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## Emission ratios of anthropogenic volatile organic compounds in northern mid-latitude megacities: Observations versus emission inventories in Los Angeles and Paris

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[1] Ground-based and airborne volatile organic compound (VOC) measurements in Los Angeles, California, and Paris, France, during the Research at the Nexus of Air Quality and Climate Change (CalNex) and Megacities: Emissions, Urban, Regional and Global Atmospheric Pollution and Climate Effects, and Integrated Tools for Assessment and Mitigation (MEGAPOLI) campaigns, respectively, are used to examine the spatial variability of the composition of anthropogenic VOC urban emissions and to evaluate regional emission inventories. Two independent methods that take into account the effect of chemistry were used to determine the emission ratios of anthropogenic VOCs (including anthropogenic isoprene and oxygenated VOCs) over carbon monoxide (CO) and acetylene. Emission ratios from both methods agree within  $\pm 20\%$ , showing the reliability of our approach. Emission ratios for alkenes, alkanes, and benzene are fairly similar between Los Angeles and Paris, whereas the emission ratios for C7–C9 aromatics in Paris are higher than in Los Angeles and other French and European Union urban areas by a factor of 2–3. The results suggest that the emissions of gasoline-powered vehicles still dominate the hydrocarbon distribution in northern mid-latitude urban areas, which disagrees with emission inventories. However, regional characteristics like the gasoline composition could affect the composition of hydrocarbon emissions. The observed emission ratios show large discrepancies by a factor of 2–4 (alkanes and oxygenated VOC) with the ones derived from four reference emission databases. A bias in CO emissions was also evident for both megacities. Nevertheless, the difference between measurements and inventory in terms of the overall OH reactivity is, in general, lower than 40%, and the potential to form secondary organic aerosols (SOA) agrees within 30% when considering volatile organic emissions as the main SOA precursors.

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### 1. Introduction

[2] Volatile organic compounds (VOCs) are known to affect urban air quality and regional climate change by contributing to the formation of ozone and secondary organic aerosols (SOA). In urban areas, VOC emissions are dominated by anthropogenic sources. Quantification of VOC emissions is a first critical step to determine effective abatement strategies and to predict their environmental impacts. Recent examples of the importance of anthropogenic VOC emissions in air quality forecast of ozone are modeling studies for industrial areas experiencing severe ozone problems: Houston, Texas [Jiang and Fast, 2004; Lei et al., 2004; Zhang et al., 2004; Kim et al., 2011] and Marseille, France [Coll et al., 2010]. While sensitivity tests of modeled SOA to its anthropogenic VOC precursor emissions are scarce and more speculative [Hodzic et al., 2009; Hallquist et al., 2009], recent modeling studies in Mexico City, Mexico, have

shown that the addition of intermediate volatility and semi-volatile organic compound emissions substantially improved the simulation of ambient SOA load [Hodzic *et al.*, 2010].

[3] The quantification of anthropogenic VOC urban emission remains challenging for several reasons. The first reason is the multiplicity of sources. Anthropogenic VOC sources encompass mobile sources (transport), stationary sources (industry), and area sources. The second reason is the spatial and temporal variability of the emissions. While the amount and composition of emissions show great variability in time (from hour to season to year), their composition variability between urban areas may be limited as suggested recently by Baker *et al.* [2008], Parrish *et al.* [2009], and von Schneidemesser *et al.* [2010]. The third reason is related to the emission inventory methodology. The emitted amount,  $E$ , of one pollutant,  $j$ , by a source category,  $i$ , is expressed as follows:

$$E = \sum A_i \times (EF)_{i,j} \times P_{i,j}$$

where  $A_i$  is an activity rate (e.g., number of kilometers travelled) and  $(EF)_{i,j}$  is the emission factor (e.g.,  $\text{mg km}^{-1}$ ), weighted by a given activity parameter  $P_{i,j}$  (e.g., vehicle with or without catalyst, vehicle speed, and cold start).

[4] Emission inventories usually combine bottom-up and top-down calculations to estimate  $E$ . Bottom-up calculations aggregate multiple local statistics on different emission source categories where possible. Top-down or downscaling calculations use regional or national activity data and reallocate emissions to finer scale by surrogate indices such as population statistics at a local level. Therefore, the uncertainties of numerous data accumulate in the estimation of  $E$ . Due to the complexity of emission inventories, it is also challenging to accurately reflect the changes in anthropogenic emissions of major air pollutants (including VOCs) due to the implementation of emission reduction measures. Indeed, non-methane hydrocarbon (NMHC) observations in northern mid-latitude urban areas over the last decades consistently show a clear decreasing trend [Warneke *et al.*, 2012; von Schneidemesser *et al.*, 2010; A. Borbon *et al.*, Multiyear trends of anthropogenic NMHC inferred from observations in French urban atmospheres, manuscript in preparation, 2013]. The reduction of gaseous pollutant emissions by the transport sector including VOC, carbon monoxide (CO), and nitrogen oxides ( $\text{NO}_x$ ) has been a main focus of European and U.S. environmental policies since the 1960s. Stringent vehicle emission standards have led to the deployment of emission control technologies at tailpipe (e.g., catalytic converter) and gasoline reformulation. In Europe, the emission standards were defined in a series of European Union directives staging the progressive introduction of increasingly more stringent standards (namely, Euro 1 to 6). In the United States, national emission standards for vehicles were first promulgated by the Clean Air Act and reinforced in the 1977 and 1990 Amendments. California was given the authority to establish their own standards because of the severity of the air pollution in the Los Angeles basin [Sawyer *et al.*, 2000]. Up-to-date emission inventories suggest that traffic emissions are no longer the dominant VOC source in urban areas. For example, the emission inventories allocate 35% and 20% of VOC emissions by mass to traffic emissions in the South Coast Air Basin (California Air Resources Board (CARB), 2008, available at [http://](http://www.arb.ca.gov/ei/maps/basins/absmap.htm)

[www.arb.ca.gov/ei/maps/basins/absmap.htm](http://www.arb.ca.gov/ei/maps/basins/absmap.htm)) and in Paris (Association de surveillance de la qualité de l'air en Ile de France, 2009), respectively. Regional emission inventories for two European cities, Paris and Zurich in 2005, point to the use of solvents from all source categories as the new dominant source of VOCs at urban scale. Conversely, source-receptor models point to traffic as the major urban source of VOCs [Niedojadlo *et al.*, 2007; Lanz *et al.*, 2008; Gaimoz *et al.*, 2011].

