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Particle and VOC emission factor measurements for anthropogenic sources in West Africa

Sekou Keita[1], Cathy Liousse[2], Véronique Yoboué[1], Pamela Dominutti[3], Benjamin Guinot[2], Eric-Michel Assamoi[1], Agnès Borbon[3], Sophie L. Haslett[4], Laetitia Bouvier[3], Aurélie Colomb[3], Hugh Coe[4], Aristide Akpo[5], Jacques Adon[2], Julien Bahino[1], Madina Doumbia[1], Julien Djossou[5], Corinne Galy-Lacaux[2], Eric Gardrat[2], Sylvain Gnamien[1], Jean F. Léon[2], Money Ossohou[1], E. Touré N'Datchoh[1], and Laurent Roblou[2]

[1]Laboratoire de Physique de l'Atmosphère, Université Félix Houphouët-Boigny, Abidjan, BPV 34, Côte d'Ivoire
[2]Laboratoire d'Aérologie, Université de Toulouse, CNRS, UPS, France
[3]Université Clermont Auvergne, CNRS, LaMP, 63000 Clermont-Ferrand, France
[4]Centre for Atmospheric Science, University of Manchester, Manchester, M13 9PL, UK
[5]Laboratoire de Physique du Rayonnement, Université Abomey-Calavi, Abomey-Calavi, Benin

Correspondence: Sekou Keita (sekkeith@yahoo.fr)

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Abstract. A number of campaigns have been carried out to establish the emission factors of pollutants from fuel combustion in West Africa, as part of work package 2 ("Air Pollution and Health") of the DACCIWA (Dynamics-Aerosol-Chemistry-Cloud Interactions in West Africa) FP7 program. Emission sources considered here include wood (hevea and iroko) and charcoal burning, charcoal making, open trash burning, and vehicle emissions, including trucks, cars, buses and two-wheeled vehicles. Emission factors of total particulate matter (TPM), elemental carbon (EC), primary organic carbon (OC) and volatile organic compounds (VOCs) have been established. In addition, emission factor measurements were performed in combustion chambers in order to reproduce field burning conditions for a tropical hardwood (hevea), and obtain particulate emission factors by size ($PM_{0.25}$, PM_1, $PM_{2.5}$ and PM_{10}). Particle samples were collected on quartz fiber filters and analyzed using gravimetric method for TPM and thermal methods for EC and OC. The emission factors of 58 VOC species were determined using offline sampling on a sorbent tube. Emission factor results for two species of tropical hardwood burning of EC, OC and TPM are $0.98 \pm 0.46\,g\,kg^{-1}$ of fuel burned ($g\,kg^{-1}$), 11.05 ± 4.55 and $41.12 \pm 24.62\,g\,kg^{-1}$, respectively. For traffic sources, the highest emission factors among particulate species are found for the two-wheeled vehicles with two-stroke engines ($2.74\,g\,kg^{-1}$ fuel for EC, $65.11\,g\,kg^{-1}$ fuel for OC and $496\,g\,kg^{-1}$ fuel for TPM). The largest VOC emissions are observed for two-stroke two-wheeled vehicles, which are up to 3 times higher than emissions from light-duty and heavy-duty vehicles. Isoprene and monoterpenes, which are usually associated with biogenic emissions, are present in almost all anthropogenic sources investigated during this work and could be as significant as aromatic emissions in wood burning ($1\,g\,kg^{-1}$ fuel). EC is primarily emitted in the ultrafine fraction, with 77 % of the total mass being emitted as particles smaller than 0.25 µm. The particles and VOC emission factors obtained in this study are generally higher than those in the literature whose values are discussed in this paper. This study underlines the important role of in situ measurements in deriving realistic and representative emission factors.

1 Introduction

Air pollution and its consequences on air quality, human health and climate are particularly worrying in Africa. First, there is a rich mixture of sources of pollutants: natural sources with Sahelian and Saharan dust emissions combine with anthropogenic sources including biomass burning, traffic, industry, residential cooking, power plant emissions and others. To date, dust and biomass burning have been considered to be predominant and many studies have been con-

ducted on these sources. A few studies only deal with anthropogenic sources. Andreae and Merlet (2001) have shown that domestic fires used for cooking are an important source of primary particle carbon worldwide and particularly in Africa. The main sources of energy in households in Africa are solid fuels such as charcoal, agricultural residues and wood (Wang et al., 2013): in Sub-Saharan Africa, these biofuels represent approximatively 80 % of the total energy consumption (Ozturk and Bilgili, 2015). Traffic emissions are also expected to be important due to the type of engine, its maintenance, its age and the fuel it uses (Robert et al., 2007; Peltier et al., 2011). Indeed, the traffic fleet in Africa is characterized by an aging fleet (more than 80 % are second-hand vehicles, with 73 % older than 10 years) (Kablan, 2010; Essoh, 2013). In Côte d'Ivoire, most of these vehicles are more than 20 years old (Ministry of Transport, 2012) and are as such highly polluting due to inefficient combustion (Boughedaoui et al., 2009). Also, there is a difference in fuel quality used in traffic between Africa and developed countries. The UNEP (2017) reports shows that in developing countries the average sulfur levels of fuel used in traffic (particularly diesel fuels) are high and may even reach 10 000 ppm, while developed countries have reduced fuel sulfur levels to 10 parts per million (ppm). In some African countries, it is also necessary to note the importance of two-wheeled vehicles (two-stroke or four-stroke engines) which use a mixture of oil and gasoline derived from smuggling that is very polluting (Assamoi and Liousse, 2010). Finally, very high levels of pollutants are associated with trash-burning emissions and this source has not been well studied in Africa. In most African countries, solid waste collection systems are insufficient, leading some people to dispose of waste using open burning (Wiedinmyer et al., 2014). In many African countries, open burning occurs at public landfills due to the lack of a modern incinerator.

All these anthropogenic sources are expected to increase in the next decades due to urbanization and population density increases. In Marticorena et al. (2010) it has been seen that they can be as important as the "well-known" dust and biomass burning sources. In Liousse et al. (2014), it may be underlined that they could be higher than Asian emissions in 2030 if no regulation occurs as quickly as possible.

One approach for quantifying air pollution and impacts, and formulating emission reduction strategies, is to use atmospheric modeling tools which require emission inventories as source data (Bond et al., 2004; Junker and Liousse, 2008; Granier et al., 2011; Smith et al., 2011; Klimont et al., 2013). Emission inventories are built based on activity and pollutant emission factor (EF) data. However, the above-mentioned sources are not well documented, especially in terms of particle carbon and volatile organic compound (VOC) EFs, leading to a scarcity of emission factors for these sources. Indeed, biomass burning EFs for a number of gaseous and particulate species have been compiled by Andreae and Merlet (2001) and Akagi et al. (2011), showing that many studies have been carried out in Africa since 1994. However, the literature shows only a few EF measurement studies on anthropogenic sources. Most existing works in that area have mainly focused on biofuel combustion. For example, particle and gas EF measurements for wood cooking fires have been performed by Brocard (1996) and Brocard et al. (1998) in Côte d'Ivoire and by Bertschi et al. (2003) in Zambia. Particle and gas EF measurements have also been performed by Bertschi et al. (2003), Brocard et al. (1998) and Kituyi et al. (2001) for charcoal cooking fire and by Pennise et al. (2001), Lacaux et al. (1994), Cachier et al. (1996) and Brocard et al. (1998) for charcoal-making fire. Unfortunately, such studies are only done for a few pollutants. To our knowledge, EF measurements for traffic vehicles in Africa are very scarce.

As a consequence, existing emission inventories for Africa extracted from global emission products use inadequate emission factors, which are not measured in Africa and consequently which are not relevant to specific fuels and combustions, and inadequate activity consumption data given by international agencies (e.g., UN, IEA). Even in the existing African Regional Inventory of Liousse et al. (2014), literature EFs issued from US or European emissions and not relevant for Africa have been sometimes used, leading to many uncertainties (Assamoi and Liousse, 2010). Moreover, if the emission inventory uncertainties result from uncertainties in the activity and emission factor data (Liousse et al., 2014; Bond et al., 2013; Zhang and Tao, 2009; Zhao et al., 2011), uncertainties are also linked to spatial keys used to geographically distribute pollutant emissions. Therefore, the use of local activity data, emission factors and adapted spatial keys derived from local measurements on Africa-specific sources may help to reduce uncertainties in emission inventories.

In Africa, the most recent regional African inventory has shown that black or elemental carbon (BC or EC) emissions are dominated by the use of diesel fuels, animal waste, fuelwood, charcoal making and coal (Liousse et al., 2014). However, animal waste, charcoal making, fuelwood and two-wheeled-vehicle fuels mostly affect organic carbon (OC) emissions. Liousse et al. (2014) also showed that West Africa has maximum emissions in the domestic and traffic sectors for EC, OC, carbon monoxide, nitrogen oxides and volatile organic compound species due to combustion of the fuels mentioned above.

In terms of pollutants from combustion process, it is necessary to focus on carbonaceous particles (OC and EC) since carbonaceous particles are the main constituents of the particle phase from combustion activity emissions. It is also interesting to study VOCs since the emission factors of these components are not well known despite their expected impact on air quality and climate through their effects on ozone and secondary organic aerosol (SOA) formation (Matsui et al., 2009; Yokelson et al., 2009; Sharma et al., 2015).

