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Ubiquity of anthropogenic terpenoids in cities worldwide: emission ratios, emission quantification and implications for urban atmospheric chemistry

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Abstract (250 words)

Terpenoids (isoprene and monoterpenes) are highly reactive Volatile Organic Compounds (VOCs) known for decades for their biogenic origin. Here, we discuss the nature and magnitude of their anthropogenic emissions. We compiled and re-analyzed fourteen datasets of in-situ VOC observations collected over the last decade in contrasting urban areas from mid-latitudes to subtropical regions. We show the systematic presence of anthropogenic terpenoids in urban ambient air with clear covariations with anthropogenic compounds ($R^2 > 0.50$) even during mid-latitude winters. Despite the emerging importance of monoterpene emissions from consumer products in North American cities, there is some evidence of monoterpene emissions from tailpipe exhaust in cities of the developing world. The traffic-related fraction of monoterpenes is estimated and can account for up to 40% of their ambient levels. The anthropogenic emission ratios (ER) of some terpenoids (isoprene, α-pinene and limonene) are estimated and spatially compared. The anthropogenic emissions of terpenoids are indirectly estimated from those ER combined to regional and global emission inventories (CAMS-GLOB-ANT_v4.2) at urban and country scale focusing on France, Lebanon and Vietnam. Those anthropogenic emissions do not represent more than 3% of other anthropogenic VOC emissions. However, they dominate by one to three orders of magnitude the reactivity of other anthropogenic VOCs regarding NO_3 oxidation and ozonolysis. This study raises two questions which need further investigations in the future.: i) the significance of terpenoid emissions from traffic, especially in urban areas of the developing world, ii) the role of anthropogenic terpenoids in nighttime and wintertime atmospheric chemistry at mid-latitudes

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Introduction

The terpenoids $(C_5H_8)_n$ are amongst the most abundant biogenic volatile organic compounds (BVOCs) in the Earth system. They include isoprene (n = 1) and monoterpenes (n = 2) with emissions of 465 $TgCyr^{-1}$ and 107.5 $TgCyr^{-1}$, respectively (Messina et al., 2016). These compounds are of great importance in atmospheric chemistry given their very high reactivity towards major oxidants (OH, NO_3, ozone). They modify the oxidizing capacity of the atmosphere and the residence time of greenhouse gases such as methane (Chiemchaisri et al., 2001, Wuebbles et al., 1989), contribute to ozone (Chameides et al., 1988, Curci et al. 2010, Jacob and Wofsy, 1988) and to the secondary organic aerosols (SOA) formation (Claeys et al., 2004, Griffin et al., 1999), which have a significant impact on the radiative balance of the atmosphere and which, at high concentrations, are also damaging to human health. On a global scale, simulations have shown that monoterpenes account for 20% of the organic aerosol in the atmosphere, with an additional 12% coming from isoprene (Pye et al., 2010).

The anthropogenic origin of isoprene from vehicle exhaust has been well described in urban atmospheres since the seminal work by Borbon et al. (2001). However, the evidence for anthropogenic sources of monoterpenes is more fragmented. The emissions of monoterpenes from biomass burning have been described in combustion chambers (Akagi et al., 2011, Gilman et al., 2015, Keita et al., 2018, Koss et al., 2018, Sekimoto et al., 2018) and in wintertime ambient air (Rouvière et al., 2006; Hellen et al., 2012). These compounds are also widely used in consumer or household products (Steinemann et al., 2011; Yeoman et al., 2020). McDonald et al. (2018) demonstrated that the use of volatile chemical products (VCPs)—including personal care products—constituted half of the fossil fuel VOC emissions in North American cities. Since then, many research efforts in the US have been put forward VCP emissions: identification of VCP emission category tracers (Coggon et al., 2018; Gkatzelis et al., 2021a), source apportionment of VCP emission contributions (Gkatzelis et al., 2021b), implementation

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of VCP emissions in emission inventories (Mc Donald et al., 2018, Coggon et al., 2018). From these studies, more than 50% of urban monoterpene load is explained by VCP-dominated emissions in Boulder, CO and New York City, NY. At the same time, near-source experiments in the developing world have recently demonstrated the potential role of fossil and non-fossil fuel combustion emissions on the urban burden of monoterpenes, including vehicle emissions in the city of Abidjan, South West Africa (Keita et al., 2018 ; Dominutti et al., 2019). In that work, speciated monoterpenes were directly measured at the exhaust pipe of the running vehicular fleet in a significant amount (Keita et al., 2018).

While the aforementioned studies suggest an anthropogenic origin for monoterpenes, their quantification remains poorly representative in space. As part of the DATAbASE project (Do Anthropogenic Terpenoids mAtter in AtmoSpheric chEmistry?), the present study (i) searches for the systematic presence of anthropogenic terpenoids (ii) estimates their anthropogenic emission ratios and discusses the potential role of traffic emissions for monoterpenes (iii) quantifies their anthropogenic emissions by combining emission ratios and emission inventories focusing on France, Lebanon and Vietnam (iv) evaluates their atmospheric impacts by implementing reactivity metrics. This study is mostly based on the re-analysis of in-situ observations collected in urban environments worldwide, complemented by new observations.

2. Measurements

VOC measurements were obtained during field campaigns over the last decade in urban areas at various latitudes, including three of the ten largest cities: Paris and London (Western Europe), Los Angeles (North America), Abidjan (West Africa), Athens, Beirut and Istanbul (Eastern Mediterranean), São Paulo (South America), Beijing (Asia). During these campaigns, a large spectrum of VOCs was measured by off-line (sorbent tubes and canisters) and/or on-line techniques (Gas chromatography –GC - coupled to a Flame Ionization Detector – FID - Mass Spectrometer – MS -, Proton Transfer Reaction MS – PTR-MS) as described in previous papers

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(Ait-Helal et al., 2014; Baudic et al., 2016; Thera et al., 2019; Borbon et al., 2013; de Gouw et al., 2018; Salameh et al., 2015; Panopoulou et al., 2018, 2020; Dominutti et al., 2019, Dominutti et al., 2020). Most of the aforementioned campaigns included additional measurements of carbon monoxide (CO) and nitrogen oxides (NOx). VOCs included isoprene, some speciated monoterpenes (α-pinene, β-pinene, camphene, limonene, myrcene, p-cimene, 1,8-cineole, Δ3-carene), total monoterpenes (protonated mass m/z 137 by PTRMS) and anthropogenic VOCs. The available species for the 14 datasets are reported in Table S1 of the Supplement Information. The protonated mass m/z 81 known as a fragment of m/z 137 (Yuan et al., 2017) has not been considered here. Erickson et al. (2014) have reported that bicycloalkanes emitted by diesel engines also show a fragment at m/z 137 commonly associated to total monoterpenes. These campaigns combined continuous ambient measurements at one or two urban/suburban sites and, for some of them, near-field source measurements like traffic, roadway, road tunnel, vehicle exhaust plume, and domestic heating. All of these observations have been re-analyzed for this study. The DATAbASE dataset has been completed by two recent ambient and/or road tunnel measurement campaigns in São Paulo, Brazil (SOPRO project - Chemical and toxicological SOurce PROfiling of particulate matter in urban air) in 2018 and an intensive field campaign in Ha Noi, Vietnam in 2019 ("A Two City study of Air Quality in Vietnam", NERC-UK in Text S1) (Dominutti et al., 2023, Duong et al., 2022). During the SOPRO project, VOC canister samples were collected in two tunnels in the São Paulo Metropolitan Area during two one-week duration field experiments as described in Nogueira et al., (2021) (Jânio Quadros Tunnel -46° 41' 36.28" W, -23° 35' 15.81 S" and Rodoanel Tunnel -46° 47' 43.85 W", -23° 27' 38.94 S"). Details on VOC sampling and analysis are provided in the Supplement Information (Text S1). During the Ha Noi project, ambient and near-source measurements at the tailpipe of representative vehicles have been silmultaneously performed. Online ambient VOCs were measured for more than 700 hours in March 2019 at an urban site in Hanoi, Vietnam (Hien et

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al., 2022, Dominutti et al., 2023) (21°0'24" N, 105°49'4"E). Ambient VOC measurements were performed using a dual channel GC-FID system. Near-source VOC measurements were performed with off-line sorbent tubes following the same strategy and analytical procedure as the one described by Dominutti et al. (2019) in Abidjan, SW Africa (Table S2). Off-line tube analysis was performed with a TD-GC-MS system. Technical details are provided in Text S1 of the Supplement Information.

The lack of metrological traceability is a critical point when combining and comparing datasets collected at different periods and by different groups. This is challenging for monoterpenes for which no harmonized calibration standards exist. Mermet and co-workers (2019) pointed out that the calibration step was the main source of uncertainty, stressing the need for certified gaseous standards for a large panel of BVOC. Therefore our results should be interpreted with caution because one cannot exclude analytical biases.

Figure 1 and Table 1 summarize the locations of the campaigns and the observed levels. The observations of isoprene are systematic in VOC urban studies. Conversely, observations of monoterpenes are scarce and heterogeneous. Pinenes, limonene and, to a lesser extent, camphene are usually the ones detected. Contrary to isoprene, the traffic origin of terpenes has received little attention compared to biomass burning and, more recently, VCP usage. While the data analysis relies on the fourteen datasets, we will put forward locations that combine ambient and near-source measurements and/or provide detailed speciation of terpenoids at different temporal scales (hourly to seasonal). These cities are Abidjan, Athens, Beirut, Istanbul, Ha Noï, Paris and São Paulo; they encompass the heterogeneity of urban environments worldwide regarding fossil, non-fossil fuel, and biogenic emissions, combustion technologies and practices, level of emission regulation, and climatic conditions (from mid-northern to subtropical latitudes).