[5] The objective of this work is to test the importance of the variability of urban VOC emission composition among northern hemisphere megacities and to evaluate the accuracy of regional emission inventories. This work relies on VOC field observations that were collected in the framework of two recent field projects: (1) Research at the Nexus of Air Quality and Climate Change (CalNex 2010) in the Los Angeles Basin and (2) Megacities: Emissions, Urban, Regional and Global Atmospheric Pollution and Climate Effects, and Integrated Tools for Assessment and Mitigation (MEGAPOLI 2009) in the Paris area.

[6] Several studies in the literature have reported on the evaluation of VOC emission inventories in urban areas. These studies either rely on direct flux measurements at ground level and on aircraft [Velasco *et al.*, 2005; Karl *et al.*, 2009; Park *et al.*, 2010], on the indirect use of ambient pollutant concentrations or on satellite retrievals [Martin *et al.*, 2003; Kim *et al.*, 2011]. Vautard *et al.* [2003, and references therein] summarized some of the studies based on in situ observations. In general, absolute or relative concentrations are compared with modeled concentrations from a chemistry-transport model (CTM). The use of inverse modeling as an alternative to direct CTM simulations is also a promising technique to evaluate emission inventories [Brioude *et al.*, 2011]. Over the last two decades, source-receptor modeling has also provided an independent evaluation of the quality of emission inventories in various urban areas worldwide [Fujita *et al.*, 1995; Niedojadlo *et al.*, 2007; Lanz *et al.*, 2008; Gaimoz *et al.*, 2010; Morino *et al.*, 2011]. The composition of urban emissions was also compared between measurements and emission inventories by studying emission ratios of various VOCs relative to an inert tracer (CO, acetylene) [Warneke *et al.*, 2007; McKeen *et al.*, 2009; Coll *et al.*, 2010]. Observed concentrations are not only the result of emissions but also of transport/mixing and chemistry. While the determination of relative emission ratios partially overcomes the effect of dilution, biases from chemistry cannot be excluded [Warneke *et al.*, 2007; Bon *et al.*, 2011] and need to be addressed.

[7] Here two independent methods that account for the effects of chemical removal were used to estimate the urban emission ratios (ERs) of various VOCs based upon the Los Angeles and Paris data sets. One method relies on linear regression fits on data that are spatially and temporally filtered to isolate fresh emissions, while the other method relies on extrapolating the photochemical age to zero. The latter method was only applied to Los Angeles data. ERs are then compared to values derived from emission inventories. Finally, the differences between ER in those two urban areas are discussed including their implications for tropospheric chemistry.

## 2. Methods

### 2.1. Ground-Based Observations

[8] During the CalNex (15 May to 15 June 2010) and MEGAPOLI experiments (1–31 July 2009), a large suite of

**Table 1.** Platforms and Measurements During the CalNex and MEGAPOLI Campaigns in Los Angeles (Pasadena) and Paris

Platforms	Species	Instruments		Time	Performances	Reference
		Resolution				
<b>Ground Level</b>						
Pasadena	VOCs (C2–C10 NMHC and OVOC)	Online GC-MS		30 min	DL: <100 ppt, precision: <15%, accuracy: <25%	<i>Gilman et al.</i> [2010]
	CO	VUV resonance fluorescence (Aerolaser 5002)		1 min	DL: 1 ppb, uncertainty: 4%	<i>Gerbig et al.</i> [1999]
Paris	C2–C6 NMHC	Online GC-FID		30 min	DL: 37–93 ppt, uncertainty: 15%	<i>Gaimoz et al.</i> [2011]
	C6–C10 NMHC	Online GC-FID		30 min	DL: 37–93 ppt, uncertainty: 20%	<i>Gaimoz et al.</i> [2011]
	CO	IR detection (Environnement SA)		1 min	DL: 100 ppb, uncertainty: 20%	AIRPARIF
Paris and other urban areas in France	C2–C9 NMHC	Online GC-FID		1 h	DL: <200 ppt, uncertainty: <8%	<i>Badol et al.</i> [2004] and <i>Borbon et al.</i> [2003b]
<b>Aircraft</b>						
Greater Paris area	VOCs	PTR-MS		40 s	DL: <150 ppt, uncertainty: <20%	See supporting information
	CO	IR detection (Thermo)		1 s	DL: 10 ppb, precision: 5 ppb	<i>Nedelec et al.</i> [2003]

VOCs including NMHC and oxygenated VOCs (OVOC) and other relevant trace gases and aerosol species were collected at two ground sites. During CalNex, the ground site was located in Pasadena, California (34.140582°N, 118.122455°W) 18 km northeast of downtown Los Angeles. The prevailing wind direction was onshore during daytime, with southwesterly winds bringing relatively unpolluted oceanic air masses over central Los Angeles to Pasadena. The transport timescale from Los Angeles to Pasadena was 3–4 h on the basis of average wind speed. More details on the site can be found in *Veres et al.* [2011] and *Washenfelder et al.* [2011]. During the summertime campaign of MEGAPOLI, the ground site in downtown Paris was located at the Laboratoire d'Hygiène de la Ville de Paris (LHVP, 48.828777°N, 2.207317°E) in the thirteenth district. This station is representative of well-mixed urban air. More details on the site can be found in *Gaimoz et al.* [2011]. In July 2009, westerly and southwesterly winds bringing clean air masses of marine origin over the Paris area were dominant (Freutel, F., et al., Aerosol particle measurements at three stationary sites in the megacity of Paris during summer 2009: Meteorology and air mass origin dominate aerosol particle loads, composition and size distribution, submitted to *Atmospheric Chemistry and Physics Discussions*, 2012).

[9] During both campaigns, VOCs were measured by online gas chromatographs (GC) coupled to a mass spectrometer in Pasadena [*Gilman et al.*, 2010] and flame ionization detectors (FID) in Paris [*Gros et al.*, 2011]. The performances of these and other instruments used in this work are reported in Table 1. For more details, the reader is referred to the listed references. To support data interpretation (see section 5), additional observations of NMHC from a long-term monitoring program launched in France in 2001 were used. One urban site in four target cities including Paris, operated by the local air quality monitoring network (Associations Agréées Surveillance Qualité de l'Air (AASQA)), was implemented with an online GC-FID for continuous, hourly measurements of 31 NMHCs. Protocols and quality control procedures have been described in detail by *Veillerot et al.* [1998] and *Badol et al.* [2004].