In this context, our study was to conduct several campaigns to measure EFs for the above-mentioned important sources and pollutants. Such a study is fully included in

the frame of the Dynamics-Aerosol-Chemistry-Cloud Interactions in West Africa (DACCIWA) program (Knippertz et al., 2015). DACCIWA aims to quantify the influence of anthropogenic and natural emissions on air quality, clouds and rainfall over southern West Africa and assess their impacts on human and ecosystem health as well as agricultural productivity. One of its aims is to develop an emission inventory of anthropogenic sources specific to this region.

The work here presented aims to provide a database of EFs for total particulate matter (TPM) mass, elemental carbon (EC), organic carbon (OC) and combustion gases (VOC) for pollution sources specific to Africa. The focus is on domestic fires using wood and charcoal mostly for cooking, charcoal making and solid trash disposal by open fires. Emissions related specifically to road traffic come from studies on vehicle categories (light duty and heavy duty), energy (gasoline or diesel engine), use (private and public transport) and age (old and recent).

In Sect. 2, this paper describes the material and the methodology used to calculate EFs of the main studied African emissions sources. Section 3 deals with the analysis of samples, whereas Sect. 4 presents the EF results of field measurements, including a comparison with literature values. In this section, combustion chamber measurements of EF are also added.

2 Methodology and materials

Two types of measurements were carried out in this study for emission factor measurement experiments: field measurements for all studied sources and combustion chamber measurements for fuelwood sources.

2.1 Emission factors

Emission factors are defined as the amount of pollutant emitted per kilogram of burned fuel. EFs are determined using the carbon balance method (Ferek et al., 1998; Radke et al., 1988; Ward and Radke, 1993). The amount of carbon emitted to the atmosphere during combustion and that contained in each fuel allow an estimation of the amount of fuel burned. Previous studies (Hall et al., 2012; Chen et al., 2007; Gupta et al., 2001) have shown that, during fuel combustion, approximately 95 % of carbon is emitted into the atmosphere as carbon dioxide (CO_2) and carbon monoxide (CO). It is therefore reasonable to estimate the emitted amount of carbon from CO and CO_2 concentrations by neglecting hydrocarbons and particles, implying a minor overestimation of EF values (Pant and Harrison, 2013; Hall et al., 2012; Chen et al., 2007; Gupta et al., 2001; Yokelson et al., 2007; Shen et al., 2010; Roden et al., 2006). The EFs are determined from concentration measurements in the plume and in ambient air outside the emission sources. Emissions factors are then calculated as follows:

$$\mathrm{EF}(x) = \frac{\frac{\Delta[X]}{\Delta[\mathrm{CO_2}]+\Delta[\mathrm{CO}]} \cdot \mathrm{MM}_x}{12} \cdot f_\mathrm{c} \cdot 10^3, \quad (1)$$

where EF (x) is the emission factor of the pollutant x in grams per kilogram fuel burned ($\mathrm{g\,kg^{-1}}$), $\Delta[x] = [x]_\mathrm{smoke} - [x]_\mathrm{background}$ is the mixing ratio of x in fresh smoke plume and background air, respectively (it is noted that ambient concentrations of TPM, EC, OC and VOC before combustion are assumed to be zero), MM_x is the molar mass of x ($\mathrm{g\,mol^{-1}}$), 12 is the molar mass of carbon ($\mathrm{g\,mol^{-1}}$) and f_c is the mass fraction of carbon in the fuel.

The modified combustion efficiency (MCE) is defined as

$$\mathrm{MCE} = \frac{\Delta[\mathrm{CO_2}]}{\Delta[\mathrm{CO_2}] + \Delta[\mathrm{CO}]}. \quad (2)$$

The ratio $\Delta\mathrm{CO}$ / $\Delta\mathrm{CO_2}$ and MCE both depend on the relative importance of the two main phases of combustion: the flaming and smoldering phases. The flaming phase is characterized by very high-temperature combustion and oxygenation, and the smoldering phase by low temperature and oxygenation (Ward and Radke, 1993). Higher $\Delta\mathrm{CO}$ / $\Delta\mathrm{CO_2}$ or lower MCE indicates more smoldering (Ward and Radke, 1993). From laboratory tests on biomass burning, several authors have demonstrated that MCE is around 0.99 for pure flaming (Chen et al., 2007; Yokelson et al., 1996) and varies between 0.65 and 0.85 for smoldering (Akagi et al., 2011). In this study, an average MCE was determined for each studied source from measurements.

Combustion chamber EFs were calculated using the carbon balance method with Eq. (1). However, using AMS and SP2 data collected in the Edinburgh combustion chamber the following equation was used:

$$\mathrm{EF} = \frac{([C_x]_\mathrm{smoke} - [C_x]_\mathrm{background}) \cdot Q_\mathrm{chamber} \cdot t}{m_\mathrm{burned}}. \quad (3)$$

In Eq. (3), EF (x) is the emission factor of the pollutant x in $\mathrm{g\,kg^{-1}}$ fuel burned, $[C_x]_\mathrm{smoke}$ and $[C_x]_\mathrm{background}$ are the concentration of x in the fresh smoke plume and the background air, respectively, Q_chamber is the air flow entering the chamber, t is the sampling time and m_burned is the mass of burned fuel.

2.2 Description of field measurements

Three field campaigns of emission factor measurements were performed as part of DACCIWA work package 2: the first in March 2015 in Abidjan (Côte d'Ivoire), the second in July 2015 in both Abidjan and Cotonou (Benin), and the third in July 2016, also in Abidjan. Locations for these field measurements are shown on a map in Supplement Fig. S1. During these campaigns, several sources were studied.

1. Open trash burning: in each eight different locations chosen to represent the combustion of waste diversity

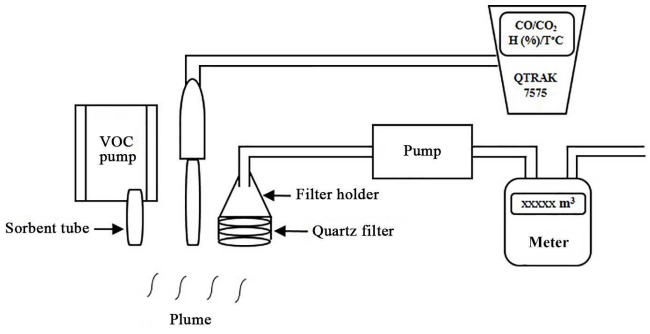

Figure 1. Schematic view of field sampling system.

(dry, wet, old or fresh waste), trash-burning plumes were sampled at "Akouédo" landfill, the largest (153 ha) and the official landfill site in the east of Abidjan District.

2. Charcoal- and wood-burning fire: eight samplings were carried out for charcoal-burning EFs, including six in Abidjan and two in Cotonou. For wood-burning EFs, four measurements were carried out in Abidjan using two different species of tropical African hardwood, hevea (*Hevea brasiliensis*) and iroko (*Milicia excelsa*). Note that hevea and iroko are both hardwood but with different properties; for example, their density differs (600 and 650 kg m^{-3}, respectively). Both are mainly used in urban areas for residential cooking, heating and in other services (bakeries, power plants, etc.). During these measurements, wood and charcoal were burned in two types of stoves traditionally used in the West African region for cooking, made of metal and of baked earth (see Fig. S2). These measurements include different phases of combustion (pyrolysis, flaming and smoldering).

3. Charcoal-making fire (CHM): eight tests were carried out on traditional charcoal-making furnaces; three of these eight tests were carried out in the outskirts of Abidjan and five tests in a rural area at 2 km from the Lamto geophysical station (Lamto is 260 km from Abidjan). The CHM kiln was prepared by charcoal producers who use all types of available dense wood. The kiln was covered with a layer of leaves and a layer of earth of about 10 cm thick. The draft, needed for the propagation of the pyrolysis, comes from air circulation between the base of the kiln and a row of holes made in a horizontal plane, which are closed when the charcoal producers open a new row below the previous one. The smoke was sampled at the holes made in the CHM kiln.

4. Combustion of fossil fuels in the traffic sector: EF measurements were carried out on several vehicle exhausts in Abidjan and Cotonou: cars, buses, trucks, mopeds, and gasoline and diesel vehicles. Both recent (under 10 years) and old vehicles (over 10 years) have been studied. For each type of vehicle, at least two tests were performed, simulating several engine speeds.

During these various measurements, samples were taken in the plume at around 1–1.5 m from the source, except for vehicles where samples were taken at the tailpipe outlet. The different EF values of the different tests are averaged for each source. For road traffic EFs, we also calculated a mean equivalent vehicle EF for both four-wheeled gasoline and diesel fleets using fleet characteristics given by Direction Generale des Transports Terrestres (DGTT) of Côte d'Ivoire: 60 % of total vehicles are considered as old models (whereas 40 % are recent ones) and 77 % of total vehicles are light-duty vehicles (whereas 23 % are heavy-duty vehicles) (SIE CI, 2010).

As with four-wheeled vehicles, we calculated an average equivalent vehicle for two-wheeled fleets assuming that 40 % are two-stroke engines (whereas 60 % are four-stroke engines) and 40 % are recent vehicles (whereas 60 % are older vehicles).