3. Urban composition and variability of terpenoids

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3.1. Spatial and temporal variability of terpenoids

The map in Figure 1 depicts concentration levels of selected anthropogenic VOCs (AVOC including acetylene, ethylene, propene, benzene, and toluene) and terpenoids at some of the target locations of the DATAbASE dataset. Regardless of location and season, the presence of isoprene and monoterpenes is always depicted at several hundreds of ppt for the former and several tens of ppt for the latter. In Ha Noi, the levels of myrcene and Δ^3-carene reach 300 ppt. Isoprene shows an opposite trend to those of AVOC, with higher concentrations in summer due to its well-known temperature and light-dependent biogenic origin. Monoterpenes show a different seasonal behavior between urban locations. Monoterpene levels are higher in summer than in winter in Beirut, while they are higher in winter in Paris and Athens (Panopoulou et al. 2020). In Paris, monoterpenes are represented by their protonated mass mz 137 ; one cannot exclude the interference from anthropogenic bicycloalkanes, as shown by Erikson et al. (2014). In summer, the presence of monoterpenes is modulated by their biogenic origin and their atmospheric reactivity. By assuming that anthropogenic emissions of monoterpenes are enriched in limonene compared to pinenes (Coggon et al., 2021), the greatest abundance of limonene in Abidjan, Beirut, and Ha Noi atmosphere (limonene/α-pinene ratios of 2.8, 1.8 and 1.3 on average, respectively) also indicates the effect of anthropogenic emissions. One should note that in Athens, this ratio falls down to 0.47 (Panopoulou et al., 2020) even in winter during which α-pinene is mostly of anthropogenic origin. The systematic detection during winter and at, sometimes, higher levels than in summer (Paris, Athens) raises the question of their anthropogenic origin associated with weaker chemical loss processes.

3.2. An examination of the wintertime variability of monoterpenes.

The time series and the diurnal variation of some monoterpenes and anthropogenic VOCs are displayed in Figure 2 for three selected cities representing various latitudes: Paris, Beirut, and

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Ha Noi. Among commonly measured anthropogenic tracers (toluene or acetylene), ETBE (Ethyl tert-butyl ether or $C_6H_{14}O$) was measured in winter in urban Paris (Roukos et al., 2009). ETBE is an oxygenated additive to reformulated gasoline with a k_{OH} of 7.38×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and is, therefore, a good single marker of traffic emissions. Indeed another origin for other AVOC cannot be excluded in winter. In Paris, Baudic et al. (2016) showed the solvent use origin of toluene and the significant contribution of wintertime wood burning combustion to VOC loads (30%).

All measured terpenes co-vary with anthropogenic VOCs in winter (R^2>0.50). On a 24-hour basis, monoterpenes show the typical bi-modal daily variation of human-made VOCs with morning and late afternoon peak maximum. The bi-modal distribution iw well-marked for Ha Noi. The correlation (R^2=0.51) of the sum of monoterpenes (m/z 137) with ETBE in the ambient atmosphere of Paris also suggests their potential origin from traffic. However, the contribution of other co-emitted anthropogenic sources like the use of personal care products (Coggon et al., 2018) or car air fresheners (Steinemann et al., 2017) cannot be excluded. Coggon et al. (2018) have highlighted that correlations between benzene and D5-dimethylsiloxane, a personal care product tracer, were rather indicative of co-emitted sources with the same emission patterns. D5-dimethylsiloxane is not available in the DATAbASE dataset. In some cases, the covariation is altered by changes in environmental conditions, such as changes in wind regimes like in Beirut (Figure 2d). In Beirut, monoterpene concentrations increased remarkably compared to the ones of toluene from February 6. At this period, the wind direction shifted to the east and the measuring site was downwind of a pine forest extending further east. Moreover, the average temperature increased (14.6°C±2.5) while the average relative humidity decreased (45%±22) compared to the average values observed under the marine influence (12.1°C ±1.8 versus 62%±15). Together with precipitation, temperature and relative humidity are the main climatic

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drivers of biogenic emissions of monoterpenes, as demonstrated in Cyprus, Eastern Mediterranean by Debevec et al. (2018).

3.3. Traffic emissions: a potential source of monoterpenes at urban scale?

While a traffic origin of monoterpenes is suspected, the contribution of co-emitted sources like personal care product usage and car air fresheners cannot be excluded based on the most recent studies in North American cities (Coggon et al., 2018; Gkatzelis et al., 2021b) and on car air freshener emissions (Steinemann et al., 2020). Because the correlation between monoterpenes and anthropogenic tracers from ambient observations cannot be unambiguously attributed to exhaust tailpipe emissions, one component of traffic emissions, we have investigated in more detail observations of monoterpenes collected in tunnels and during near-source tailpipe experiments. This review is based on the literature and the DATAbASE dataset (Figure 3 and Table S3).

While the number of observations is limited (Table S3), some monoterpenes (pinenes and limonene) have been already detected in tunnels in Asia, in the Middle East, and northern mid-latitudes (Paris, Guy Moquet tunnel, this study); emission factors or mixing ratios are usually in the same order of magnitude. In Figure 3A, we show the clear covariation of α-pinene and limonene with benzene in the Guy Moquet tunnel in Paris with correlation coefficients higher than 0.90. Similarly to benzene, the concentration levels of monoterpenes clearly peak at traffic rush hours when vehicle speed drops down and traffic becomes congested: an enhancement of more than a factor of 20 is observed compared to periods of wind speed above 80 $km.h^{-1}$. Coggon and co-workers have demonstrated that the D5-dimethylsiloxane emitted by personal care products worn by car passengers could mix with tailpipe emissions when the vehicle fan is on. Steinemann et al. (2020) report the occurrence of limonene and pinenes as well as benzene and toluene, in car air fresheners. Therefore, the co-emission of monoterpenes commonly used in fragranced VCP with the ones from tailpipe exhaust cannot be excluded in tunnels. While

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measurements and detection of monoterpenes from the transport sector are scarce, recent measurements in Côte d'Ivoire (Dominutti et al., 2019) and Vietnam (this study and Dominutti et al., 2023) reveal the systematic and significant presence of terpenoids (Table S3). Monoterpenes are usually higher in diesel exhaust compared to gasoline vehicle exhaust and are strongly emitted by 4 strokes -2 wheelers and 3-wheelers in these two cities of the developing world. Only one European study reports the presence of a-pinene in biofuel diesel exhaust (Lopes et al., 2014). The paucity of monoterpene measurements might be explained by the fact that they are usually not the compounds of interest when exhaust emissions are investigated.

In Figure 3B, we report the quantities of speciated emitted monoterpenes from the aforementioned studies relative to the ones of benzene. While the number of near-source studies is limited, we show the presence of monoterpenes in traffic emissions in the four target regions. They can represent up to 60% of the benzene (in mass), but they usually do not exceed 20%. While the presence of monoterpenes in tunnels could be a combined effect of co-emission of personal care and exhaust, their detection at the exhaust of various categories of vehicles indicates their potential fossil fuel combustion origin, and even for limonene. In other words, traffic constitutes a direct source of monoterpenes by combustion or a vector of other emission-types like personal care products. In the following section, we will discuss the traffic-related component of anthropogenic emissions of terpenoids. The traffic-related component of anthropogenic emissions of terpenoids not only includes their direct exhaust emission by fuel combustion but also their potential release from their fragranced VCP from the interior of the vehicle.

5. Contribution of traffic-related emissions to urban monoterpene concentrations

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The method adapted from Borbon et al. (2018) consists of estimating the fraction of each monoterpene originating from traffic at some urban sites. The fraction of monoterpenes coming from traffic is calculated by dividing their calculated concentrations from traffic over their measured ambient concentrations. The monoterpene concentration originating from traffic emissions ($[terpene]_{traffic}$) is expressed as follows:

$$[terpene]_{traffic} = ([tracer]_{traffic} - [tracer]_{bckgd}) \times ER_{traffic}. \quad \text{(Equation 1)}$$

where $[tracer]_{traffic}$ is the concentration of a traffic tracer, $[tracer]_{bckgd}$ is the regional background concentration of the traffic tracer and $ER_{traffic}$ is the traffic emission ratio between terpenes and the traffic tracer.

This equation is derived from the one developed by Borbon et al. (; 2018). The $[terpene]_{traffic}$ term is available for Abidjan, Athens, Beirut, and Paris datasets for which near-traffic observations have been collected in addition to the ones at urban sites (Table 1). $ER_{traffic}$ is determined from the slope of a two-sided linear regression fit between terpenes and an anthropogenic tracer at traffic rush hours measured at the traffic sites (Borbon et al., 2013; Warneke et al., 2007). Except in Abidjan, where terpenes have been directly detected at exhaust pipes (Table 1), one cannot exclude that the $ER_{traffic}$ include co-emissions from personal care product and exhaust in Athens, Beirut, and Paris. $[tracer]_{bckgd}$ is determined on an hourly basis in Paris from a linear interpolation of minimum concentrations observed over a 4-day period and described in Borbon et al. (2018). Those background values were shown to be consistent with the ones reported at two rural French stations (Borbon et al., 2018). In Beirut and Athens, we use the concentrations measured at the East Mediterranean background site of Cyprus (Debevec et al., 2018). In Abidjan, we used the concentrations measured over the Guinea Gulf by the Safire French ATR 42 aircraft, representing the regional background levels (Brito et al., 2017).

The calculated traffic-related fraction should be seen as an upper limit because one cannot exclude the potential effect of chemistry that alters total monoterpene concentrations. The

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calculated average fractions and their standard deviation are reported in Figure 4 for Abidjan, Athens, Beirut, and Paris. The contribution of traffic varies spatially for a given compound and between species. Except for limonene in Athens and α-pinene in Paris in winter, the fraction of monoterpenes from traffic never exceeds 40% on average and goes down to 10% with high relative standard deviations. In winter, limonene is fully explained by traffic emissions in Athens within the uncertainties of the calculated contributions. Given the high standard deviations, a moderate seasonality is depicted for α-pinene and limonene in Athens and Beirut, respectively. In Paris, the traffic-related fraction of α-pinene shows a well-marked seasonal variability. While displaying space-dependent patterns, the fraction of monoterpenes from traffic can be significant at the urban scale. This fraction is expected to be modulated by the intensity of other sources like VCP-related ones and controlled by climatic drivers like biogenic emissions in summer and domestic burning.

5. Determination of anthropogenic emission ratios of urban terpenoids

The anthropogenic emission ratios (ER) of urban terpenoids versus seven anthropogenic tracers (ethyne, ethylene, propene, benzene and toluene, CO and NOx) were estimated from ambient data. As for $ER_{traffic}$ in the previous section, the anthropogenic ERs are derived from the slope of a linear least square regression fit as described in Borbon et al., 2013. Here, the data have been first carefully examined in order to exclude the effects of biogenic emissions of terpenoids and the daytime and nighttime chemistry on the distribution of the scatterplots (see sections 4.1 and 4.2). The selected AVOC tracers were discussed previously (Borbon et al., 2018).