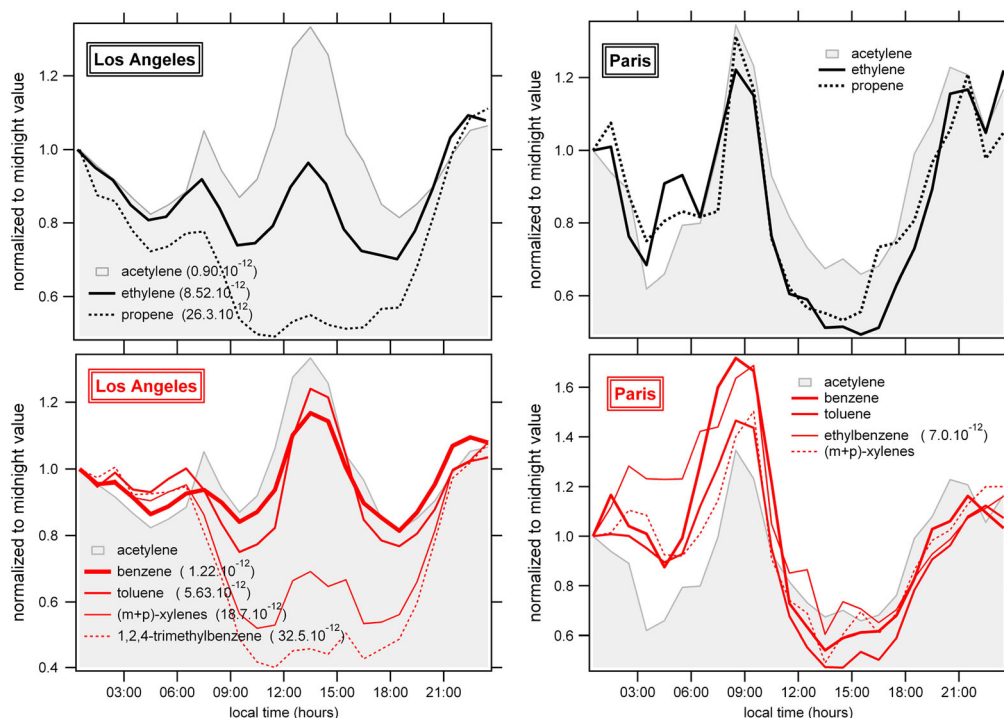
## 2.2. Aircraft Observations

[10] During the summertime campaign of MEGAPOLI, VOCs and other relevant trace gases and aerosol species were measured on board the French research aircraft, the ATR-42. In particular, a new online proton transfer reaction mass spectrometer (PTR-MS) was deployed for the first time. The principle of the proton-transfer reaction mass spectrometer technique has been described elsewhere [*Lindinger et al.*, 1998; *de Gouw and Warneke*, 2007]. Here a high-sensitivity PTR-MS from Ionicon Analytik (Innsbruck, Austria) was re-designed to fit in an ATR-42-rack and to meet aircraft safety rules. A scheme of the PTR-MS configuration and operating conditions on board are provided in the supporting information (Figure S1).

[11] During MEGAPOLI, the ATR-42 was based at the airport of Cergy Pontoise in northwest Paris (49.09667°N, 2.0408349°E). The aircraft performed pseudo-Lagrangian flights downwind from Paris in eight predefined sectors according to prevailing wind directions. Four hour flights were performed in the afternoon in a well-developed boundary layer, at constant altitude (1500–2000 feet). First, the aircraft circled Paris followed by four transects perpendicular to plume axis at increasing distances from the Paris urban center (50–150 km; see section 3). One vertical sounding between 500 and 10,000 feet was performed at the end of the four transects.

## 2.3. Anthropogenic Emissions Database

[12] The anthropogenic VOC emissions databases considered here for Los Angeles (4 km × 4 km resolution) are based upon the U.S. EPA's 2005 National Emission Inventory (NEI 2005) released in December 2008 and the regional California Air Resources Board's (CARB 2008) 2008 emission inventory (<http://www.arb.ca.gov/ei/emissiondata.htm>). The NEI emission database has been described in detail in recent papers [*Brioude et al.*, 2011; *Kim et al.*, 2011]. Both anthropogenic VOC emission databases separate emissions into four source categories: on road, non-road, point, and area. In general, emission databases are designed



**Figure 1.** Normalized diurnal profiles of the mixing ratios of selected aromatics and alkenes to midnight values at the Los Angeles and Paris ground sites. Numbers in parentheses are the rate coefficient with OH in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  according to *Atkinson and Arey* [2003].

for regional-scale photochemical modeling. Anthropogenic VOCs are partitioned into 41 and 31 individual and lumped VOC species in the NEI and CARB inventory, respectively, as defined by the Statewide Air Pollution Research Center (SAPRC-99) condensed photochemical mechanism [Carter, 2000]. Emissions are hourly resolved.