2.3 Field measurement and sampling equipment

Two types of sampling were performed during our EF measurement experiments: collection of particles on Whatman quartz fiber filters and speciated VOCs (alkanes, alkene, carbonyl and aromatic compounds) on sorbent tubes. Figure 1 shows the particles and VOC schematic sampling system in the field. According to Eq. (1), it is necessary to quantify the amounts of CO_2 and CO emitted to the atmosphere to determine the amount of carbon emitted during the combustion and calculate the MCE. The QTRAK-7575 (Kam et al., 2011; Li et al., 2017), developed by TSI, was used to measure CO_2 and CO gas concentrations. This allows the measurement of real-time atmospheric CO_2 and CO concentrations. The CO concentration is determined using an electrochemical sensor with a sensitivity of 0 to 500 ppm with ±3 % accuracy. The CO_2 concentration is measured using a non-dispersive infrared detector with a sensitivity of 0 to 5000 ppm with an accuracy of ±3 %. The QTRAK-7575 was calibrated in the laboratory prior to each field measurement. The difference between CO_2 and CO in the fresh smoke plume and the background air allowed the amount of carbon emitted into the atmosphere during each sampling to be obtained.

VOCs were actively sampled using sorbent tubes (Perkin-Elmer® and TERA-Environnement) containing multisorbent materials. Duplicates were performed for 15 min using a manual pump (Accuro 2000, from Dräger) with a controlled flow of 100 mL min^{-1}. For each emission source studied, samples were taken at the same levels as those from the filter holder and QTRAK-7575 probe (see Fig. 1). While offline field measurements are essential to characterize the composition from real emissions from an unrestricted number of sources, they are limited as only a small fraction of compounds and only some combustion processes can be measured. Therefore, in order to capture a large spectrum of

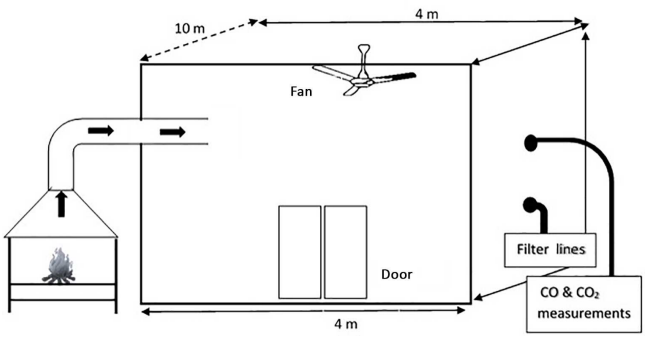

Figure 2. Schematic view of the Lannemezan combustion chamber.

VOC species from the largest number of emission sources in the region, two types of sorbent tubes were used: Tenax TA 60–80 meshes (250 mg, 2,6-diphenyl-p-phenylene oxide) and multi-sorbent tubes composed of Carbopack C (200 mg) and Carbopack B (200 mg) 60–80 mesh (graphitized black carbon). The identification and quantification of each tube type was performed at different places and using different analytical techniques.

The particle collection line consisted of a pump with a flow rate of 9.5 liters per minute ($L\,min^{-1}$) for sampling total particulate matter, a volumetric counter for quantifying sampled air volume and a filter holder on which a 47 mm diameter quartz-fiber filter (QM/A®, Whatman Inc.) was mounted. Before sampling, the filters were cleaned by heating for 48 h at 340 °C. After sampling they were kept at a temperature of 5 °C to avoid any contamination of the samples.

2.4 Measurements in the combustion chamber in the diluted wood combustion plume

This sampling took place in a chamber where the plumes of hevea wood fire were convoyed. Therefore, concentrations were diluted compared to the measurements carried out in the field at the sources. The tests were conducted in two combustion chambers with different configurations. Only hevea wood from Côte d'Ivoire was studied in both combustion chambers. The combustion chamber of Lannemezan (Guillon et al., 2013) (Laboratoire d'Aérologie, UMR 5560, Toulouse, France) and the combustion chamber at the University of Edinburgh's School of Engineering were used. In Lannemezan, the dark dilution chamber (10 m × 4 m × 4 m) allowed measurement of concentrations at the absence of any solar radiation with no photochemistry. A fan stirs the air in the chamber to mix it well. For this combustion, the fuels were burned in a metal stove similar to the one used in the field and the plume is conveyed into the chamber through a chimney 1.5 m high and 15 cm wide (Fig. 2). Two QTRAKs were used to measure CO_2 and CO concentrations, temperature and associated relative humidity in the room. The chamber remained closed during all phases of combustion, monitored from an adjacent room to the combustion chamber. After homogenization of the plume within the chamber, five filter sampling lines corresponding respectively to the cut-off heads for $PM_{0.25}$, PM_1, $PM_{2.5}$, PM_{10} and TPM were used to collect aerosols for 15–25 min on average. For each of the five lines, the pumps were coupled to flow regulators to allow aerosol selection by particle size classes. Between two experiments, the chamber was opened (ventilated) to allow all sensors to return to their background values. Four tests were carried out with hevea wood from Côte d'Ivoire.

Hevea wood combustion experiments were also conducted using the FM-Global Fire Propagation Apparatus (FPA) at the Edinburgh University School of Engineering facility. The FPA allows the burning of small samples of fuel under controlled conditions (Brohez et al., 2006). The sample holder was placed on a mass balance that provides sample mass evolution during the experiment. The samples were surrounded by four infrared lamps, irradiating uniformly at $30\,kWm^{-2}$ (low heat) or $50\,kWm^{-2}$ (high heat), and subjected to an air flow entering from below at rates of $50\,L\,min^{-1}$ (low flow) or $200\,L\,min^{-1}$ (high flow). A large part of these chamber measurements has already been discussed in detail in Haslett et al. (2018), mainly focusing on active analyzer results but not on filter sampling. The configuration used in this chamber is shown in Fig. 3.

The fuel used in Edinburgh was hevea wood from Côte d'Ivoire. The plume was collected in a hood before entering the exhaust tube. Air samples were collected simultaneously at two points. The first was in the exhaust tube, where CO and CO_2 were measured directly and a further sample was diluted in pure nitrogen by a factor of 100 for the online measurement of EC and OC concentrations. An aerosol mass spectrometer (AMS) was used to measure the concentration of organic aerosols and other non-refractory species and a single-particle soot photometer (SP2) to measure refractory black carbon (EC) mass concentration. The CO_2, CO and O_2 concentrations in the plume were measured at a frequency of 1 Hz at the exhaust tube by the FPA analyzers using non-dispersive infrared techniques (Servopro 4200). The second was at the exit of the exhaust pipe for filter sampling (offline measurement). A QTRAK analyzer was used to continuously measure CO and CO_2 concentrations. Two aerodynamic sampling lines ($PM_{2.5}$ and TPM) were used with pumps, counter, cut-off heads and filter holders with 47 mm quartz fiber filters.

Eight combustion tests were carried out during this experiment. Two of them were made with infrared lamps set at $30\,kWm^{-2}$ and incoming airflow of $200\,L\,min^{-1}$ (low heat and high flow: hFl), three tests at $50\,kWm^{-2}$ and $200\,L\,min^{-1}$ (high heat and high flow: HFl) and three other tests at $50\,kWm^{-2}$ and $50\,L\,min^{-1}$ (high heat and low flow: Hfl).

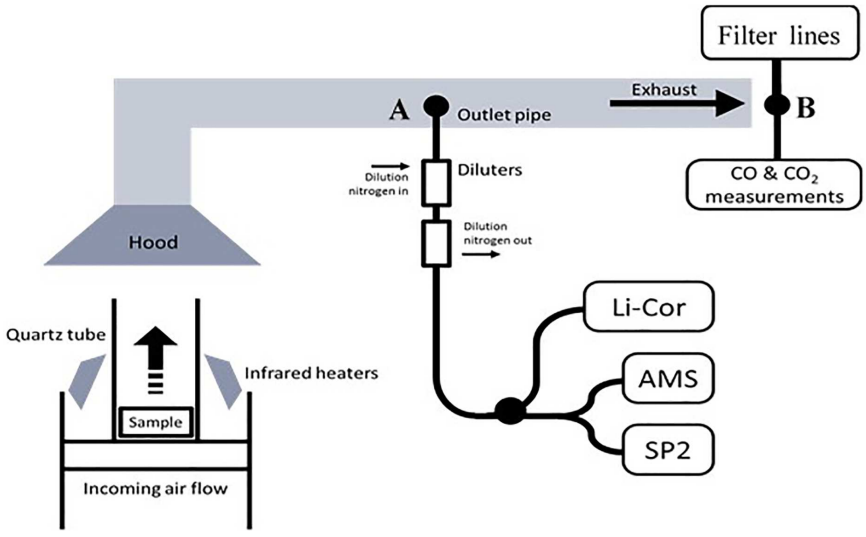

Figure 3. Schematic view of the FM-Global Fire Propagation Apparatus with a diagram of the gas and particle sampling system (adapted from Haslett et al., 2018).

3 Sample analysis

3.1 VOCs analysis

The analysis of Tenax 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) connected to an automatic thermal desorption unit (Turbomatrix ATD). Each cartridge was desorbed at 270 °C for 15 min at a flow rate of 40 mL min^{-1}, reconcentrated on a second trap, at −10 °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. The separating column used was a capillary PE-5MS (60 m × 0.25 mm × 0.25 µm, 5 % phenyl–95 % PDMS, Perkin Elmer) and the GC temperature profile was ramped from 35 °C for 5 min, heating at 8 °C min^{-1} to 250 °C and hold for 2 min. The mass spectrometer was operated in a total ion current (TIC) chromatogram from 35 to 350 m/z amu, and all chromatography parameters were optimized to enable the separation of 16 compounds from C_5–C_{10} VOCs. Calibration was performed by analyzing conditioned cartridges doped with known masses of each compound, present in standard low-ppb-level gas solutions (purchased from the National Physical Laboratory, UK). The cartridges were then analyzed with the aforementioned method and calibration curves were obtained for each compound. Carbopack cartridges were analyzed at the SAGE Department (IMT Lille Douai) with an ATD-GC-FID analytical system, already described in Detournay et al. (2011) and Ait-Helal et al. (2014). This method allowed the separation and identification of 58 compounds, from C_5–C_{16} VOCs, including 7 carbonyls, 2 ketones, 12 terpenes and 6 intermediate VOCs (C_{11}–C_{16}). The application of both methods allowed the comparison of common compounds (benzene, toluene, ethylbenzene, $m+p$-xylene, o-xylene, trimethylbenzenes, n-heptane, iso-octane, n-octane, α-pinene, β-pinene, limonene, isoprene) and the analysis of analytical techniques' performance.