5.1. Effect of biogenic emissions

The effect of biogenic emissions is investigated by plotting the terpenoid mixing ratios versus those of anthropogenic tracers by making a distinction between daytime and nighttime and winter and summer datasets. In summer, regardless of the city, a common pattern is depicted for isoprene (Figure 5): its daytime scatterplots are diffuse due to the presence of its temperature

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and light-dependent biogenic emissions, as already depicted in past studies (Borbon et al., 2001). At night, the scatterplots get narrower and lie along a linear regression fit due to a common anthropogenic origin and the lack of isoprene biogenic emissions. In winter, two patterns are depicted. As illustrated by London (Figure 5), daytime and nighttime distributions are well-superimposed due to a common anthropogenic origin and the lack of isoprene biogenic emissions. In contrast, in Athens (not shown) and São Paulo, the diffuse scatterplots during the day indicate the presence of biogenic emissions of isoprene as in summer. These wintertime emissions are favored by the presence of evergreen trees in São Paulo and temperatures high enough to stimulate isoprene emissions in winter (Dominutti et al., 2016). As a consequence, a nighttime temporal filter has been applied to the summertime observations due to the lack of biogenic isoprene emissions and the Athens and São Paulo wintertime dataset (figure 5c and 5d). In winter, the effect of biogenic emissions is negligible, and no filter is applied (Figure 5b). For monoterpenes, different patterns are depicted (Figure 6). Camphene and limonene in Beirut behave similarly to isoprene in summer. Other monoterpenes (pinenes), total monoterpenes (Paris), p-cymene, and Δ3-carene (Ha Noi) significantly correlate with anthropogenic tracers during the day and night, either during both seasons or in winter. In Beirut, an additional meteorological filter has been applied, as illustrated in Figure 2, by retaining observations under oceanic wind regime in winter. The emissions of biogenic monoterpenes cannot be excluded at night and have been already depicted in various compartments of the forest canopy (branch, stem and litter) (Staudt et al., 2019). Unlike isoprene, monoterpenes are stored in specialized structures in many plants and can be released into the atmosphere by temperature-controlled diffusion even at night. However, the significant correlation between monoterpenes and anthropogenic tracers at night suggests that the nighttime biogenic contribution is negligible in the explored urban environments (Fuentes et al., 2000).

5.2. Effect of chemistry

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The effect of daytime OH photochemistry and nighttime chemistry is investigated by looking at the daytime over nighttime average concentrations versus k_{OH} kinetic constants and the nighttime R^2 versus k_{O3} and k_{NO3} following de Gouw et al. (2018). Those effects are investigated in two contrasting urban environments, Paris and Beirut, regarding emissions, emission policies and meteorology and for which a full-detailed description of the VOC dataset is available (Borbon et al., 2013; Salameh et al., 2017) (Figure 7 and 8). We also report the data from Athens as described in Panopoulou et al. (2020) in Figure 8. In winter, the day-to-night ratios are usually higher than 1 and are independent of $k_{OH,}$ suggesting that the effect of photochemistry can be neglected even for the most reactive compounds like alkenes and terpenoids (Figure 7). Dilution and emissions control the diurnal variability of VOC concentrations, as already suggested by Borbon et al. (2013) in Paris and Salameh et al. (2015) in Beirut. In summer, the feature is different: the ratios lie along the single exponential fit derived by de Gouw (2018) on VOC data in Los Angeles. This suggests the potential effect of daytime photochemistry. However two groups of compounds deviate from the fit: C4-C5 alkenes and terpenoids (isoprene, limonene). Regardless of the city, alkenes deviate from the fit with higher ratios than the ones predicted by the only daytime chemistry. First reason is the effect of nighttime chemistry on the daytime-to-nighttime ratio. While there is no clear degradation of the quality of the nighttime fit towards ozone chemistry in both cities in Figure 8, R^2 decreases with increasing k_{NO3} while staying statistically significant. However some differences exist among terpenes and the most reactive ones like a-pinene, that shows good correlation at night in Beirut and in Athens with an R^2 higher than 0.6 (Panopoulou et al., 2020). Second reason is the additional effect of other sources during the day like biogenic emissions. The effect of chemistry at night for alkenes have been already shown by de Gouw and co workers in Los Angeles due to ozone chemistry and to a less extent NO_3 radical (de Gouw et al., 2018). This resulted for instance in a small upward correction of the isoprene-to-CO

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emission ratios from 0.30 ppt/ppb CO (Borbon et al., 2013) to 0.52 ppt/ppb CO (de Gouw et al., 2018). In our case, the effect of nitrate radical chemistry is not excluded but not systematic among terpenes. As a consequence, the anthropogenic emission ratio has been derived from the nighttime regression fit in summer. However this ER should be seen as a lower limit in further discussions.

5.3. Spatial variability of anthropogenic ER of urban terpenoids

The estimated anthropogenic emission ratios of terpenoids worldwide are compared in Figure 9 for isoprene (figure 9A) and the two commonly measured terpenes in DATAbASE : α-pinene and limonene (figure 9B and C). The anthropogenic emission ratios follow the same trend along with the tracer and are in the same range of values for all terpenoids: the range of variability at the global scale span one order of magnitude and sometimes more when including the literature for CO (figure 9A). The emission ratio of isoprene-to-NOx is much less scattered, probably reflecting the single traffic origin of isoprene and NOx regardless of the urban area. In mid-latitude regions (Paris, London), the wintertime emission ratio is usually higher than the summertime one, while in Mediterranean or subtropical regions (Beirut, São Paulo), the emission ratios do not show any seasonal cycle. One explanation is the heating activities during the winter season that are expected to emit AVOC and CO in addition to other fossil fuel combustion sources. Interestingly, the spatial ranking of anthropogenic emission ratio values for isoprene is different from the ones of terpenes. For instance, the ERs are the highest in Paris for isoprene while they are the lowest in Paris for α-pinene. This suggests that all terpenoids need to be measured in cities.

6. Indirect quantification of anthropogenic terpenoid emissions and impact on atmospheric chemistry

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The evaluation of the effect of anthropogenic terpenoid emissions on atmospheric chemistry consists of i) estimating the anthropogenic emissions of terpenoids ($E_{A\text{-terpenoids}}$ for all anthropogenic emission sectors) from the product between anthropogenic terpenoids-to-tracer ER (isoprene and sum of monoterpenes) and annual emissions of anthropogenic tracers (AVOC, CO, NOx) extracted from emission inventories ii) weighting $E_{A\text{-terpenoids}}$ by reactivity metrics. Reactivity metrics describe the ability of VOC precursors to contribute to oxidation transformations and to form secondary pollutants (ozone and SOA).

6.1. Emission inventory and emission calculation

The evaluation is carried out at both national (country level) and urban scales. Indeed, the relative importance of BVOC emissions compared to AVOC emissions is scale-dependent. France, Lebanon, and Vietnam have been selected to illustrate countries of Northern, Mediterranean, and subtropical latitudes, and they also offer a detailed in-situ dataset (see previous section). The French city of Paris is selected to represent the ERs determined at the city level. We also assume that the ERs determined at the city level represent the whole country. When comparing the worldwide isoprene and monoterpene ERs from figure 9, their spatial variability spans one order of magnitude at the global scale. As a consequence, the error propagation from the extrapolation of urban ER to country-level will not exceed a factor of 10.

The emissions of AVOC, CO and NOx at the urban and country levels are extracted from the regional emission inventories released by the local air quality monitoring network AIRPARIF in Paris and from the global CAMS-GLOB-ANT_v4.2 (Granier et al., 2019) for France, Lebanon, and Vietnam. The year of reference is 2010, except for Vietnam (2019) to be consistent with the periods of the campaigns. In addition to the five AVOC tracers (acetylene, ethene, propene, benzene, toluene), our estimation also includes other AVOC of atmospheric interest regarding their reactivity with major oxidants: C8- and C9-aromatics and C4-C6 alkenes. Those latter species are sometimes lumped in the emission inventory in a category

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including other chemical VOC functions: this is the case, for instance, for alkenes and alkynes in CAMS. The methodology for the construction of the regional anthropogenic emission database by AIRPARIF has been already decribed in Borbon et al. (2013). In CAMS-GLOB-ANT_v4.2, emissions are provided for the main pollutants and greenhouse gases, together with speciation of non-methane VOCs from Huang et al. (2017). Emissions are provided for 12 anthropogenic sectors, depending on the species. Some sectors have been excluded for the calculation: ships, agricultural activities and solid waste and waste water. The spatial resolution of the inventory is 0.1x0.1 degree. The global emissions have been obtained from the ECCAD emissions database (https://permalink.aeris-data.fr/CAMS-GLOB-ANT). The mean emissions of anthropogenic (A) terpenoids (A-isoprene and A-terpenes) are calculated from the emission ratios through the following expression:

$$E_{A-terpenoids} = {}^{1}/_{n} \times \sum_{1}^{n}\left(ER \times \frac{MW_i}{MW_{terpenoids}}\right) \times E_i \qquad \text{(Equation 2)}$$

where i is the tracer and n the number of tracers (here, 5), ER is the ambient emission ratio (ppb per ppb_{tracer} i), MW the molecular weight ($g.mol^{-1}$) of the tracer i, E_i the total anthropogenic emission of the tracer by the inventory in Gg or Tons. The standard deviation of $E_{A\text{-}terpenoids}$ is also calculated.

The results of this emission-derived approach are presented in section 6.3. It depends on the quality of the emissions estimated by the inventories for which high uncertainties are expected, as already shown for cities of the Eastern Mediterranean (Salameh et al., 2016; Thera et al., 2019). Therefore, a second approach (ER-relative-to-CO derived approach) is also implemented and reported in the Supporting Information (Figure S1) from the Paris and Beirut datasets. This second approach does not depend on the absolute emissions of anthropogenic tracers: it only takes into account relative anthropogenic emission ratios without considering the biogenic ones.

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6.2. Reactivity-weighted anthropogenic emissions

Reactivity metrics describe the ability of VOC precursors to contribute to oxidation transformations and to form secondary pollutants (ozone and SOA). They were described in detail by (Gilman et al., 2015) and (Dominutti et al., 2019). The novelty here is the use of kinetic constants with ozone and nitrate radicals. While during daytime, OH-initiated oxidation is the main pathway for the chemical removal of most of the VOCs, during nighttime, when the photolytic source of OH becomes negligible, the NO_3 mixing ratios can increase significantly, and the reactions with NO_3 become an important oxidation sink for many VOCs, especially for unsaturated alkenes like isoprene, monoterpenes, and sesquiterpenes (Warneke et al., 2004). The loss of biogenic VOCs is usually dominated by the reaction with NO_3. Their lifetime is up to 4 orders of magnitude compared to the ones with OH. The absolute emissions $E_{A\text{-terpenoids}}$ have been weighted by the different reactivity metrics as described below. Then, they are compared to the anthropogenic ones of the 5 tracers and the biogenic ones.