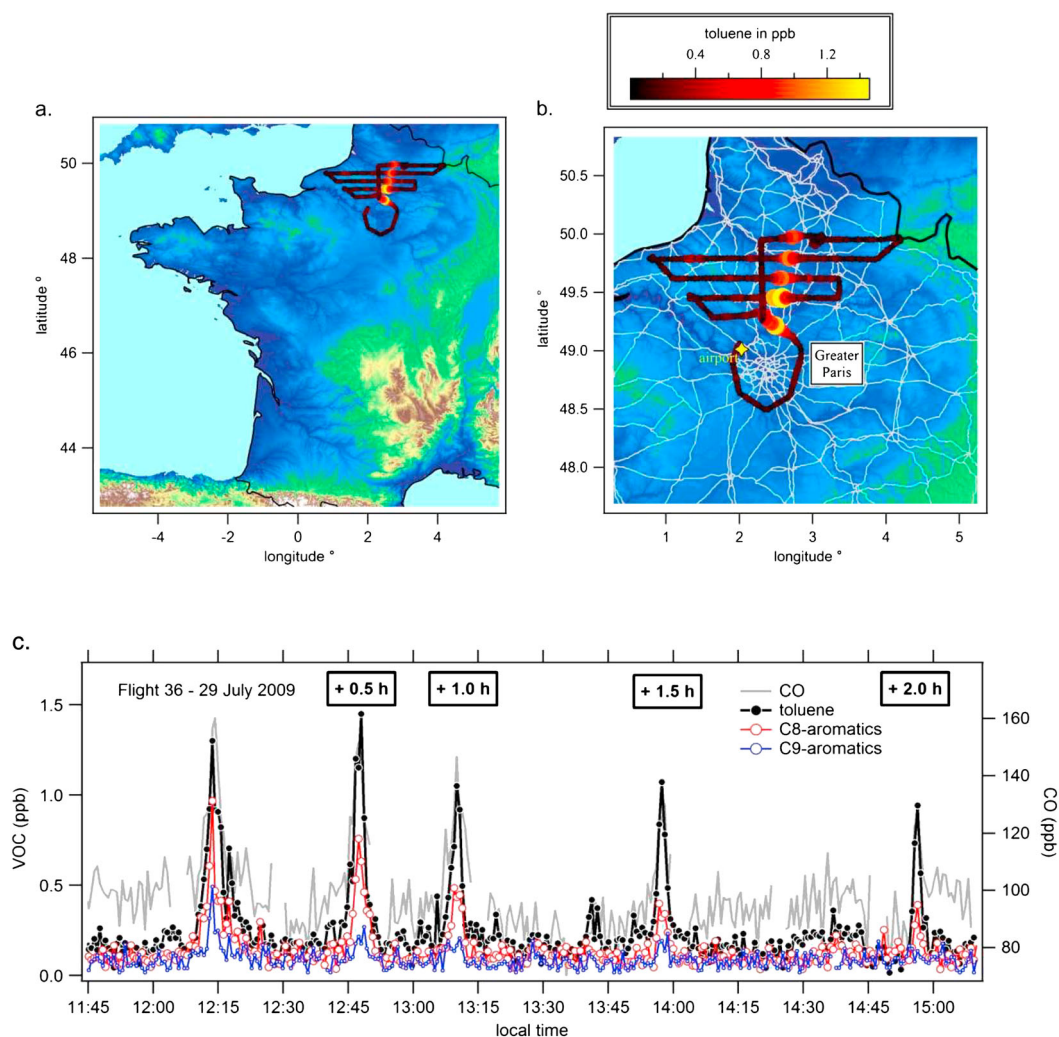
[13] The anthropogenic VOC emission database in Paris and Ile de France region is based upon the 2005 regional emission inventory released in April 2010 by the air quality monitoring network AIRPARIF. The inventory is compiled according to the Core Inventory Air (CORINAIR) emissions European methodology. The methodology was described in *Gaimoz et al.* [2011]. The anthropogenic VOC emission database from AIRPARIF separates emissions into nine source nomenclature for atmospheric pollution (SNAP) source categories: public power (SNAP 1); residential combustion (SNAP 2); industrial combustion (SNAP 3); industrial processes (SNAP 4); extraction, first processing, and distribution of fossil fuels (SNAP 5); solvents (SNAP 6); on-road transport (SNAP 7); non-road transport (SNAP 8); and waste disposal and treatment (SNAP 9). Emissions are temporally resolved on a monthly, daily, and hourly basis. Emissions of individual VOCs are extracted from the database by disaggregating the total emission of HC per emission sector or SNAP code from emission profiles (in %) available in the literature and widely used by the scientific community. Emission profiles are the ones used for chemistry-transport models in Europe and France (e.g., CHIMERE model) derived from *Passant et al.* [2002] and the ones compiled by the IER-Stuttgart [*Friedrich and Reis*, 2004; *Theloke and Friedrich*, 2007]. For the latter, the emissions of more than 300 species can be assigned.

[14] The inventories are respectively compiled for the same period of the year as the 31 day campaign of CalNex and MEGAPOLI, applying standard profiles for the monthly, weekly, and diurnal variability.

### 3. Emission and Chemistry of VOCs in Paris and Los Angeles

[15] The relative importance of emissions, chemistry and transport is first examined through the average diurnal profiles of the mixing ratios of some representative VOCs. The diurnal profiles of VOC absolute mixing ratios can be affected by emissions, chemistry (removal or photochemical production), and dilution, with the relative importance of each of these processes changing throughout the day. One can derive the diurnal normalized profiles of a given VOC relative to an inert tracer to examine the relative importance of these processes. The average profiles of primary VOCs are reported in Figure 1 for the Los Angeles and Paris ground sites. To facilitate comparison with the relatively inert tracer acetylene, the diurnal profile of acetylene is shown in each panel and the absolute values of all diurnal profiles are normalized to a midnight value of one.

[16] The diurnal profiles of primary VOCs in Los Angeles with a midday maximum for the less reactive VOCs and a midday minimum for the more reactive VOCs are explained by the transport of the photochemically processed LA plume to the Pasadena site [*Veres et al.*, 2011] during the day and the accumulation of local emissions at night in a shallower boundary layer. The degree of chemical removal during the day is  $k_{\text{OH}}$  dependent and increases with  $k_{\text{OH}}$  as illustrated for alkenes and aromatics. The diurnal profiles of primary



**Figure 2.** (a and b) Flight track color coded by toluene mixing ratios and (c) associated time series of aromatic VOCs and CO measured on board the ATR-42 downwind of Paris on 29 July. Only data collected at constant altitude (500 m) are reported. Framed bold values are the estimated transport time (in hours) of the urban plume since the first plume encounter at an average wind speed of  $7.5 \text{ m s}^{-1}$ .

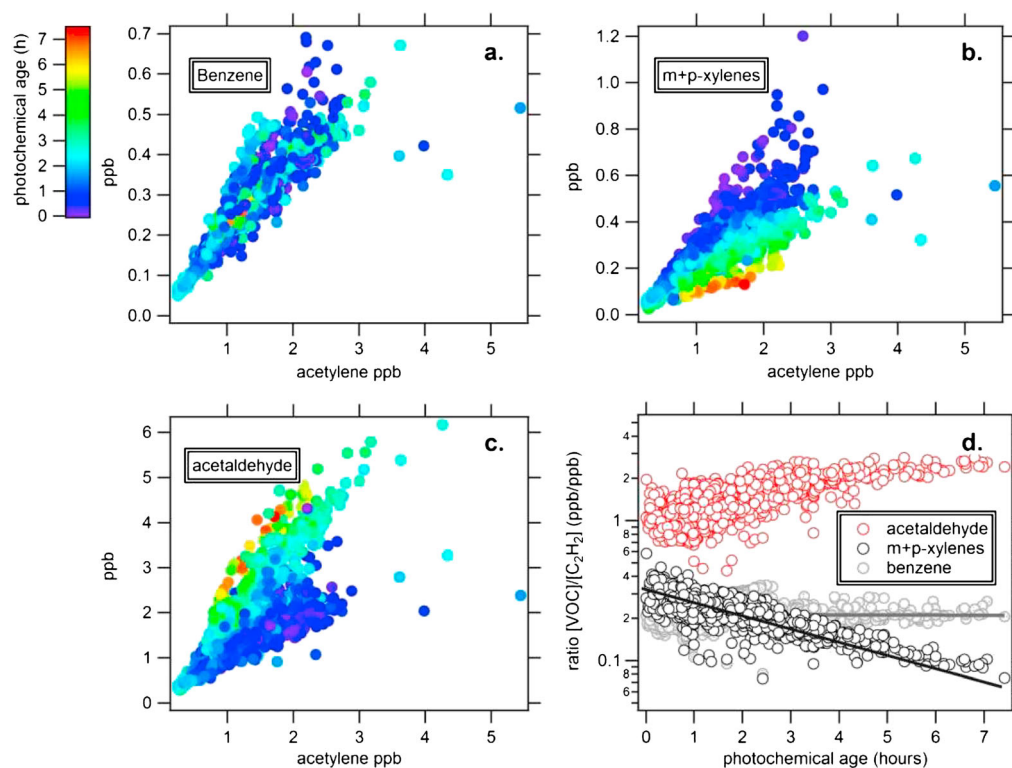
VOCs in Paris with maximum concentrations at morning and late afternoon traffic rush hours are typical of the profiles of traffic-emission-related compounds [Borbón *et al.*, 2003a; Gros *et al.*, 2011]. While photochemical removal cannot be excluded at midday in Paris, there is no evidence of its effect as no clear difference is seen between the diurnal profiles of VOCs with different reactivity. The minimum observed at midday in Paris is rather explained by differing emissions and dilution in a deeper afternoon boundary layer than by VOC chemical removal. On an hourly average basis, primary emissions combined with dilution dominate the variability of anthropogenic VOCs in downtown Paris while chemistry combined with advection strongly affects the variability of anthropogenic VOCs in Pasadena.