The tubes were previously conditioned by flowing purified nitrogen through them at a rate of 100 mL min^{-1}, for 5 h at 320 °C using an adsorbent thermal regenerator. The quality assurance parameters of both methods (uncertainties and detection limits) are described in the Supplement (Tables S1 and S2).

3.2 Particulate matter filters

Gravimetric analysis of quartz fiber filters (providing TPM, PM_{10}, $PM_{2.5}$, etc.) was performed by comparing the difference in weight of the filters before and after exposure. Weighing was performed using a SARTORIUS microbalance with 1.95 µg sensitivity. After the gravimetric analysis, the laboratory two-step thermal method from Cachier et al. (1989) was applied for the separation and the analysis of elemental and organic carbon particulate contents (EC and OC, respectively). Note that the detection stage was modified since in our instrument (G4 ICARUS), particulate carbon content is quantified from CO_2 by a non-dispersive infrared (NDIR) detector, instead of coulometry as in Cachier et al. (1989). The relevance of the use of thermal method was validated by comparing results of 10 samples also analyzed using a thermo-optical method (IMPROVE method; Chow et al., 1993, 2001). We performed a linear regression analysis of all values obtained for both methods for TC, EC and OC. The analysis of the regression coefficients (given here in terms of R^2) shows that suitable correlations were found among the

thermal and thermo-optical methods for TC, EC and OC values. The thermal method gives 94 % of OC and 90 % of the EC measured with the thermo-optical method. Examples of regression plots are given in the Supplement with the Fig. S3. After this comparative study of analyses by these two methods, the thermal method was used for the subsequent analyses because of the high filter load. Two similar aliquots of the same filter were then separately analyzed. One portion was directly analyzed for its total carbon content (TC). The other portion was firstly submitted to a pre-combustion step (2 h at 340 °C under pure oxygen) in order to eliminate OC and then analyzed for its EC content. Organic carbon (OC) concentrations were calculated as the difference between TC and EC. The analyzer calibration is checked before each series of analyses by analysis of the filter punches each containing a sucrose solution of known concentration.

4 Results and discussions

4.1 Field measurements

Field measurements allowed determination of mean values of EF for residential fuel fires (charcoal burning, CH; fuelwood burning, FW), charcoal-making fires (CHM), open trash-burning fires (WB) and vehicle exhaust (car, bus, truck, light-duty vehicles, two-wheeled two-stroke and four-stroke vehicles) by energy source (diesel and gasoline) and by model age (recent, less than 10 years old; old, 10 years and over). As mentioned above, the studied species are CO, CO_2, carbonaceous particles (EC, OC and TC), speciated VOCs compounds (C_5–C_{16} alkanes, C_5–C_{11} carbonyls, C_4-ketones, C_6–C_9 aromatics and 13 species of terpenes) and total particulate matter (TPM).

4.1.1 Particulate EFs for biofuel combustion sources

The EFs for fuelwood burning sources were calculated following Eq. (1), and using $f_c = 46\,\%$ (Brocard et al., 1996). EFs are expressed in grams of pollutant per kilogram of fuel burned ($g\,kg^{-1}$). Results of OC emission factor (EF(OC)) values given in Table 1 are 15.61 ± 6.44 and $6.50 \pm 1.98\,g\,kg^{-1}$ for hevea and iroko wood respectively, while for EC, EFs were found to be 1.45 ± 0.61 and $0.52 \pm 0.39\,g\,kg^{-1}$, respectively. Hevea wood emitted more carbonaceous particles than iroko wood. To have a mean EFs for wood cooking fire, we averaged the EFs of the two types of wood studied here (iroko and hevea). Following this, a value of $0.98 \pm 0.46\,g\,kg^{-1}$ for EC and $11.05 \pm 4.55\,g\,kg^{-1}$ for OC is assumed to be representative of the EFs typical for this area. On the one hand, EC and OC EFs for iroko wood cooking fire are of almost the same order of magnitude as those of Brocard et al. (1996), but EFs of hevea wood cooking fire from this study are higher than other literature values in Table 1. On the other hand, comparison of mean EFs of EC and OC with those used by Liousse et al. (2014) and Akagi et al. (2011) showed that EF(EC) is of the same order of magnitude while EF(OC) of this study is 4 times higher than those values reported by Liousse et al. (2014) and Akagi et al. (2011) (see Table 1). Thus, the use of new EF(OC) from this study should show that previous values of EF(OC) underestimated OC emissions in West Africa. These differences may be explained by the wide variety of wood used in the different studies as well as the different burning conditions as shown by the different MCE values in Table 1. However, our MCE value for iroko wood cooking is reasonably similar to those of Brocard et al. (1996). This reveals that these two combustions take place mainly in the flaming phase because $MCE \approx 0.92$.

Particles EFs for charcoal cooking fire were obtained by averaging EFs of several tests and using f_c of 71.5 % (Brocard et al., 1996) to express EFs in $g\,kg^{-1}$ of charcoal burned. Table 1 also presents the mean EF for charcoal cooking fire with literature data. EC and OC EFs were found to be 0.65 ± 0.30 and $1.78 \pm 2.80\,g\,kg^{-1}$, respectively. It can be seen here that our EF(EC) for charcoal cooking fires are 3 times higher than those reported by Brocard et al. (1996) and Roden and Bond (2006) but of the same order of magnitude as those used by Liousse et al. (2014). However, the EFs are almost the same for OC. For charcoal burning, we can say that Liousse et al. (2014) give values of the same order of magnitude for EC and OC emissions in West Africa compared to those we would obtain using these study values and the same activity data. The mean value of MCE (0.83 ± 0.06) found for charcoal cooking fire shows that this also burned mainly in the flaming phase.

The carbon balance method cannot be used directly to calculate charcoal-making (CHM) EF (Bertschi et al., 2003) in the same way we calculate wood- and charcoal-burning EFs. Indeed, during the CHM process, part of the burned carbon is found in charcoal, ash and pyroligneous liquid. Thus, less than 50 % is emitted into the atmosphere. As shown previously, Lacaux et al. (1994), Cachier et al. (1996), Smith et al. (1999) and Bertschi et al. (2003) estimate the fraction of carbon emitted as atmospheric gases to be 35, 35, 37, and 45 % respectively. Moreover, Cachier et al. (1996) estimate that if 35 % of the carbon content of wood is emitted into the atmosphere during CHM, 89 % is emitted as CO and CO_2 during the smoldering phase. Since the CHM conditions described in Cachier et al. (1996) are similar to those of this study (pure smoldering phase because of an average MCE of 76 %; Fig. 4; Akagi et al., 2011), we considered that 35 % of the carbon content of wood is emitted into the atmosphere and 89 % of this carbon is emitted as CO and CO_2 for CHM. Thus, 0.35 was the factor used in order to obtain an EF in $g\,kg^{-1}$ of wood burned from EF in grams per kilogram of carbon (Cachier et al., 1996). As shown in Table 1, CHM EFs of this study are comparable to those of Brocard (1996) and Cachier et al. (1996) for OC and are a factor of 2 lower for EC. This difference could be explained by a wide variety of wood used for CHM (e.g., wood type or wood mois-

Table 1. EFs of residential sources for this study and those from the literature (mean values from this study in bold).

Emission sources	Type	Reference	EF ($g\,kg^{-1}$ fuel)			OC / EC	MCE
			EC	OC	TPM		
Wood cooking fires	Iroko	This work	0.52 ± 0.39	6.50 ± 1.98	16.50 ± 2.58	12.8	0.92 ± 0.02
	Hevea		1.45 ± 0.61	15.61 ± 6.44	65.74 ± 30.00	10.7	0.76 ± 0.12
	Mean		$\mathbf{0.98 \pm 0.46}$	$\mathbf{11.05 \pm 4.55}$	$\mathbf{41.12 \pm 24.62}$	**11.2**	$\mathbf{0.76 - 0.92}$
		Brocard (1996)	0.55 ± 0.30	5.0 ± 3.60	nd	9.1	0.93
	Open	Akagi et al. (2011)	0.83 ± 0.45	2.89 ± 1.23	4.55 ± 1.53	3.5	
	stove	Akagi et al. (2011)	0.74 ± 0.37	1.92 ± 0.90	3.34 ± 1.68	2.6	
		Liousse et al. (2014)	0.90	2.70			
Charcoal cooking fires		This work	$\mathbf{0.65 \pm 0.30}$	$\mathbf{1.78 \pm 2.80}$	$\mathbf{12.75 \pm 9.03}$	**2.7**	$\mathbf{0.83 \pm 0.06}$
		Brocard (1996)	0.20	2.00	nd	10	
		Roden et al. (2006)	0.20	1.50	nd	7.5	
		Liousse et al. (2014)	0.75	2.30	nd	3	
Charcoal making		This work	$\mathbf{0.22 \pm 0.16}$	$\mathbf{3.93 \pm 1.01}$	$\mathbf{40.12 \pm 22.26}$	**17.5**	$\mathbf{0.76 \pm 0.05}$
		Cachier et al. (1996)	0.46 ± 0.10	4.40 ± 0.60	nd	9.6	
		Brocard (1996)	0.40	3.60	nd	9	