VOC-OH, VOC-NO_3 and VOC-ozone reactivity represents the sink reaction of each VOC with the hydroxyl radical (OH) and is equal to

$$E_{oxidant-reactivity} = \left({}^{E_{VOC} \times k_{oxidant}}/_{MW}\right) \times 6.02 \times 10^{35} \quad \text{(Equation 3)}$$

where E_{VOC} are the absolute anthropogenic emissions of a given VOC (in Tg/year), $k_{oxidant}$ is the second-order reaction rate coefficient of VOC with the hydroxyl or nitrate radicals or ozone (in cm^{-3}.$molecules^{-1}$.sec^{-1}), MW is the molar mass of the VOC (in $g.mol^{-1}$). $k_{oxidant}$ are reported in Table S4.

The SOA formation potential represents the propensity of each VOC to form secondary organic aerosols and is equal to : $E_{SOAP} = E_{VOC}$ x SOAP

where E_{VOC} are the absolute anthropogenic emissions of a given VOC (in Tg/year), and SOAP is a non-dimensional model-derived SOA formation potential (Derwent et al., 2010); (Gilman et al., 2015).

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All SOAP values represent the modelled mass of organic aerosol that was 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).

6.3. Quantification and implication for chemistry

The $E_{A\text{-terpenoids}}$ are reported in Figure 10 at urban (Paris) and country scales and are compared to AVOC and BVOC emissions from the inventories. Table S5 reports the calculated anthropogenic emissions of terpenoids. At the national level, the estimated absolute amounts of emitted anthropogenic terpenoids vary between 0.22 $Gg.year^{-1}$ (Lebanon) to 5.70 $Gg.year^{-1}$ (France) with a coefficient of variation of ± 39% on average. Those numbers are equivalent to a 13 - 284 $person^{-1}.day^{-1}$ emission rate range for monoterpenes. Coggon et al. (2021b)'s estimates vary between 520 to 860 $mg.person^{-1}.day^{-1}$ in Manhattan, NYC. In typical indoor environments, emissions rates of monoterpenes from humans are less than 5 $mg.day^{-1}.person^{-1}$ and even lower (0.24 $mg.day^{-1}.person^{-1}$) from the only body without the use of additional personal care products (Wang et al., 2022). The order of magnitude of emission rates calculated here is larger than those calculated as being directly emitted from people suggesting that traffic is a potential emission source to be taken into account.

In Paris, those numbers fall to 25.4 $tons.year^{1}$ with a higher average coefficient of variation of ±78%. These numbers represent less than 3% of AVOC emissions and usually less than 1% of biogenic terpenoid emissions.

While the absolute anthropogenic emissions of terpenoids appear negligible, a different picture arises when weighting those emissions by their atmospheric reactivity. While the OH-reactivity from anthropogenic terpenoids accounts for 20% of the total AVOC reactivity, the OH-reactivity of terpenoids remains dominated by their biogenic component, especially in summer,

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during the day at the maximum of photochemistry and biogenic emissions. Remarkably, the ozone- and NO_3-reactivity from anthropogenic terpenoid emissions exceed three orders of magnitude and one order of magnitude, respectively, the ones from other AVOC, a difference even greater than potential analytical bias from the measurement. Indeed, isoprene and monoterpenes react a million times faster with ozone and NO_3 than other alkenes and aromatics, respectively (Table S4). Ozonolysis and NO_3 oxidation reactions, especially at night, are known as major sinks of terpenoids responsible for the formation of secondary gaseous (e.g. formaldehyde, organic nitrates) and particulate organic products (e.g. SOA) (Lee et al., 2006). Here, the ozone reactivity is dominated by isoprene, and the NO_3-reactivity is dominated by monoterpenes. Similar conclusions are drawn from the ER-relative-to-CO derived approach in Figure S1 with two exceptions: A-isoprene and A-monoterpenes make a greater contribution to relative SOAP, respectively (60% in Paris and 5% in Beirut) and C4-C6 alkenes dominate the NO_3-reactivity in Beirut compared to terpenes. The propensity of anthropogenic emissions to form SOA is dominated by anthropogenic aromatics in which saturated functional groups and anthropogenic terpenoids play a minor role. This is consistent with previous work by Gilman et al. (2015) and Dominutti et al. (2016). However, the use of SOA potential (SOAP) should be carefully considered as it is in contrast to measured aerosol yields, which are approximately 1.7 times higher for monoterpenes compared to toluene (Pandis et al., 1992).

Our results highlight the potential role of anthropogenic terpenoids in nighttime and wintertime chemistry at mid-latitudes when the biosphere is dormant. However, those transformations have always been investigated from a biosphere origin perspective. Alkenes like isoprene and terpenes are known to react rapidly with NO_3 during the night, with consequences on the SOA and nitrogen species budget through the formation of organic nitrates. Because isoprene biogenically emitted in the late afternoon is not fully photooxidized, it accumulates in a shallow nocturnal boundary layer constituting a reactive reservoir towards NO_3 and ozone, especially

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in areas impacted by urban and biogenic emissions (Brown et al., 2009; Warneke et al., 2004). More recently, Haskins and coworkers explored the wintertime chemistry in the Eastern United States within the framework of the WINTER aircraft experiment (Haskins et al., 2019). The authors point out formaldehyde (HCHO) as the largest wintertime radical source over land. Contrary to summer, the dormant wintertime biosphere implies that the HCHO sources are anthropogenic, either through direct HCHO emissions or emissions of short-lived precursors, such as primary alkenes. Anthropogenic terpenoids from inefficient combustion, manufacturing processes, and consumer products, and actually disregarded, are expected to contribute to wintertime HCHO ambient levels at mid-latitudes.

7. Conclusion and implications

The re-analysis of different VOC observations collected over the last decade has shown the systematic presence of anthropogenic isoprene and monoterpenes in cities worldwide and also recently demonstrated in Delhi, India (Bryant et al., 2023). Here we show that monoterpenes, as well as isoprene, are potentially emitted at the exhaust of fossil fuel vehicles by re-examining the DATAbASE dataset and the literature and by collecting new observations in the developing world (Vietnam). However, these results are modulated in northern mid-latitudes by the recent evidence of co-emitted personal care products won by car passengers in Northern US cities. The traffic-related fraction of monoterpenes can be significant (up to 40% of the observed levels) but is strongly space-dependent. This fraction might not be as significant nowadays in OECD (Organisation for Economic Co-operation and Development) Annex 1 countries in an era of efforts to reduce emissions from traditional mobile sources. Decreasing trends in VOC emissions from road transportation in northern mid-latitudes (by 70% in France, for instance, as estimated by the CAMS-GLOB-ANT_v4.2) over the last decade suggest that those emissions might not be as significant nowadays. However, a systematic screening of terpenoids at exhaust pipe is required to corroborate this statement. On the opposite, increasing trends in road

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transport emissions in countries of the developing world (by 1.5 to 3.7 fold in Côte d'Ivoire and Vietnam, respectively - https://eccad.aeris-data.fr/) suggest that traffic-related emissions still make a significant contribution. Given the high standard deviations of the calculated fractions, deeper investigation is needed in the future, and a more systematic search and quantification of terpenoids at the exhaust of vehicles in different regions of the world is needed to evaluate their real importance. While absolute anthropogenic emissions of terpenoids represent less than 3% of other anthropogenic VOC emissions, they dominate the reactivity of anthropogenic VOC emissions by one to three orders of magnitude regarding nighttime oxidation by NO_3 and ozonolysis, respectively. This study suggests the need to evaluate the effect of the anthropogenic terpenoid fraction on nighttime and wintertime atmospheric chemistry in the future, especially at mid-latitudes. Such evaluation may bring some answers to unresolved questions regarding nighttime and wintertime chemistry.

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involved in the VOC field experiments: W. Aït-Helal, L. Bouvier, B. Cetin, C. Gaimoz, J, Gilman, J. de Gouw, M. Keles, T. Leonardis, N. Marchand, B. Termine, F. Oztürk, N. Viet Thanh.

Data availability statement

The concentrations of VOCs from the 14 datasets used in the paper and some trace gases are all available either in the project database or in repositories as described in Table 1 for different cities. The dataset references are listed below for each target city:

Abidjan : Borbon et al., 2019 https://baobab.sedoo.fr/Data-Download/?datsId=1787&project_name=DACCIWA

Athens: Panopoulou, A., Sauvage, S., Liliakou, E., 2021 [Dataset], https://zenodo.org/record/4545775

Beijing : Gros, V., 2021, https://doi.org/10.5281/zenodo.4555438

Beirut : Sauvage, S., Salameh, T., 2021. https://mistrals.sedoo.fr/TRANSEMED/

Istanbul: Borbon, A., 2017. [Dataset], https://mistrals.sedoo.fr/TRANSEMED/

Paris: Sauvage, S., and Locoge, N.. 2011, https://cds-espri.ipsl.upmc.fr/megapoli/DescPlateforme.do?idPlat=16, Gros, V., 2010. https://cds-espri.ipsl.upmc.fr/megapoli/DescPlateforme.do?idPlat=15, Gros, V., 2021, https://doi.org/10.5281/zenodo.4555438,

Ha Noi: Hopkins, JR., and Dominutti, P., 2021. https://doi.org/10.5281/zenodo.4545790

Los Angeles: Gilman, J., and de Gouw, J., 2011, https://csl.noaa.gov/groups/csl7/measurements/2010calnex/Ground/DataDownload/index.php?page=/groups/csl7/measurements/2010calnex/Ground/DataDownload/

São Paulo, Nogueira, T., and Dominutti, P., 2021. https://doi.org/10.5281/zenodo.4544398, Fornaro, A., and Dominutti, P., 2021, https://doi.org/10.5281/zenodo.4544267,

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Figures

Figure 1: Locations of field campaigns used for data re-analysis (in white characters) or reported by published studies (blue and green characters). References highlighted in blue have reported an anthropogenic origin for isoprene. References highlighted in green have reported an anthropogenic origin of monoterpenes. Figures show the mean concentrations in pbb of VOCs measured at some of these locations from the DATAbASE datasets (Los Angeles - 2010, Paris 2009/2010, Beijing 2007, São Paulo – 2013, Adidjan – 2016, Beirut – 2011/2012). Anthropogenic VOC are in grey: Et (Ethylene) Pr (propene) Ac (acetylene) Be (benzene) To (toluene). Terpenoids are in green: Is (isoprene) aP (α-pinene) bP (β-pinene) Ca (camphene) Li (limonene) mz stands for m/z 137 (sum of monoterpenes measured by PTRMS), My (myrcene), pCym (p-cymene), 3Car (Δ3-carene), 1,8Cin (1,8-cineole). The absence of bars means that the compounds were not determined.