[17] The relative importance of emissions and chemistry is now explored in the Paris plume sampled by the ATR-42 as illustrated in Figure 2 during flight 36 on 29 July 2009. This flight was performed in the Northern sector of Paris (Figures 2a and 2b). Time series of aromatics measured by PTR-MS and CO, a passive tracer of anthropogenic emissions on the timescale of observations, are also

reported in Figure 2c. When the aircraft intercepted the Paris plume, the mixing ratios of toluene (Figure 2b) and all other trace gases of anthropogenic origin increased in parallel (Figure 2c). After 1.5 h of transport time, the Paris plume was still well defined. As transport time increased, the degree of removal was  $k_{\text{OH}}$  dependent. The enhancement ratios of toluene and benzene (not shown here for clarity) relative to CO remained constant, as they are little affected by photochemical processing within a 1.5 h transport time. Conversely, the enhancement ratios of C8 and C9 aromatics relative to CO decreased. The depletion is even faster for C9 aromatics compared with C8 aromatics as their rate coefficient with OH is a factor of 2 to 3 higher (Figure 1). After 30 min, C8 and C9 aromatics were depleted by 17% and almost 40%, respectively, in the Paris plume.

#### 4. Determination of VOC Emission Ratios

[18] The goal of this paper is to determine urban VOC emission ratios. In the previous chapter, we showed that



**Figure 3.** Scatterplots of (a) benzene, (b) (m+p)-xylenes, and (c) acetaldehyde versus acetylene in Pasadena color coded by the photochemical age. (d) Measured ratios of benzene/acetylene, (m+p)-xylenes/acetylene and acetaldehyde/acetylene as a function of photochemical age.

VOCs can be strongly affected by chemical transformation processes, so that the measured enhancement ratios, especially for shorter-lived VOCs, can be significantly different from the emission ratios. In this chapter, we show how emission ratios can be determined by looking at “no-chemistry” conditions. It should be noted that the urban emission ratios determined here represent the total urban emissions as individual source categories cannot be distinguished in either megacity.

#### 4.1. The Photochemical Age Method Applied to Ground-Based Observations

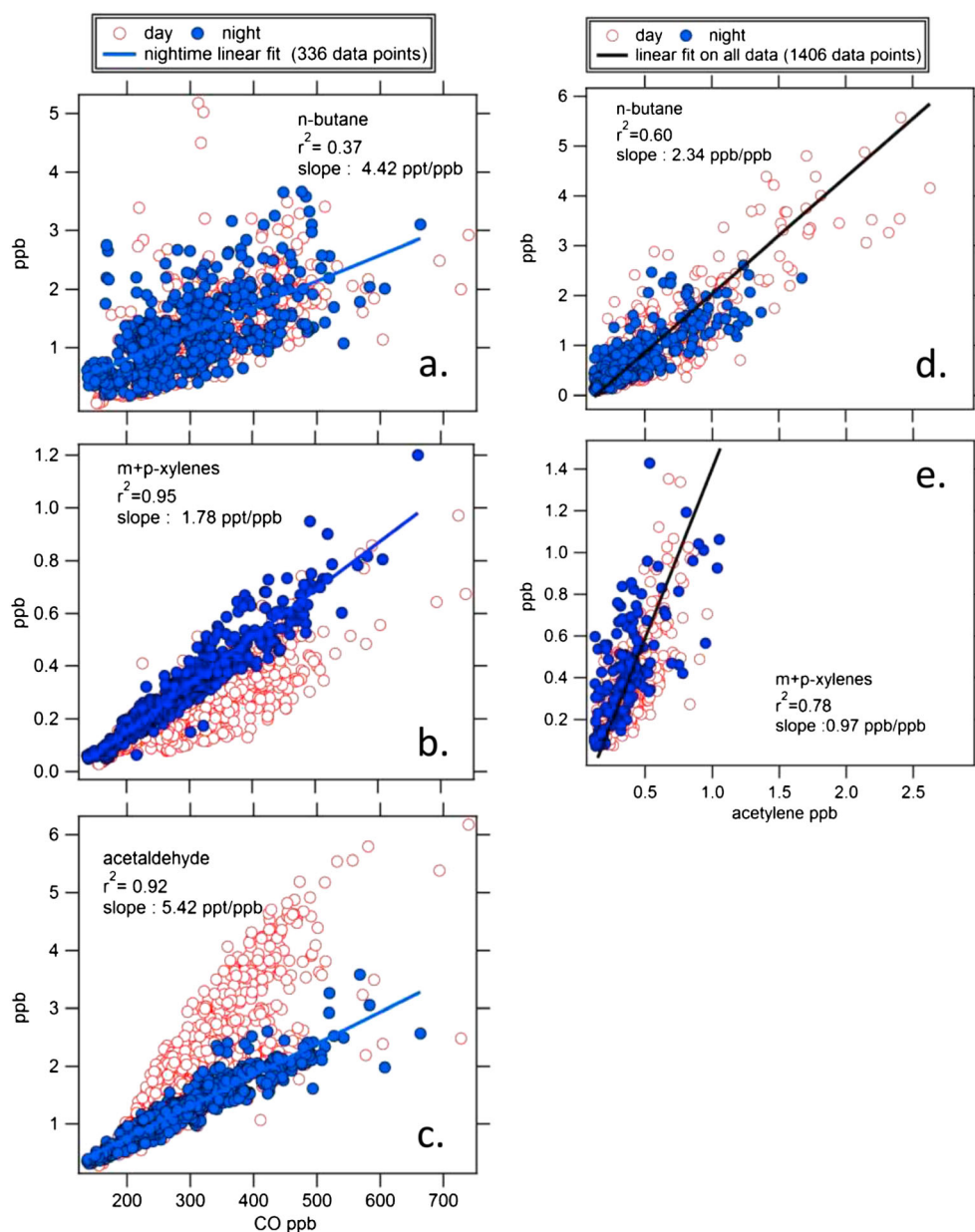
[19] The estimation of emission ratios using the photochemical age is adapted from *de Gouw et al.* [2005] and *Warneke et al.* [2007]. In this method, the degree of photochemical processing (photochemical age) of air masses is estimated from hydrocarbon ratios, and the enhancement ratios of VOCs are extrapolated to zero photochemical age to estimate the emission ratios. The calculation of the photochemical age and equations used for emission ratio determination are described in details in the supporting information (section S2). The principle of the method is illustrated in Figure 3. The scatterplots of a less reactive primary VOC (benzene), a reactive primary VOC ((m+p)-xylenes), and a secondary VOC (acetaldehyde) versus acetylene are color coded by the photochemical age in Figures 3a–3c. The slope of the scatterplot is clearly affected by the photochemical age for the chemistry-dependent VOCs ((m+p)-xylenes and acetaldehyde): higher in freshly emitted air masses for short-lived primary VOCs and lower for secondary VOC. The ratios of measured benzene/acetylene,