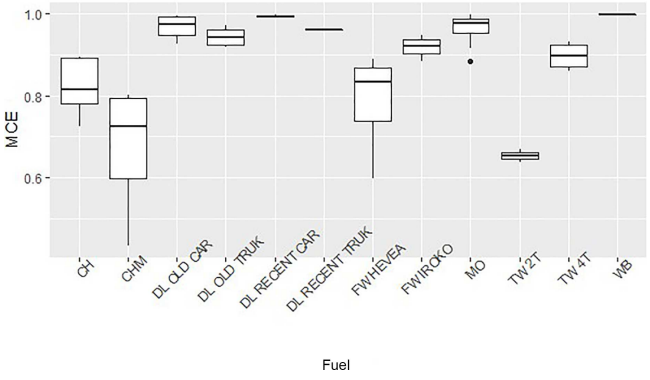

Figure 4. Modified combustion efficiency of different sources studied (charcoal burning: CH; charcoal making: CHM; diesel: DL; wood burning: FW; gasoline: MO; two-wheeled vehicles: TW; and trash burning: WB).

ture). For charcoal-making fires, mean MCE is found to be 0.76 ± 0.05, a value lower than those found for other biofuels tested in this study.

4.1.2 Particulate EFs for road traffic sources

EFs for road traffic sources were calculated following (Eq. 1). The fraction of carbon contained in diesel (Eggleston et al., 2006; Kirchstetter et al., 1999) and in gasoline (IPCC, 2006; Ban-Weiss et al., 2010) was assumed to be 85 % in order to obtain an EF expressed in g of pollutant per kg of fuel burned ($g\,kg^{-1}$). Table 2 summarizes EC, OC and TPM EFs from our measurements by two vehicle age categories (old, 10 years and over; recent, less than 10 years old), by energy or fuel type (gasoline and diesel) and by those used in emissions inventories.

The results show that the EF(EC) ($1.03 \pm 0.83\,g\,kg^{-1}$) and EF(OC) ($1.80 \pm 1.26\,g\,kg^{-1}$) of this study for old light-duty gasoline vehicles (LDGVs) are larger than those of recent vehicles by a factor of 1000 and 40 respectively for EC and OC, showing that older the LDGV becomes, the more EC it emits. Like LDGVs, EF(EC) and EF(OC) for old vehicles are higher than those of recent vehicles for light-duty diesel vehicles (LDDVs) (Table 2). The high emission factors for older vehicles in Africa can be explained by the lack of regulations on vehicle emissions (catalytic converter and diesel particulate filters, e.g., EURO standards). In addition, EC EFs are higher than OC EFs for both old and recent LDDVs as previously shown by some studies such as Pant and Harrison (2013), Chiang et al. (2012), and Grieshop et al. (2006). EFs of all tested vehicles are reported in Table S3 of the Supplement. It was reported in the literature (measurements not performed in Africa) that the EC EFs of diesel vehicles were in the range of 0.11 to $2.20\,g\,kg^{-1}$ fuel (Kirchstetter et al., 1999; Gillies and Gertler, 2000; Streets et al., 2001; Westerdahl et al., 2009; Wang et al., 2012, 2016). Our results of EF(EC) of diesel vehicle are in this range with the exception of old vehicles.

Mean EFs of EC, OC and TPM for LDDVs, including private cars and taxis, are estimated to be respectively 3.35 ± 2.20, 2.03 ± 1.13 and $35.82 \pm 21.40\,g\,kg^{-1}$. They are higher than mean EFs for heavy-duty diesel vehicles (HDDVs), including trucks and buses, respectively of the order of 2.20 ± 1.05, 2.50 ± 1.43 and $31.00 \pm 15.80\,g\,kg^{-1}$. Regarding gasoline vehicles, EF measurements were carried out only for LDGVs, which constitute the majority of the fleet using gasoline. Mean EC, OC and TPM EFs are lower than LDDVs with 0.62 ± 0.49, 1.10 ± 0.77 and $7.0 \pm 2.80\,g\,kg^{-1}$ respectively.

Table 2. Emission factors for gasoline and diesel vehicles by age group and those in the literature, from different measurement methods (mean values in bold).

Fuel	Age	EFs ($g\,kg^{-1}$ fuel)				Study
		EC	OC	TPM	MCE	
Gasoline	Recent LDGV	0.001 ± 0.001	0.042 ± 0.04	3.02 ± 0.3	0.99 ± 0.00	This work
	Old LDGV	1.03 ± 0.83	1.80 ± 1.26	9.63 ± 4.44	0.94 ± 0.04	
	LDGV	$\mathbf{0.62 \pm 0.49}$	$\mathbf{1.10 \pm 0.77}$	$\mathbf{7.00 \pm 2.80}$	$\mathbf{0.94 - 0.99}$	
		0.15	0.73	nd		Liousse et al. (2014)
		0.08–0.43	0.19–5.40	nd		Bond et al. (2004)
Diesel	Recent LDDV	1.26 ± 0.66	0.60 ± 0.25	9.13 ± 4.08	0.99 ± 0.00	This work
	Old LDDV	4.74 ± 3.2	2.97 ± 1.71	53.62 ± 33.0	0.97 ± 0.02	
	Recent HDDV	0.35 ± 0.01	0.72 ± 0.15	6.70 ± 0.58	0.96 ± 0.00	
	Old HDDV	3.43 ± 1.7	3.71 ± 2.3	47.14 ± 28.8	0.94 ± 0.02	
	LDDV	$\mathbf{3.35 \pm 2.20}$	$\mathbf{2.03 \pm 1.13}$	$\mathbf{35.82 \pm 21.44}$		
	HDDV	$\mathbf{2.20 \pm 1.05}$	$\mathbf{2.50 \pm 1.43}$	$\mathbf{31.0 \pm 15.80}$		
	ROAD (mean)	$\mathbf{3.08 \pm 1.96}$	$\mathbf{2.14 \pm 1.20}$	$\mathbf{34.70 \pm 20.13}$		This work
	ROAD (mean)	5.00	2.50	nd	nd	Liousse et al. (2014)
	ROAD (mean)	1.30–3.60	0.40–1.10	nd	nd	Bond et al. (2004)

nd: not determined

Finally, mean road equivalent vehicle EFs (Table 2) by fuel types were compared with EF values used in Bond et al. (2004) inventory and in the most recent African emissions inventory by Liousse et al. (2014). For gasoline vehicles, the EF(EC) value of our mean road equivalent vehicle is higher than the upper limit value used by Bond et al. (2004), which is the value used by these authors for countries where there are the most super emitters such as in West Africa. Unlike EF(EC), our EF(OC) is within the range of values given by Bond et al. (2004), but it is lower than the upper limit given by Bond et al. (2004). For diesel vehicles, while our EF(EC) value for mean road equivalent vehicle is close to the upper limit given by Bond et al. (2004), our EF(OC) is higher than their upper limit value. In addition, the EF values obtained in this study for gasoline are higher than those observed in Liousse et al. (2014) (4 times higher for EC and 2 times higher for OC), while they are slightly lower for diesel (Table 2). This shows that the use of Liousse et al. (2014) EFs underestimates EC and OC emissions for on-road gasoline motors compared to what would happen if using our EF values, whereas they are of the same order of magnitude for on-road diesel motor.

EFs for two-wheeled (TW) vehicles were also classified according to their age (old and recent), and their engine type (two- or four-stroke). Indeed, it is important to note that due to the use of a very polluting mixture of gasoline and oil, the two-stroke engines were distinguished from the four-stroke engines. For recent TW two-stroke engines, EC and OC EFs are 2.26 ± 1.40 and $25.71 \pm 1.10\,g\,kg^{-1}$ respectively, while 0.11 ± 0.01 and $0.45 \pm 0.13\,g\,kg^{-1}$ are found for recent TW four-stroke engines. In addition, for old TW two-stroke engines, EC and OC EFs are 3.45 and $124.21\,g\,kg^{-1}$ respectively, while 3.66 and $25.46\,g\,kg^{-1}$ are found for old TW four-stroke engines (Table 3). This shows that TW two-stroke engines globally emitted considerably more carbonaceous particles (especially OC particles) than TW four-stroke engines. These high EC and OC EFs for two-stroke engines can be explained by incomplete combustion due to the gasoline–oil mixtures used in these engines. This has already been highlighted by Volckens et al. (2008) for particulate emissions when studying two-stroke engines. In addition, the old / recent ratio of EF(EC) for TW two-stroke engines is around 1.5, while the same ratio for EF(OC) is around 5, which is 3 times greater than that of EF(EC). Similarly, for TW four-stroke engines, the old / recent ratio of EF(OC) is a factor of 2 greater than the ratio of EF(EC). That shows that OC emissions are more enhanced (doubled or tripled) in older TW vehicles compared with those of EC.

Mean road equivalent two-wheeled-vehicle EFs obtained for EC and OC (Table 3) are both very close to the values used by Assamoi and Liousse (2010), which is the only regional two-wheeled-vehicle inventory specific to Africa. These values were used in Liousse et al. (2014). Also, EF(EC) and EF(OC) mean values from this study are both above the upper limit of the TW EFs given by Bond et al. (2004), which correspond to the TW EFs that these authors consider for Africa. Comparison of these new values with those used in the Bond et al. (2004) inventory shows that this global inventory underestimates EC and OC emissions from two-wheeled vehicles in Africa, particularly in West Africa.