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Figure 10: Estimated anthropogenic emissions of terpenoids (A-Terp) at urban (Paris) and national levels in France, Lebanon and Vietnam compared to the ones of anthropogenic VOC (A-VOC) and biogenic terpenoids (B-Terp). From left to right, we report the absolute emissions and OH-reactivity-weighted, ozone-reactivity-weighted, NO_3-reactivity-weighted and SOAP-weighted emissions. The blue boxes reports the total A-Terp absolute emissions. In AIRPARIF inventory, 3 anthropogenic sectors are used: transportation, solvent, wood burning. In CAMS, anthropogenic emissions sectors exclude agriculture, solid waste and ships.

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Tables

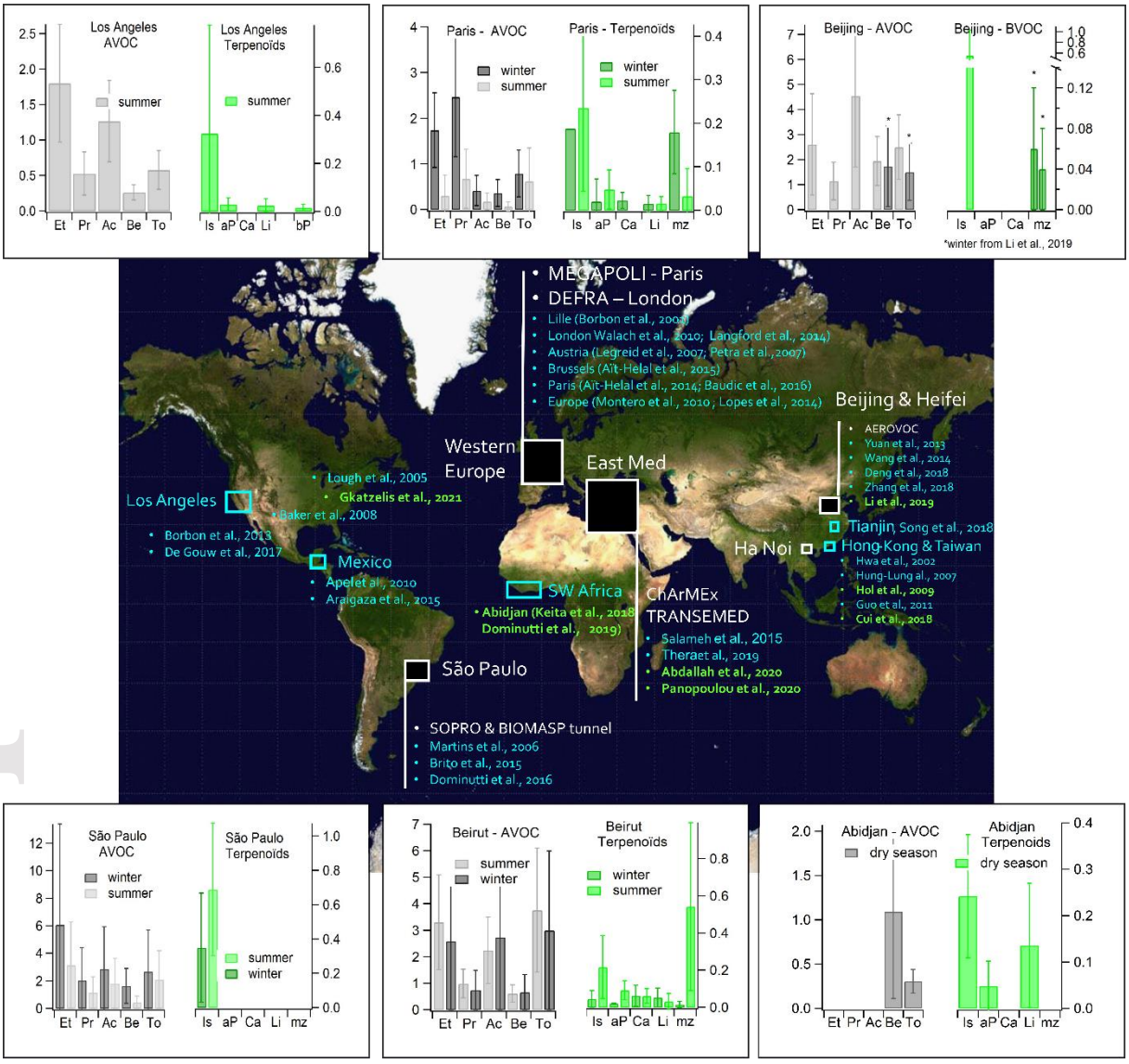
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Index	Region	City - country	Site type	Coordinates	Period	Campaign	References	Data citation
1	**Europe**	Paris - France	Suburban	48°42"36' N, 2°12"36' E	Jan.-Feb. 2010	MEGAPOLI	Ait-Helal et al., 2014	Sauvage, S., and Locoge, N.. 2011. SIRTA VOC tubes. https://cds-espri.ipsl.upmc.fr/megapoli/DescPlateforme.do?idPlat=16
2		Paris - France	Urban	48°49' N, 2°49'41"E	Jul. 2009- Jan.-Feb. 2010	MEGAPOLI	Baudic et al., 2016	Gros, V., 2010. LHVP VOC and Air Quality. https://cds-espri.ipsl.upmc.fr/megapoli/DescPlateforme.do?idPlat=15
3		Paris - France	Tunnel	48°46'16"N, 2°23'24"E	Oct-12	IZNOGOUD	Ammoura et al., 2016	Gros, V., 2021, Paris and Beijing VOC and air quality datasets, 10.5281/zenodo.4555438
4		London - UK	Urban	51°31'7" N, 0°8'59" W	JJA 2009- DJF 2010	UK Network	Dollard et al., 2007	https://uk-air.defra.gov.uk/data/data_selector_service
5	**North America**	Los Angeles	Suburban	34.140582 N, 118.122455 W	May-10	CalNex	Borbon et al., 2013 ; de Gouw et al., 2018	Gilman, J., and de Gouw, J., 2011, G01-VOCs-GCMS. https://csl.noaa.gov/groups/csl7/measurements/2010calnex/Ground/DataDownload/index.php?page=/groups/csl7/measurements/2010calnex/Ground/DataDownload/
6	**East Mediterranean**	Istanbul - Turkey	Urban / Roadway	41°02"33' N, 29°00"26' E	Sept. 2014	TRANSEMED	Thera et al., 2019	Borbon, A., 2017. Istanbul VOC online PTRMS. https://mistrals.sedoo.fr/TRANSEMED/
7		Athens - Greece	Urban background Roadway	37°58'12" N 23°43'12" E	Year 2016	CHARMEX	Panopoulou et al., 2020	Panopoulou, A., Sauvage, S., Liliakou, E., 2021, Athens dataset for DATAbASE, 10.5281/zenodo.4545775
8	**Middle East**	Beirut - Lebanon	Urban	33°51'55"N, 35°56'51" E	Jul. 2011 - Jan.-Feb. 2012	TRANSEMED	Salameh et al., 2015, 2016, 2017	Sauvage, S., and Salameh, T., 2021. Beirut_VOC_tubesoffline, https://mistrals.sedoo.fr/TRANSEMED/
9		Beirut - Lebanon	Tunnel	33°52'17"N, 35°29'41"E	Oct. 2016	ECOCEM-tunnel	Abdallah et al., 2020	-
10	**Africa**	Abidjan - Côte Ivoire	Urban Combustion sources	Multiple	Jan-16	DACCIWA	Dominuti et al., 2019	https://baobab.sedoo.fr/Data-Download/?datsId=1787&project_name=DACCIWA
11	**South America**	São Paulo - Brésil	Urban	23°33"33.6'S, 46°44"0.3'W	2013 to 2015	USP/IAG monitoring	Dominutti et al., 2016	Fornaro, A., and Dominutti, P., 2021. São Paulo dataset at IAG for DATAbASE, 10.5281/zenodo.4544267
12			Tunnels	RT: -46° 47' 43.85", -23°27' 38.94" JQT: -46° 41'36.28", -23°35'15.81	Nov-18	SOPRO	*This study*	Nogueira, T., and Dominutti, P., 2021. São Paulo dataset at two tunnels for DATAbASE, 10.5281/zenodo.4544398
13	**Asia**	Beijing - China	Urban	39°55'56"N, 116°19'27"E	Jan. 2007	AEROCOV	Gaimoz et al., 2007	Gros, V., 2021. Paris and Beijing VOC and air quality datasets, 10.5281/zenodo.4555438
14		Ha Noi - Vietnam	Traffic urban Traffic sources	21°0'24" N, 105°49'4"E	Mar-19	Air Quality in Vietnam	*This study*	Hopkins, JR., and Dominutti, P., 2021, Ha Noi VOC 10.5281/zenodo.4545790