(m+p)-xylenes/acetylene, and acetaldehyde/acetylene are reported in Figure 3d as a function of photochemical age. As observed above, the benzene/acetylene ratio is fairly constant with photochemical age on these photochemical timescales, whereas the (m+p)-xylene/acetylene ratio decreases by almost a factor of 5 and the acetaldehyde/acetylene ratio increases by almost a factor of 3. Following *de Gouw et al.* [2005] and *Warneke et al.* [2007], the data on Figure 3d for primary VOCs and secondary OVOCs can be described by an equation in which the emission ratio is the extrapolation of the measured ratios to a zero photochemical age (see equations (S1) and (S2) in the supporting information). For primary VOCs, the emission ratio corresponds to the value of the intercept of the linear fit with the y axis (Figure 3d).

#### 4.2. The Linear Regression Fit Method Applied to Ground-Based Observations

[20] A commonly used method to determine emission ratios is to utilize a linear regression fit (LRF) to calculate the slope of the scatterplot between two compounds, here a particular VOC versus acetylene or CO. As observed in Figure 3, the distribution of points within the scatterplot can be affected by photochemistry. To prevent an overestimation or underestimation of the emission ratio, spatial and temporal filters need to be applied to account for the influence of chemistry. Scatterplots of some selected VOCs are shown in Figure 4.

[21] In the Los Angeles-Pasadena area, the measured ratios of VOCs to an inert tracer can be affected by their chemistry with the OH radical during daytime as seen in Figures 1 and 3. At night, chemistry with OH can be

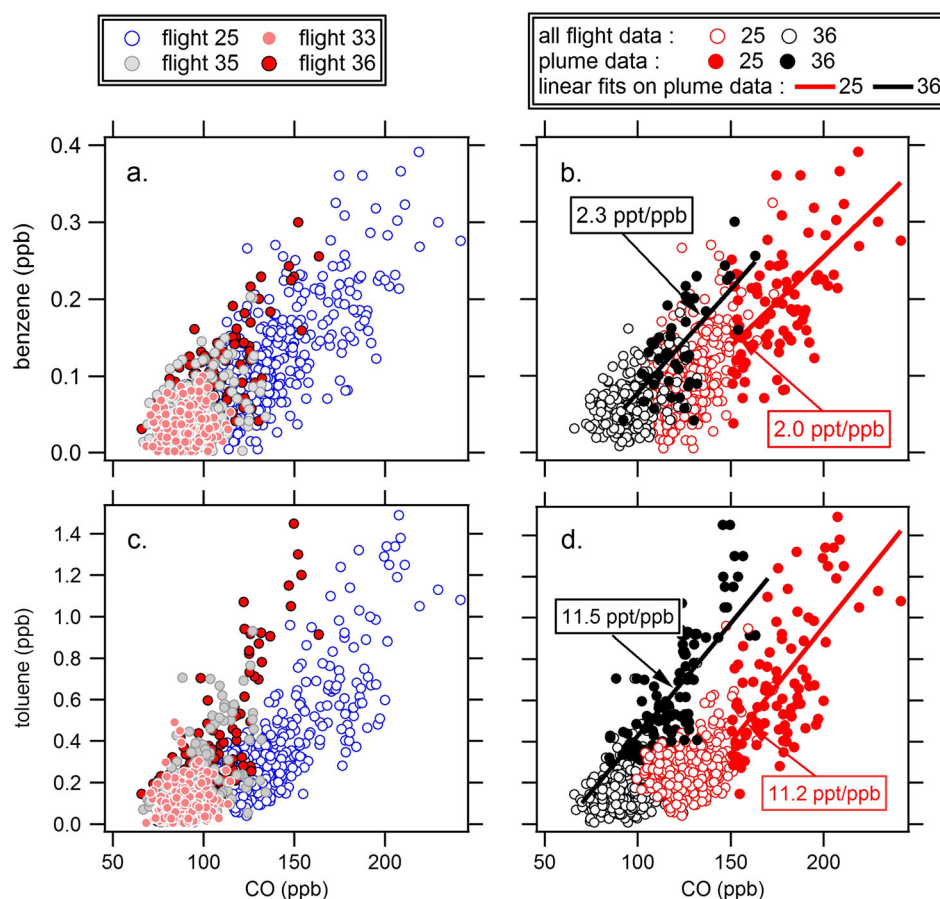


**Figure 4.** Daytime and nighttime scatterplots of some representative VOCs over two inert tracers. (a–c) CO in Los Angeles and (d, e) acetylene in Paris. The two-sided linear fit is applied on nighttime data in Los Angeles and all data (day and night) in Paris.

neglected as discussed in section 4.1. However, alkenes could be affected by their chemistry with ozone and  $\text{NO}_3$  radicals at night. Given its reaction rate constant with ozone of  $0.190 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [Atkinson and Arey, 2003] and with  $\text{NO}_3$  of  $9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [Ambrose *et al.*, 2007], trans-2-butene is the most reactive alkene at night measured during CalNex at the ground site. The nighttime average mixing ratio was 20 ppb for ozone and 7 ppt for  $\text{NO}_3$  provided by the differential optical absorption spectroscopy (DOAS) instrument [Alicke *et al.*, 2002; Stutz *et al.*, 2009] at the ground site. A lifetime of about 10 min toward  $\text{NO}_3$  against 2.9 h toward ozone is deduced for trans-2-butene. Nighttime chemistry with  $\text{NO}_3$  and to a lesser extent ozone can therefore be significant for cis- and trans-2-butenes, and results for those species

will be discussed with caution. Except for butenes, nighttime chemistry is not significant for most measured VOCs, and nighttime data (22:00–06:00 local time) can be used for the LRF method. Figures 4b and 4c highlight the importance of this temporal filter for reactive primary VOCs (alkenes, C7–C9 aromatics) and VOCs with an additional secondary origin (aldehydes and ketones). In addition, isoprene from anthropogenic emissions can be derived from nighttime data in the absence of its light-dependent biogenic origin [Borbon *et al.*, 2001]. In Paris center, there is no clear evidence of a strong effect from active photochemistry at ground level, as seen from Figure 1. As for n-butane in Los Angeles (Figure 4a), a non-reactive VOC at the timescale of interest, the nighttime and daytime scatterplots in Paris cannot be distinguished regardless of