These higher EFs may be explained by the fact that African TW two-stroke vehicles are often older and second-hand (used) vehicles imported from Europe. Moreover, As-

Table 3. EC and OC EFs for two-wheeled (TW) vehicles of our study and those of the literature (mean values in bold).

Emission source	Type	EFs ($g\,kg^{-1}$ fuel)			OC / EC	Reference
		EC	OC	TPM		
TW two-stroke vehicles	Recent	2.26 ± 1.4	25.71 ± 1.1	238.3 ± 193	11.37	This work
	Old	3.45	124.21	883	36	
	Mean	**2.74**	**65.11**	**496**	23.8	
TW four-stroke vehicles	Recent	0.11 ± 0.01	0.45 ± 0.13	5.37 ± 4.64	4.1	This work
	Old	3.66	25.46	500	7	
	Mean	**1.53**	**10.46**	**203**	6.8	
Road TW	Mean	$\mathbf{2.13 \pm 0.42}$	$\mathbf{28.46 \pm 0.40}$	**420.52**	13.36	This work
Road TW		2.31	30.56	nd	13.23	Assamoi and Liousse (2010)
Road TW		0.71–1.40	11.25–22.50	nd	22.89	Bond et al. (2004)

samoi and Liousse (2010) have shown that a large proportion of the fuel used by two-wheeled vehicles in West Africa is adulterated and smuggled and thus of poor quality compared to European standards as shown by UNEP (2017). It can be seen in Fig. 4 that fossil fuel (FF) sources (diesel, gasoline) have MCEs in the range between 0.9 and 1, aside from two-wheeled two-stroke engines (TW 2T), which have a MCE of 0.65. As expected, TW 2T with a mixture of gasoline and oil has less efficient combustion with more abundant smoldering products.

4.1.3 Particulate EFs for open trash burning

EFs of pollutants for open trash burning were calculated using Eq. (1) adapted for this source. In that case, Eq. (1) was multiplied by a carbon oxidation factor (COF), defined as the ratio between the amount of burned carbon and the amount of carbon initially present in the sample. Carbon content of household waste (trash) of 46 % was used (Lundin et al., 2013; Wiedinmyer et al., 2014) with a COF of 58 % (Fiedler et al., 2010). The averaged EFs for open trash burning are presented in Table 4 with associated standard deviation. During our measurements, different phases were observed during each test/sample with different predominance from one test to another (Fig. S4): the flaming phase was predominant during the combustion of dry trash, while the smoldering phase was predominant for wet trash burning. These various fire types and the trash composition explain the relatively high value of the associated standard deviation. EF expressed in grams per kilogram of trash ($g\,kg^{-1}$) of EC, OC and TPM are 2.80 ± 3.30, 6.44 ± 4.60 and 87.90 ± 32.90, respectively. As expected, trash burning emits more OC than EC. In addition, the relatively high value of TPM suggests that other kinds of particulate matter (such as ions or metals) are also emitted during trash burning. When comparing values found during this study to those of Christian et al. (2010) which deals with carbonaceous particles EFs, it is noted that EF(OC) is of the same order of magnitude, while the EF(EC) of our work is higher than that of Christian et al. (2010) by a factor of 4. This high EF(EC) found in the present work may be explained by differences in the solid trash composition from Côte d'Ivoire and Mexico, where the measurements of Christian et al. (2010) were carried out. Moreover, it can be also explained by the fact that more flaming was sampled during our measurements. Finally, the use of EC EFs from Christian et al. (2010) in several global inventories would underestimate EC emissions from trash burning in West Africa.

4.1.4 Emission factors of volatile organic compounds

VOCs were measured and emission factors estimated for the first time to our knowledge in West Africa. Fifteen common VOC species (C_5 to C_{10}) were identified and quantified from sorbent tube measurements and are reported in Table 5. The selection of these VOC was related to their identification by both analytical methods implemented during this study.

Globally, the dominant VOC species emitted during EF measurements include toluene, $m + p$-xylene, 1,2,4-trimethylbenzene (124-TMB), ethylbenzene, o-xylene, 1,3,5-trimethylbenzene (135-TMB) and heptane. These compounds are important species in terms of atmospheric reactivity, generally involved in photochemistry processing and in the formation of secondary pollutants like ozone (Pandis and Seinfeld, 2006). Aromatic compounds also have high secondary organic aerosol potentials (Derwent et al., 2010). While they are usually associated with biogenic emissions (Kesselmeier and Staudt, 1999), isoprene and terpenes (limonene, α-pinene and β-pinene) were also observed in the EFs of almost all anthropogenic sources. Table 5 presents EF values of such species for all the studied sources. It is important to note that standard deviation values are high, reflecting the range of uncertainties linked to the two sets of analysis (see "Methodology and materials" section) and also

Table 4. EF for open solid trash burning of this study and other studies.

Emission source	EF ($g\,kg^{-1}$ trash)			Reference
	EC	OC	TPM	
Trash burning	2.80 ± 3.33	6.44 ± 4.60	87.9 ± 32.9	This work
	0.70	5.30	nd	Christian et al. (2010)

Table 5. EF values of VOC species for the studied sources: heavy-duty diesel vehicles (HDDV), light-duty diesel vehicles (LDDV), light-duty gasoline vehicles (LDGV), two-wheeled two-stroke vehicles (TW 2T), two-wheeled four-stroke vehicles (TW 4T), fuelwood (FW), charcoal (CH), charcoal making (CHM) and trash burning (WB) (in bold the EFs of the first four major species).

EF ($g\,kg^{-1}$ fuel)	HDDV	LDDV	LDGV	TW 2T	TW 4T	FW	CH	CHM	WB
Heptane	0.23 ± 0.16	0.18 ± 0.13	0.44 ± 0.15	473 ± 371	13.7 ± 6.10	0.04 ± 0.04	0.55 ± 0.40	$\mathbf{2.93 \pm 2.70}$	9.34 ± 11.6
Octane	$\mathbf{0.74 \pm 0.46}$	0.21 ± 0.10	2.36 ± 0.40	470 ± 423	8.09 ± 4.00	$\mathbf{2.38 \pm 2.30}$	0.87 ± 0.50	2.25 ± 1.70	6.31 ± 9.10
Iso-octane	0.09 ± 0.07	0.21 ± 0.15	0.04 ± 0.03	204 ± 217	0.74 ± 0.17	0.37 ± 0.60	0.42 ± 0.59	0.14 ± 0.04	0.40 ± 0.60
Benzene	$\mathbf{0.68 \pm 0.27}$	$\mathbf{5.60 \pm 2.80}$	4.78 ± 0.40	379 ± 279	32.0 ± 8.50	$\mathbf{2.00 \pm 1.98}$	$\mathbf{8.64 \pm 12.0}$	$\mathbf{4.20 \pm 0.12}$	$\mathbf{19.1 \pm 19.0}$
Toluene	0.58 ± 0.17	$\mathbf{3.10 \pm 1.80}$	$\mathbf{34.7 \pm 18.6}$	$\mathbf{1134 \pm 830}$	$\mathbf{95.0 \pm 32.2}$	1.53 ± 1.52	$\mathbf{3.60 \pm 4.30}$	$\mathbf{4.64 \pm 2.00}$	$\mathbf{35.5 \pm 45.6}$
$m + p$-Xylene	$\mathbf{0.70 \pm 0.26}$	$\mathbf{1.06 \pm 0.27}$	$\mathbf{63.4 \pm 1.07}$	$\mathbf{1334 \pm 810}$	$\mathbf{56.3 \pm 21.0}$	1.43 ± 1.42	$\mathbf{2.17 \pm 2.04}$	$\mathbf{2.63 \pm 1.70}$	5.50 ± 8.60
o-Xylene	0.32 ± 0.15	0.56 ± 0.22	$\mathbf{30.1 \pm 3.43}$	793 ± 536	25.0 ± 9.33	0.16 ± 0.47	0.51 ± 0.50	0.73 ± 0.22	0.37 ± 0.43
Ethylbenzene	0.25 ± 0.11	0.82 ± 0.37	15.6 ± 3.15	$\mathbf{814 \pm 590}$	$\mathbf{40.6 \pm 16.1}$	0.24 ± 2.07	1.74 ± 2.07	0.80 ± 0.25	$\mathbf{27.8 \pm 34.3}$
135-TMB	0.33 ± 0.21	0.52 ± 0.14	10.8 ± 0.56	484 ± 386	9.17 ± 4.00	0.07 ± 0.02	0.02 ± 0.02	0.35 ± 0.14	2.01 ± 2.88
124-TMB	$\mathbf{1.29 \pm 0.96}$	$\mathbf{1.73 \pm 0.34}$	$\mathbf{34.6 \pm 0.84}$	$\mathbf{1122 \pm 729}$	$\mathbf{30.5 \pm 13.9}$	0.06 ± 0.08	0.11 ± 0.08	0.94 ± 0.32	1.75 ± 2.12
123-TMB	0.50 ± 0.40	0.71 ± 0.14	5.84 ± 0.36	309 ± 195	6.62 ± 3.12	0.65 ± 12.7	$\mathbf{7.74 \pm 12.7}$	1.58 ± 0.55	0.57 ± 0.77
Isoprene	0.02 ± 0.02	0.06 ± 0.06	0.41 ± 0.35	28.3 ± 28.6	1.97 ± 0.84	$\mathbf{1.69 \pm 0.20}$	0.20 ± 0.20	0.70 ± 0.25	2.67 ± 4.32
Limonene	0.07 ± 0.06	0.02 ± 0.01	0.00 ± 0.00	7.03 ± 10.0	0.08 ± 0.07	$\mathbf{1.91 \pm 1.87}$	0.20 ± 0.20	0.30 ± 0.28	$\mathbf{68.3 \pm 77.3}$
α-Pinene	0.04 ± 0.02	0.00 ± 0.00	0.01 ± 0.01	28.7 ± 29.3	0.13 ± 0.13	0.00 ± 1.50	0.83 ± 1.40	0.04 ± 0.01	0.21 ± 0.37
β-Pinene	0.06 ± 0.05	0.01 ± 0.00	0.05 ± 0.03	17.4 ± 22.0	0.15 ± 0.01	0.03 ± 1.72	0.99 ± 1.72	0.05 ± 0.04	1.02 ± 1.20

to the different sources associated with the emission sector analyzed.