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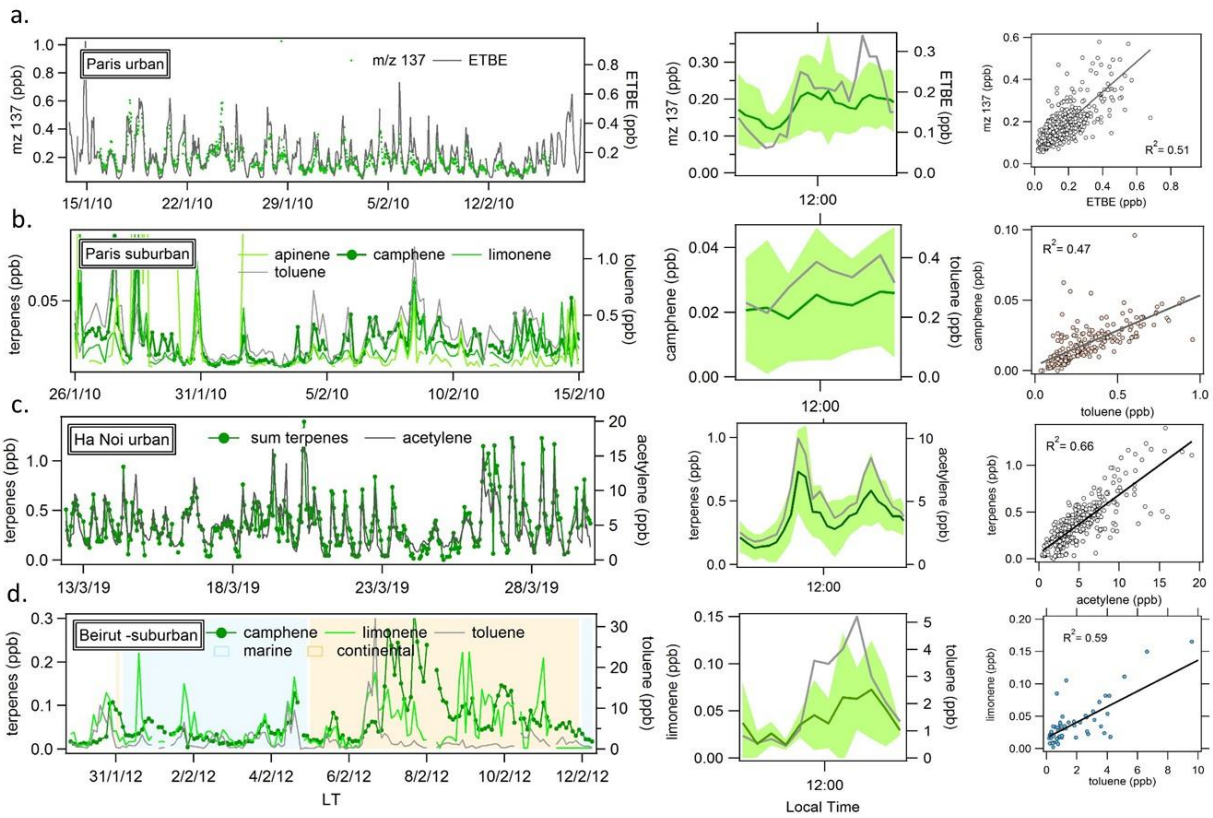
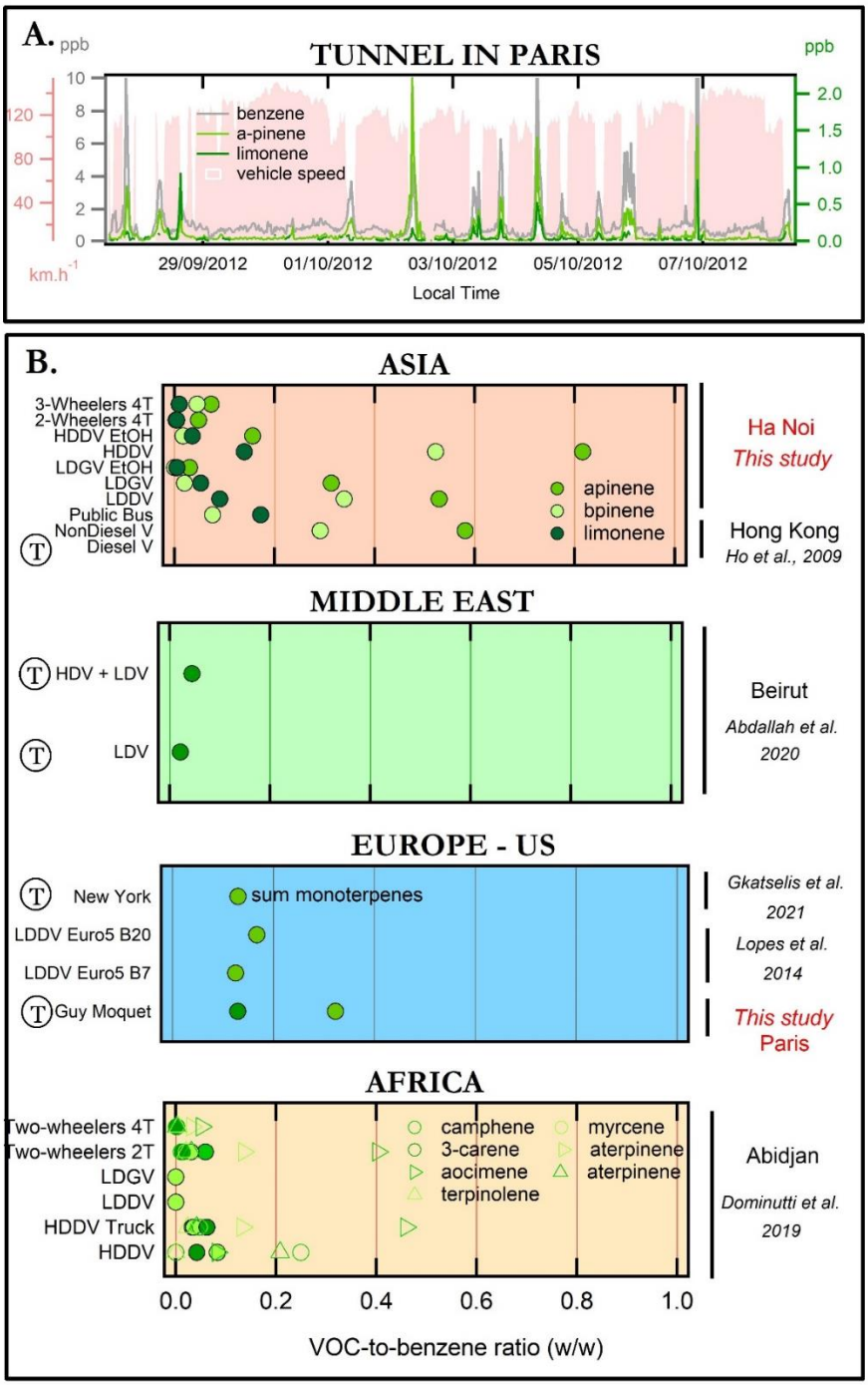


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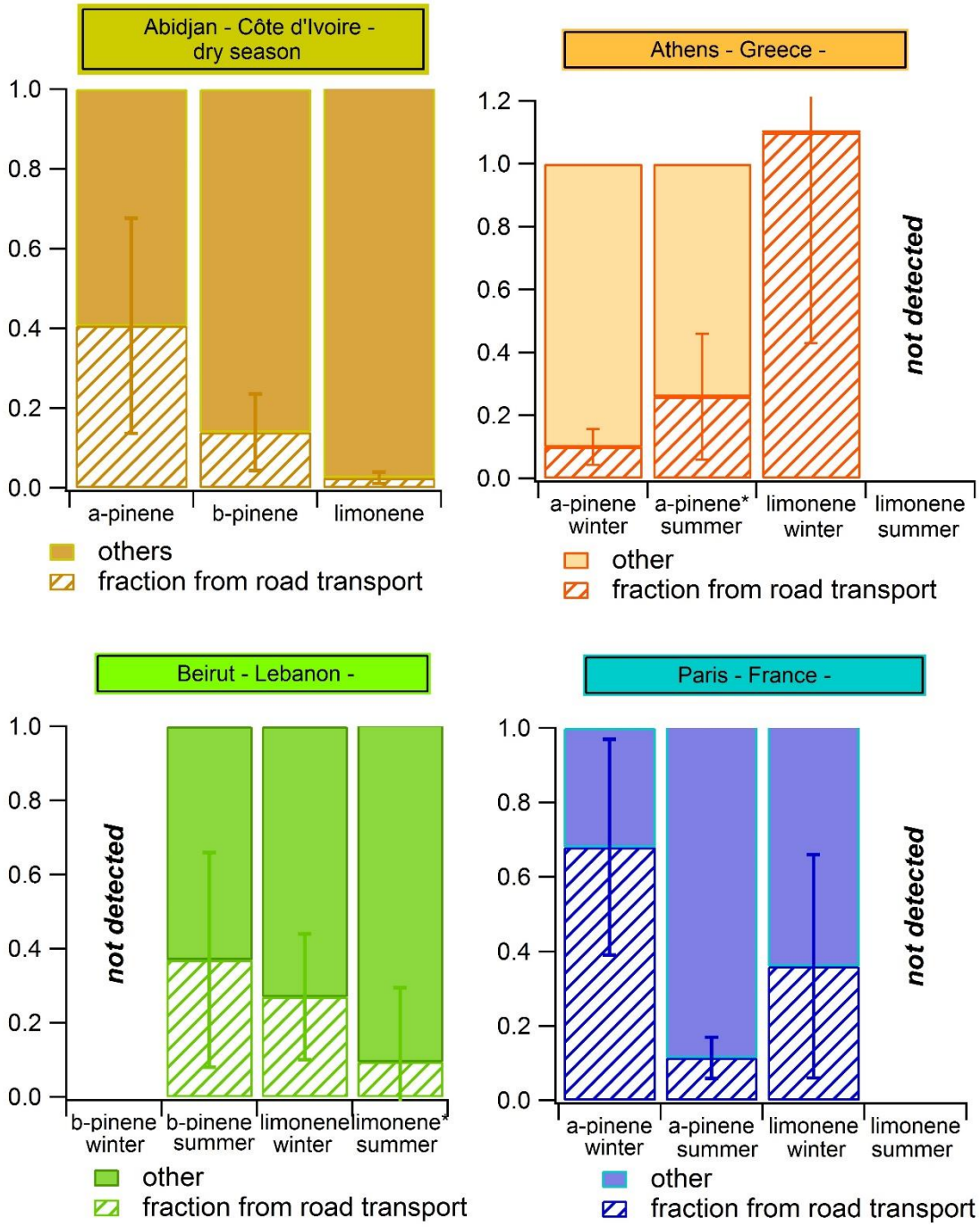