**Figure 5.** Scatterplots of benzene and toluene versus CO mixing ratios from the ATR-42 airborne observations in the boundary layer of Paris. (a, c) The scatterplots are color coded by four typical flights. (b, d) The lines and numbers are the linear regression fits and slope values, respectively, on data within the Paris plume during flights 25 and 36.

the VOC reactivity (Figures 4d and 4e). Daytime and nighttime data can be used for the LRF method.

[22] The nighttime LRF approach relies on the assumption that the composition of urban emissions relative to CO, and acetylene does not change between day and night. In particular, one could expect some changes in the composition of evaporative emissions from fuel for light alkanes due to diurnal changes in temperature. However, daytime and nighttime scatterplots agree very well as seen from n-butane (Figures 4a and 4d) suggesting that emission composition does not change between day and night for either data set. Previous studies in spring time have shown that the contribution of continental transport from source regions located in northeastern and eastern Europe could contribute to the observed pollutant levels downtown Paris [Gros *et al.*, 2011; Sciare *et al.*, 2010], at least for the long-lived species. The VOC emission ratio to acetylene and CO could be then underestimated. In summer 2009, westerly winds that brought clean air masses from the Atlantic were the most frequent (W. Ait-Helal *et al.*, Gaseous organic carbon in suburban Paris: Importance of intermediate VOCs in SOA formation, manuscript in preparation, 2013). Therefore, the import of air masses from the continent did not significantly affect the distribution of points within the scatterplots.

[23] In both megacities,  $>C_4$  alkanes, aromatics, alkenes, and carbonyls are correlated with acetylene and CO with values of  $r^2$  higher than 0.70. Gasoline-powered vehicles are the dominant primary emission source for CO [Allan *et al.*, 2010] and therefore are also the likely sources of acetylene, aromatics and alkenes,  $>C_4$  alkanes, and carbonyls.  $C_2$ – $C_4$  alkanes in both megacities and alcohols in Los Angeles show a lower  $r^2$  ( $0.5 < r^2 < 0.8$ ). While part of their primary anthropogenic emissions is gasoline-powered vehicles, other diffuse and non-combustion sources are known to contribute to their emissions including fuel evaporation and natural gas leakage for alkanes, and oceanic and biogenic sources for methanol.

### 4.3. The LRF Method Applied to Airborne Observations

[24] Since the time series of benzene and toluene in the Paris plume also suggest the absence of significant chemical removal on the transport timescales studied here, the emission ratio can be also derived from a linear regression fit of aromatics versus CO within the Paris plume after a flight-by-flight examination. Benzene, toluene, C8 aromatics, and C9 aromatics are detected at 79, 93, 107, and 121 amu, respectively. With PTR-MS, unambiguous identification of

**Table 2.** Urban Emission Ratios of VOCs Relative to Acetylene and CO in Los Angeles and Paris Obtained by Calculating a Linear Regression Fit to Data<sup>a</sup>

VOC	$\Delta\text{VOC}/\Delta\text{C}_2\text{H}_2$ (ppb/ppb)		$\Delta\text{VOC}/\Delta\text{CO}$ (ppb/ppb)	
	Los Angeles	Paris	Los Angeles	Paris
Ethane	2.86	4.94	18.4	23.4
Propane	1.91	1.90	11.2	9.02
n-butane	1.22	2.34	4.42	10.1
i-butane	0.60	0.96	3.08	4.53
n-pentane	0.66	0.65	3.26	3.08
i-pentane	1.36	2.27	8.69	10.8
2-methyl-pentane	-	0.27	-	1.29
n-hexane	0.18	0.24	1.13	1.15
3-methyl-hexane	-	0.45	-	2.14
cyclohexane	-	0.07	-	0.33
n-heptane	-	0.43	-	2.03
2,3-dimethylpentane	-	0.79	-	3.74
3-methyl-heptane	-	0.02	-	0.09
n-octane	-	0.04	-	0.19
2,2,4-trimethylpentane	-	0.15	-	0.71
n-nonane	0.03	0.06	0.22	0.26
n-decane	0.03	0.10	0.18	0.46
Undecane	0.04	-	0.29	-
Acetylene	1.00	1.00	5.87	4.74
Ethene	1.75	0.61	10.35	7.64
Propane	0.64	0.44	3.74	2.07
1-butene	0.05	nd	0.34	nd
cis-2-butene	0.01	nd	0.09	nd
trans-2-butene	0.01	0.07	0.10	0.34
1,3-butadiene	0.05	0.08	0.35	0.39
Isoprene	0.04	nd	0.30	nd
Benzene	0.20	0.23	1.30	1.07(2.50) <sup>c</sup>
Toluene	0.51	2.59	3.18	12.3(11.4) <sup>c</sup>
m + p-xylenes	0.28	0.97	1.79	4.59
o-xylenes	0.10	0.23	0.67	1.09
Ethylbenzene	0.09	0.19	0.57	0.95
C8-aromatics <sup>b</sup>	-	1.15	-	4.75(5.50) <sup>c</sup>
n-propylbenzene	0.02	0.21	0.11	0.87
Isopropylbenzene	0.01	-	0.03	-
1-ethyl-2-methyl-benzene	0.02	-	0.12	-
1-ethyl-3,4-dimethylbenzene	0.05	-	0.35	-
Styrene	0.04	-	0.22	-
1,3,5-trimethylbenzene	0.05	0.08	0.31	0.38
1,2,3-trimethylbenzene	0.04	0.12	0.24	0.59
1,2,4-trimethylbenzene	0.10	0.16	0.62	0.74
Acetaldehyde	0.93	-	5.42	-
Butanal	0.04	-	0.25	-
Propanal	0.17	-	1.13	-
Benzaldehyde	0.16	-	0.03	-
Acetone	2.52	-	11.78	-
Methylvinylketone	0.03	-	0.24	-
Methacrolein	0.02	-	0.12	-
2,3-butadiene	0.02	-	0.14	-
Methanol	2.48	-	21.72	-
Ethanol	6.81	-	48.01	-
Isopropanol	2.62	-	10.60	-
Carbon monoxide	170	242	1.00	1.00

<sup>a</sup>See Table S2 in the supporting information for complement. A hyphen (-) indicates unmeasured VOC; nd is non-determined.