As can be seen, road traffic VOC EFs presented the highest values, especially for two-wheeled two-stroke engines (TW 2T). The EFs for TW are up to 3 orders of magnitude greater than those observed for diesel vehicles (HDDVs and LDDVs) and LDGVs. They are dominated by alkanes and aromatic compounds (Tsai et al., 2003). Likewise, we highlight the presence of isoprene and terpene emissions in TW sources, whose contribution cannot be neglected. In terms of engine differences, four-stroke engine emissions had lower EFs than those observed for two-stroke engines. This result is in agreement with other works (Tsai et al., 2000; Montero et al., 2010) which analyzed the concentration of individual VOC in the tailpipe exhaust, showing the differences between two-stroke and four-stroke engine emissions.

Gasoline vehicle EFs are higher than diesel vehicles and they are dominated by aromatic compounds, including xylenes, trimethylbenzenes and toluene (45, 25 and 15 % respectively, in relative contribution, % wt). The main differences associated with both fuel emission profiles were related to the higher relative contribution of benzene (37 % for LDDV) and alkanes (18 % for HDDV) for diesel vehicles. Charcoal making (CHM), wood (FW) and charcoal burning (CH) emissions were characterized by the abundant presence of alkanes, benzene, and xylenes. Particularly in the case of FW, terpenes and isoprene show important contribution to the total sum of emissions (15 and 13 % respectively). The most abundant VOC species observed for open trash burning (WB) were terpenes (38 %) followed by toluene, trimethylbenzenes, benzene and alkanes. The sum of C_5–C_{10} VOC for this study shows a similar EF range in comparison with the sum of volatile organic compounds found in the literature (Christian et al., 2010). Despite the uncertainties associated with each method, high variabilities were found from different measurements related to the same emission source. For instance, the WB emission factors presented a high standard deviation (up to 100 %). This deviation could be related to the effect of many factors the can impact the burning process, including the combustion processes, the fuel chemistry, moisture, and geometry (Andreae and Merlet, 2001).

Individual VOC species were aggregated into species groups as proposed by the GEIA initiative that were introduced in the last EDGAR VOC inventory (Huang et al., 2017) (Tables S4, S5 and S6). In this way, a larger VOC database was considered, including 12 species of terpenes, intermediate VOCs (iVOCs from C_{11}–C_{16} n-alkanes), ketones and carbonyl compounds for a reduced number of sources (Table S4). The main differences obtained from this exhaustive speciation were related to the contribution of heavy alkanes (VOC6, with iVOCs the most important fraction, 50 %) and aldehydes (VOC22, 13 %) for HDDV

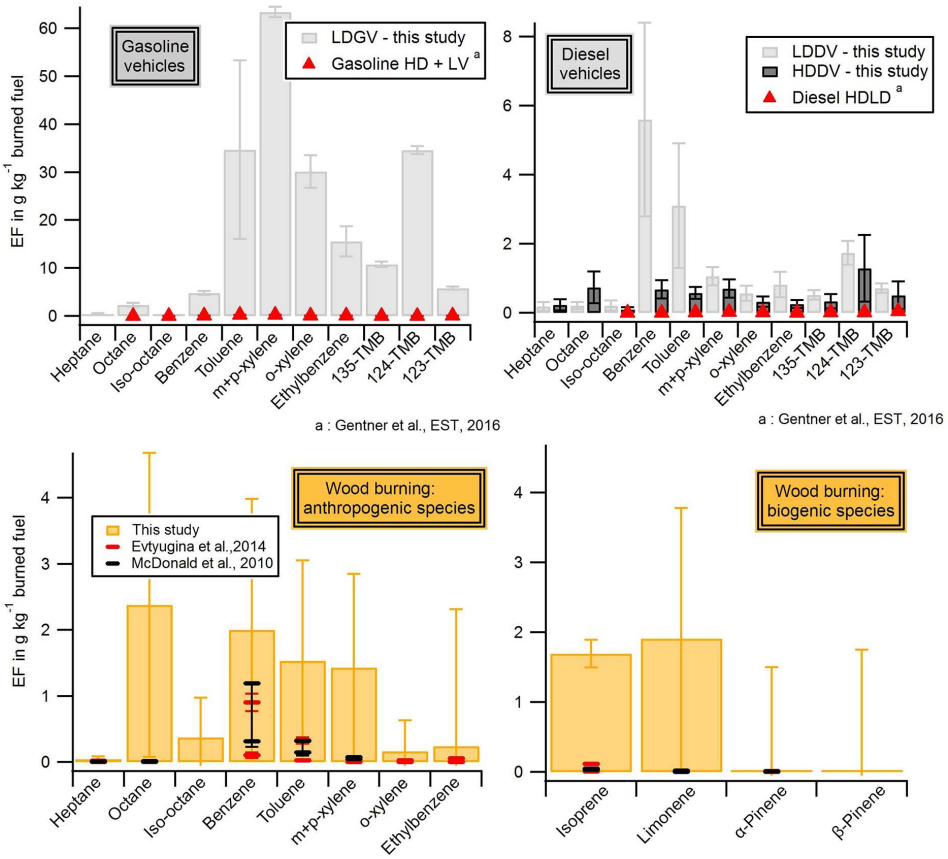

Figure 5. Comparison of VOC EF with the literature for traffic (light-duty gasoline vehicles, LDGV; light-duty diesel vehicles, LDDV; and heavy-duty diesel vehicles, HDDV) and wood burning. The bars correspond to the standard deviations of measurements

sources. The contribution of heavy alkanes from diesel was also observed in other studies (Ait-Helal et al., 2014; Dunmore et al., 2015). In the same way aldehydes presented a considerable contribution in CH and CHM emissions and terpenes were also significant (14 %) in wood-burning emissions (FW).

The determined EFs for gasoline (LDGV) and diesel (LDDV and HDDV) vehicles and wood burning have been compared (Fig. 5) to the ones from the literature (McDonald et al., 2000; Gentner et al., 2013; Evtyugina et al., 2014) in order to evaluate the magnitude of the West African anthropogenic emissions of VOCs. Numbers are reported in Table S7 of the Supplement. Regardless of the motorization, the EFs in West Africa are higher than the most recent ones reported in California in the Caldecott Tunnel by Gentner et al. (2013). The differences span 2 orders of magnitude. The EFs for wood burning are also higher by between a factor of 2 and a factor of 100 than those reported in the literature for different types of hardwood used in woodstoves and fireplaces (Fig. 5). The presence of isoprene and monoterpenes in WB emissions is also observed in the literature. However, in this study, their levels are as significant as the ones of aromatic compounds.

These new VOC data were also used to evaluate the emission inventories in Côte d'Ivoire as a first case study. VOC emissions were calculated by combining the new speciated VOC EFs and statistical activity data provided by International Energy Agency (IEA) and then compared with those provided by the EDGAR inventory (EDGAR v4.3.2) for the road transport sector. For that purpose, the 15 VOCs were aggregated according to GEIA VOC groups (Table S4, Huang et al., 2017). In Fig. 6 the road transport emissions for the year 2012 in Côte d'Ivoire are compared. Notwithstanding the selected number of VOC species, a large discrepancy can be noted between both profiles (Fig. 6a): the EDGAR inventory underestimates VOC emissions by a factor of 50. In terms of composition, the main differences are observed for the VOC6 group ($> C_6$ alkanes), which presents a greater contribution in the EDGAR inventory. This disparity could also be related to the few VOC species that were analyzed for the VOC6 group in our study. In contrast, aromatic compounds dominate the updated emission inventory, especially for C_8 and C_9 compounds (40 and 25 %, respectively, Fig. 6b). Since the reactivity is different for each species, the inaccuracies in the VOC speciation also have consequences in the estimation of their impacts. The scarcity of measure-