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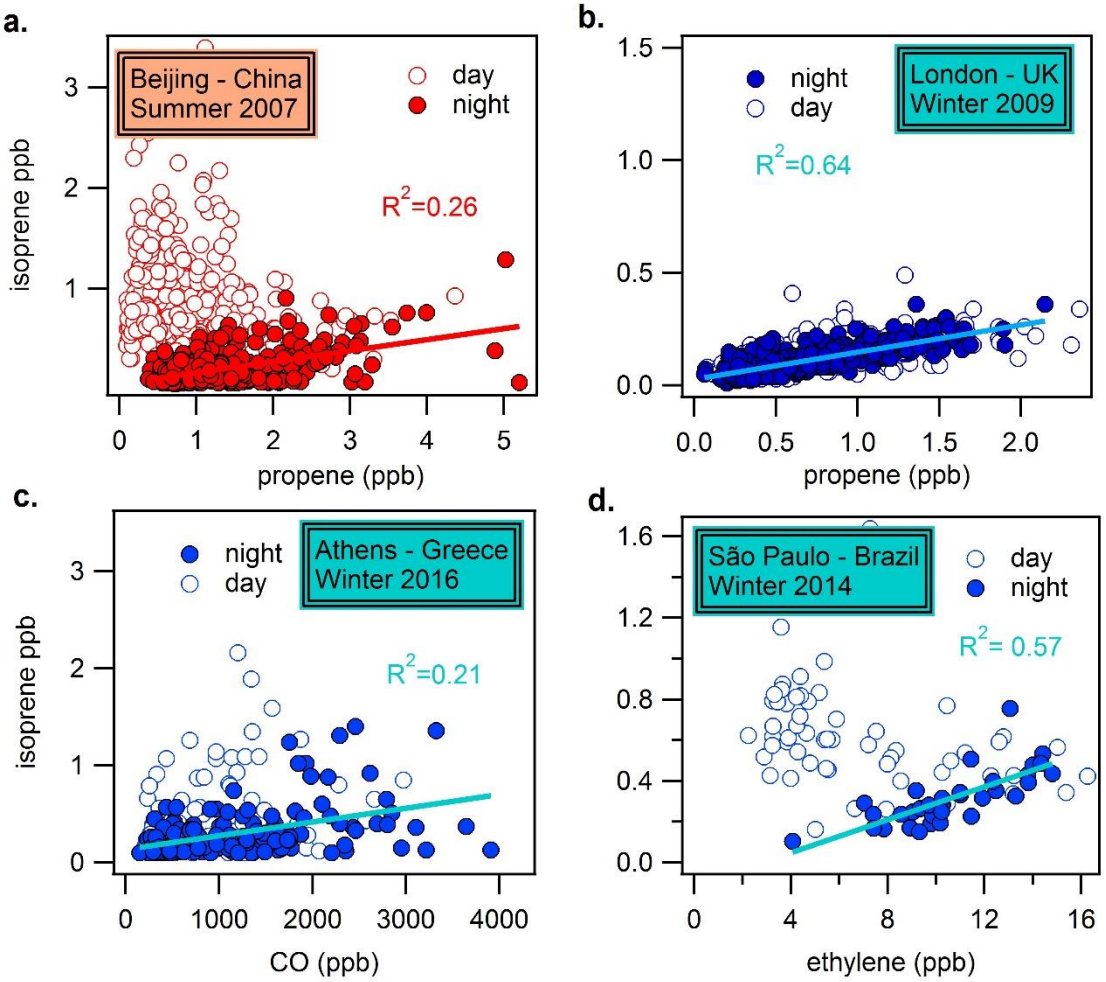


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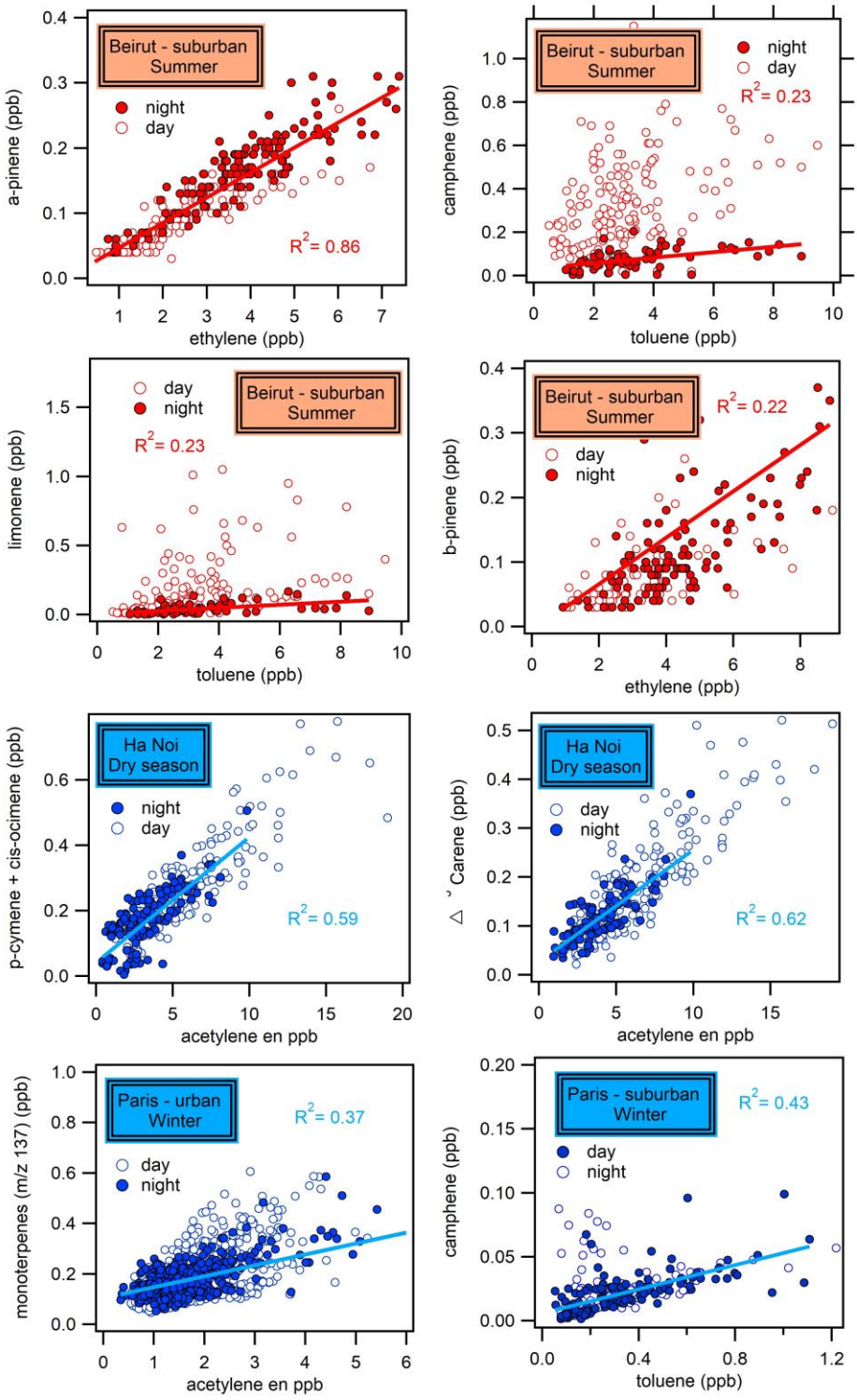


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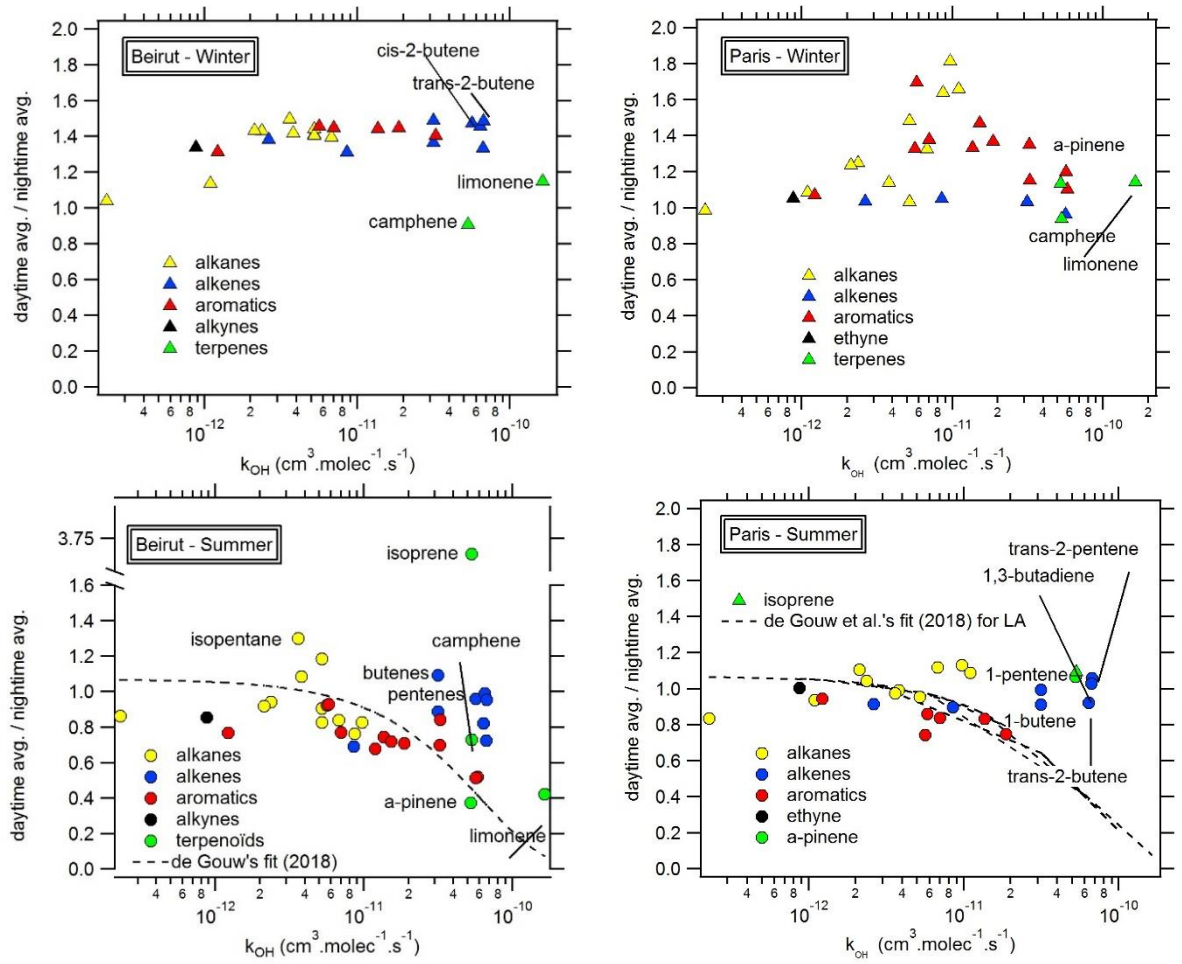


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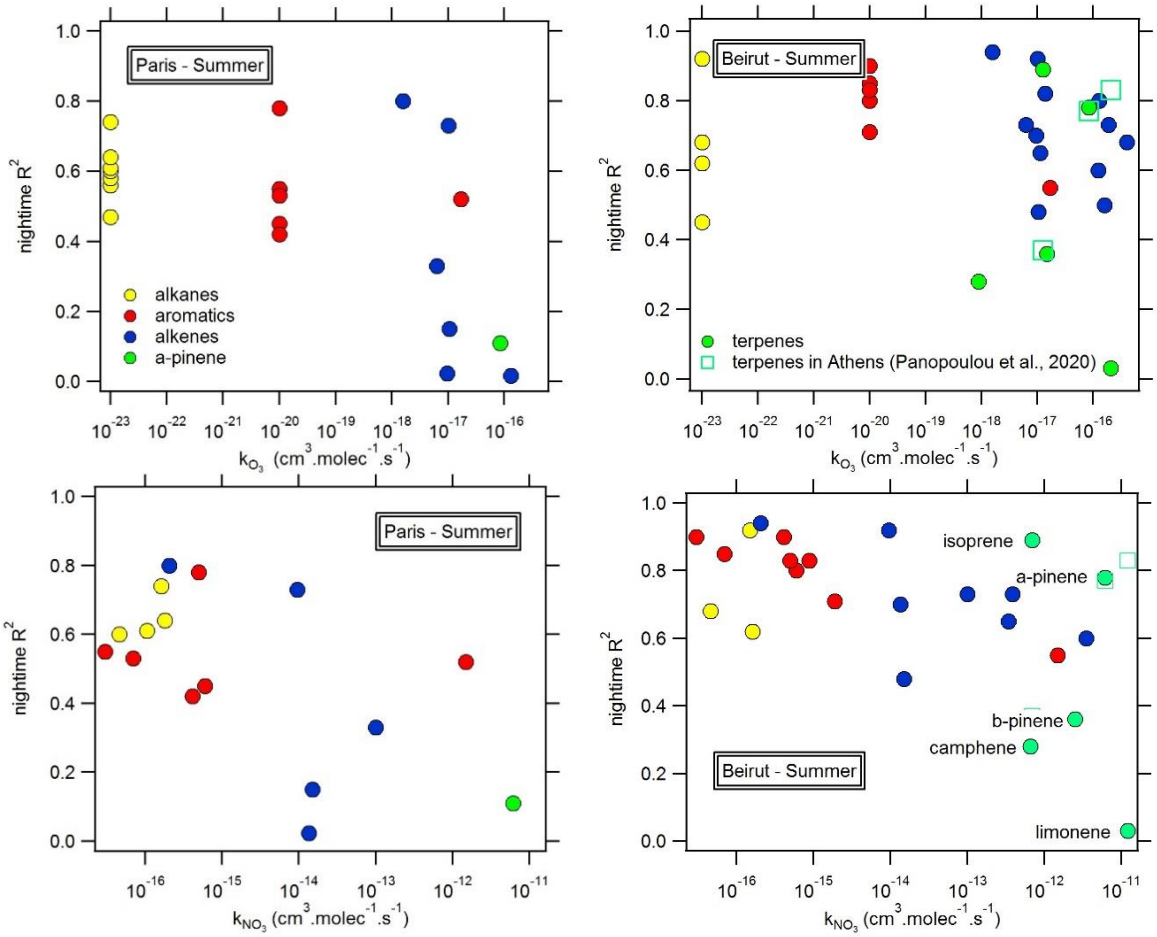


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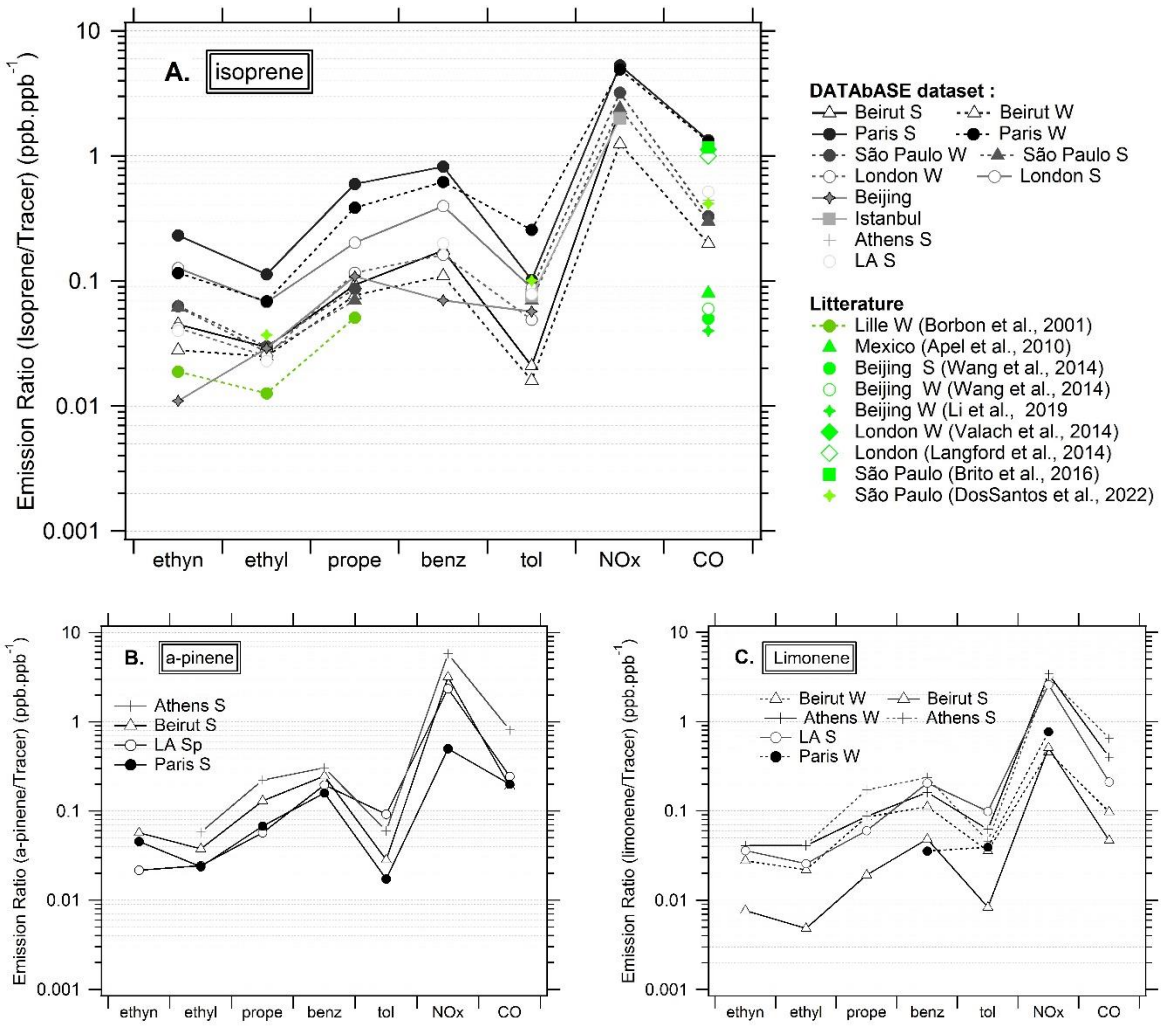


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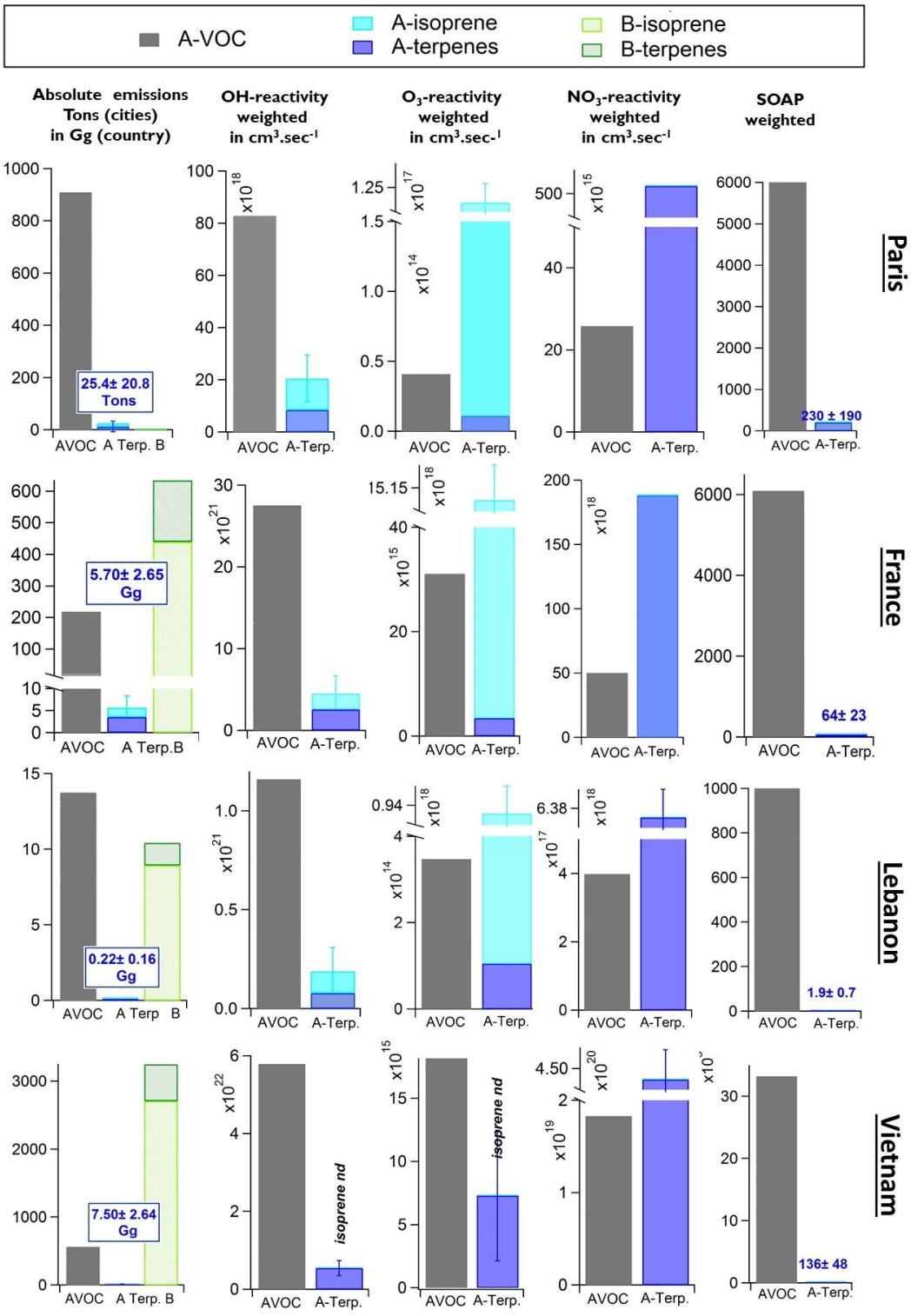


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