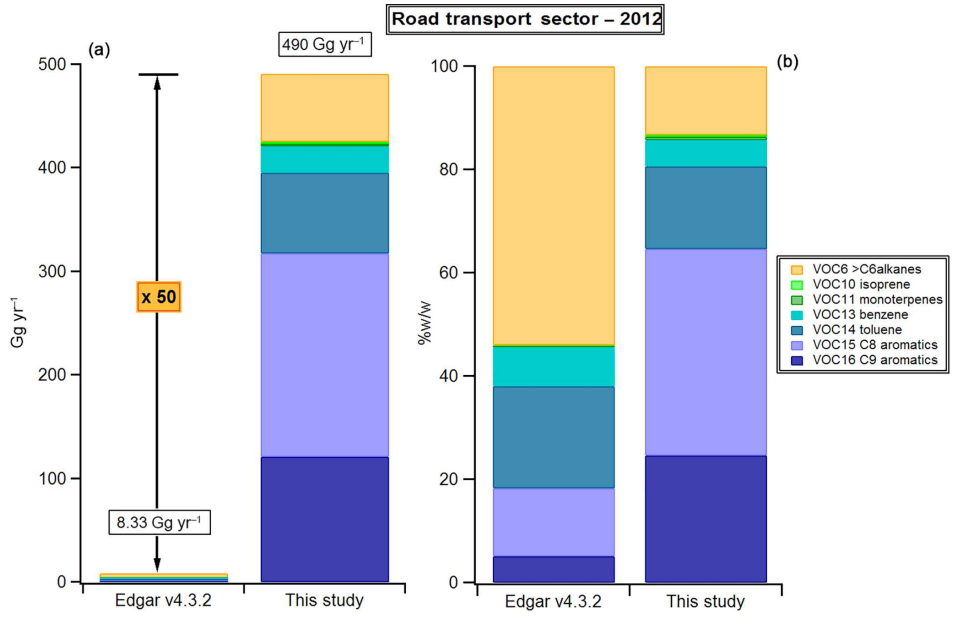

Figure 6. Comparison of Côte d'Ivoire VOC emissions with the Edgar v4.3.2 inventory (Huang et al., 2017) for the road transport sector in 2012: **(a)** absolute emissions in Gg yr^{-1} and **(b)** relative mass emissions for selected VOC groups.

Table 6. EF for fuelwood burning of this study for field and combustion chamber measurements.

Measurements	Methods	EF (g kg^{-1} fuel)			MCE
		EC	OC	TPM	
Field	Filter	1.216	13.11	55.22	0.76
Lannemezan	Filter	0.078	1.13	6.658	0.94
Edinburgh	HF1 filter	0.095	0.557	2.790	0.93
	hF1 filter	0.049	0.356	2.194	0.95
	HF1: AMS, SP2	0.444	0.742	nd	0.97
	hF1: AMS, SP2	0.352	0.674	nd	0.98

ment and source profile data in Africa was previously pointed out in the development of the EDGAR inventory, which leads to considering the priority of this region for future inventory improvements (Huang et al., 2017). Our results show that emissions of anthropogenic VOCs by actual emission inventory are largely underestimated and show the usefulness of in situ measurements in real conditions to derive realistic emission factors and subsequent emissions of better quality.

4.2 Combustion chamber measurements for fuelwood burning

4.2.1 EF comparison between field and combustion chamber measurements for wood burning

Table 6 summarizes EFs of EC, OC and TPM experiments carried out in the combustion chambers. As can be seen, field EF values obtained with the same methodology of "filter sampling" are a factor of 16 and 11 higher than those of the Lannemezan combustion chamber for EC and OC respectively, and a factor of 16 and 28 higher than those of the Edinburgh combustion chamber. Quantitatively, it can be seen that a dilution factor of around 8 exists between field and combustion chamber measurements. Indeed, CO / CO_2 field measurements (≈ 0.32) are 8 times higher than that of Lannemezan (≈ 0.04), and CO_2 is roughly the same. The same factor is obtained for the EF_{field} / $EF_{Lannemezan}$ ratio for EC and total mass. This is not so clear with the Edinburgh results. Edinburgh and Lannemezan MCE results show that there is more flaming during these tests than during the field tests due to higher MCE (≈ 0.94) rather than in the field (≈ 0.76). This important difference between field and combustion chamber results may be linked to many factors such as the different combustion conditions (different MCE) and the high dilution of plumes occurring in combustion chambers. Indeed, field EF measurements are performed within the plume before its dispersion. In terms of quantities, field values are representative of primary emissions, which have to be computed in emission inventory algorithms. Finally, we have compared EFs (EC and OC) obtained at the Edinburgh combustion chamber with two sampling methods: the method using the filter sampling and QTRAK-7575 on the one hand and the AMS-SP2 and FPA CO-CO_2 analyzer method on the other hand. MCEs obtained with FPA are slightly higher than those of QTRAK, which shows a stronger flaming condition. But the differences are more pronounced with EFs, where EFs(EC) obtained from AMS-SP2 measurements are 100 times higher than those obtained from filter methodology. These differences in addition to those listed above may be due to the carbon measurement method (thermal method for

Table 7. Relative contribution of EFs (EC and OC) for wood burning per size class to total size.

Size class	EF (EC)	EF (OC)	EC / TC
PM_{10}	86 %	72 %	0.064
$PM_{2.5}$	81 %	72 %	0.062
PM_1	82 %	59 %	0.078
$PM_{0.25}$	77 %	51 %	0.094

filters (EC) and incandescence method using single-particle methods for SP2 (BC); Petzold et al., 2013).

However, it should be underlined that combustion chamber measurements are very complementary for field measurement. First, it allows more measurements to be performed than on the ground. Second, it allows a better understanding of the impact of combustion processes on aerosol composition and size class (e.g., $PM_{2.5}$, PM_1).

4.2.2 Wood burning EFs per size class

Relative contributions of different size classes (PM_{10}, $PM_{2.5}$, PM_1, and $PM_{0.25}$) to total size of EC and OC EFs are shown in Table 7. As can be seen, such a contribution is less variable for EC EFs from fine particles ($PM_{2.5}$: 81 %) to ultrafine particles ($PM_{0.25}$: 77 %) than for OC EFs, which varies from 72 to 51 % for $PM_{2.5}$ and $PM_{0.25}$, respectively. This means that EC EFs particularly predominate in the ultrafine size fraction. These results are in line with those reported by previous works on fuelwood burning (Guofeng et al., 2012; Danielsen et al., 2011; Purvis et al., 2000). Table 7 also shows that EC / TC is consequently different in the different aerosol size fraction with larger values in the ultrafine sizes (0.094) than in the coarse ones (0.064). The domination of fine particles from fuelwood burning is a health concern for those who use wood for cooking, since fine particles can penetrate deeper into the lungs and are often associated with many toxic compounds (Englert, 2004; Pope et al., 2009; Val et al., 2013).

5 Conclusions

This study characterizes the emissions of many sources specific to Africa. EFs of EC, OC, TPM and specified VOCs were determined for biofuel (tropical fuelwood, charcoal and charcoal making), fossil fuels used in traffic (gasoline and diesel) and trash burning. Field EF measurements were performed for all studied sources as well as in combustion chambers for hevea fuelwood in order to obtain EFs per size fraction.

During field measurements, several tests were performed per source studied here in order to get the more representative EFs for each source. The mean EFs of EC, OC and TPM are 0.98 ± 0.46, 11.05 ± 4.55 and $41.12 \pm 24.62\,g\,kg^{-1}$ fuel for wood burning and 0.65 ± 0.30, 1.78 ± 2.80 and $12.75 \pm 9.03\,g\,kg^{-1}$ fuel for charcoal burning, respectively. Note that wood burning emits more particles than charcoal burning. Particle EFs for biofuel burning are comparable to the range of those found in the literature (measurements and values used in inventories in Africa) excepted EF(OC) for wood burning. In the combustion chamber measurements, the EFs of the particles for hevea wood burning per size class show that EC is mainly in the fine fraction. The significant difference between the combustion chamber and field measurements suggests that EFs and chemical composition are strongly affected by variables that differ according to field and laboratory procedures. Even if field values are more representative of primary emissions, combustion chamber allows for more measurements to be performed than in the field, allowing for better understanding the impact of wood combustion processes on aerosol composition and size class: these two types of measures remain complementary. EFs for fossil fuel burning in traffic are strongly dependent on vehicle age. The older the vehicles, the higher EF values for carbonaceous particles are; these values are sometimes up to 100 times higher than the EF values found in the literature generally for recent vehicles. These older vehicles are the most used in African countries and can be characterized as typical "African EFs". In contrast, particles EFs for recent (under 10 years old) vehicle models are similar to published EF values for gasoline and of the same order of magnitude for diesel. The mean EFs of EC, OC and TPM are 0.62 ± 0.49, 1.10 ± 0.77 and $7.0 \pm 2.80\,g\,kg^{-1}$ fuel for road gasoline and 3.08 ± 1.96, 2.14 ± 1.20 and $34.70 \pm 20.13\,g\,kg^{-1}$ fuel for road diesel, respectively.

Finally, the EFs of more than 50 VOCs have been determined for the first time in West Africa and integrated into the GEIA VOC groups available for the development of emission inventories. These EFs showed that emission profiles are dominated by aromatics (up to 80 % for some traffic-related sources). The greatest emissions are observed for two-stroke two-wheelers, which can be higher than 3 orders of magnitude compared to the EFs observed from LD and HD vehicles. The presence of terpenes in biofuel burning emissions was considerable, as were heavy alkanes (iVOCs), reaching up to 50 % in diesel-related sources. Comparison to recent literature worldwide points out the greatest levels of anthropogenic African EF for VOC and the relevance of in situ measurements to derive realistic and representative emission factors. Such measurements should be complemented with experiences under controlled conditions.

This original database will be useful for improving and updating African emission inventories, which will reduce emission uncertainties and help to better assess impacts on climate, air quality and health. The emissions obtained with these new EFs in this study can also help to identify key source categories. This could help policy makers implement new policies to mitigate emissions from major emission sources.

Data availability. The emission factor data from this study are original and are publicly available in the Supplement.

The Supplement related to this article is available online at https://doi.org/10.5194/acp-18-7691-2018-supplement.

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

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