<sup>b</sup>Xylenes (m + p + o) + ethylbenzene at m/z 108.

<sup>c</sup>Numbers in parenthesis are the emissions ratios determined from airborne measurements by PTR-MS in Paris plume.

chemical species is not possible. However, no large interferences for aromatic VOCs are known in urban air from past inter-comparisons with chromatographic techniques [*de Gouw and Warneke, 2007*].

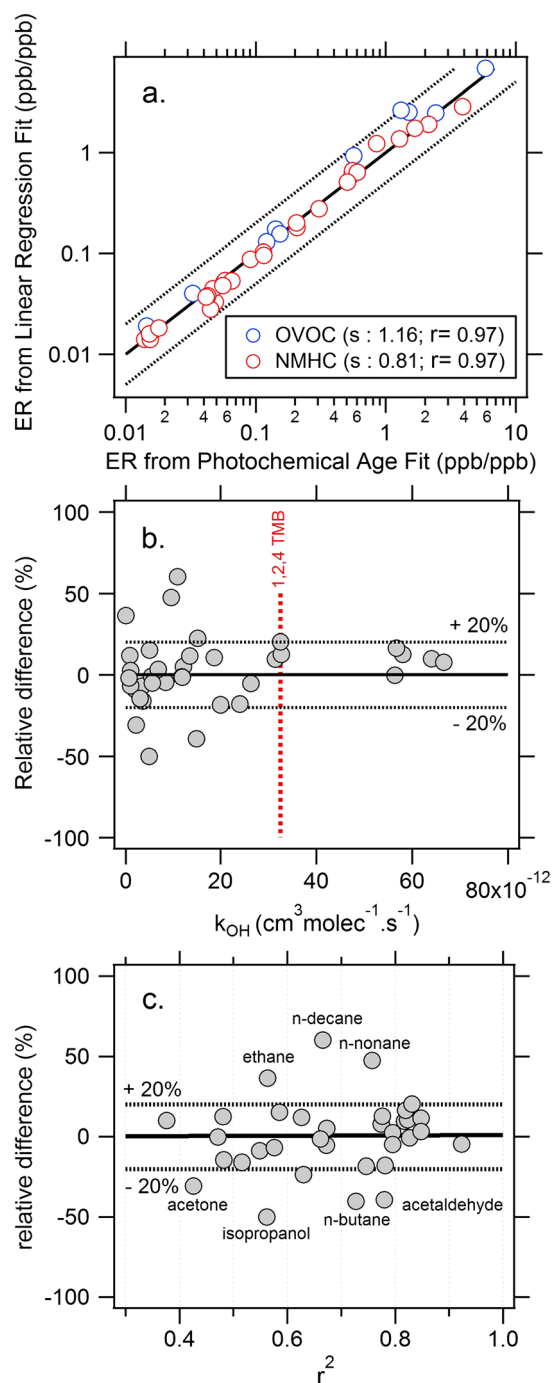
[25] Scatterplots are reported in Figure 5 for four flights over Paris area during the MEGAPOLI summertime campaign (Figures 5a and 5c). The emission ratios of benzene and toluene were derived from the average of their linear fits versus CO within the Paris plume as illustrated in Figures 5b and 5d for flights 25 and 36.

#### 4.4. Performance of the Different Methods

[26] All emission ratios (ERs) determined as described above are given in Table 2 for the LRF method and in the supporting information for the photochemical age method applied to ground-based data in Los Angeles (Table S1).

[27] The performance of the ER determination is illustrated in Figure 6 for the Los Angeles data. ER from the photochemical age and LRF methods are compared in Figure 6a, and their relative differences (in %) are analyzed as a function of the rate coefficients relative to OH (Figure 6b) and  $r^2$  (Figure 6c). *de Gouw et al. [2005]* and *Warneke et al. [2007]* have shown that the accuracy of the photochemical age method estimation could be limited for the most reactive compounds, especially for the ones with a rate coefficient relative to OH higher than that of the compound used in the numerator in the photochemical age calculation (here 1,2,4-trimethylbenzene in equation (S1) in the supporting information). The  $r^2$  coefficient indicates the quality of the linear fit in the LRF method; the uncertainty of the slope is expected to increase at lower  $r^2$ . In general, the relative differences between both methods are within  $\pm 20\%$  and outliers remain within the uncertainties expected from the photochemical age method as discussed in section 4.3. From Figures 6b and 6c, the relative differences do not seem to depend on neither the reactivity rate with OH nor the quality of the linear fit. The LRF results for cis- and trans-2-butenes should be seen as a lower limit as an effect of NO<sub>3</sub> nighttime chemistry cannot be excluded (see chapter 4.2). However, their relative difference remains within the  $\pm 20\%$  interval. The relative differences are much higher for some alkanes (ethane, n-butane, n-nonane, and n-decane), acetaldehyde, acetone, and isopropanol. Vehicle exhaust is not the dominant source of these compounds, which also have important contributions from area sources. Overall, the good agreement between the two methods in Los Angeles confirms that the selection of nighttime data in the LRF method does not bias the results. While the absolute fluxes of urban emissions decrease at night (CARB, 2008), the composition of those emissions remains approximately constant.

[28] The performance of the ER determination in Paris can be evaluated for the benzene, toluene, and C8 aromatics ratios relative to CO by comparing the results of ground-based and airborne LRF reported in Table 2. The values for toluene and C8 aromatics are within 10%, whereas the one for benzene derived from the GC-FID ground site data is almost two times higher than that from the airborne PTR-MS observations. The airborne value of 2.5 ppt/ppb [CO] is consistent with the value of 2.4 ppt/ppb found at a motorway location in Austria [*Schnitzhofer et al., 2008*]. The difference between airborne and ground-based measurements remains within the range of variation that can be expected for the benzene to CO emission ratio in European urban areas.



**Figure 6.** Performance of the emission ratio (ER) estimation methods relative to acetylene in Los Angeles. (a) Comparison of the ER estimated by the nighttime linear regression fit and the photochemical age fit. (b) Relative differences between the ER from both methods versus the reaction rate coefficient with OH ( $k_{OH}$ ). (c) Relative differences between the ER from both methods versus the determination coefficient ( $r^2$ ).

A factor of 2 is also the maximum difference expected from the photochemical age and LRF method (see Figures 6b and 6c). The consistency between emission ratios from airborne and ground-based observations shows that the LHVP ground

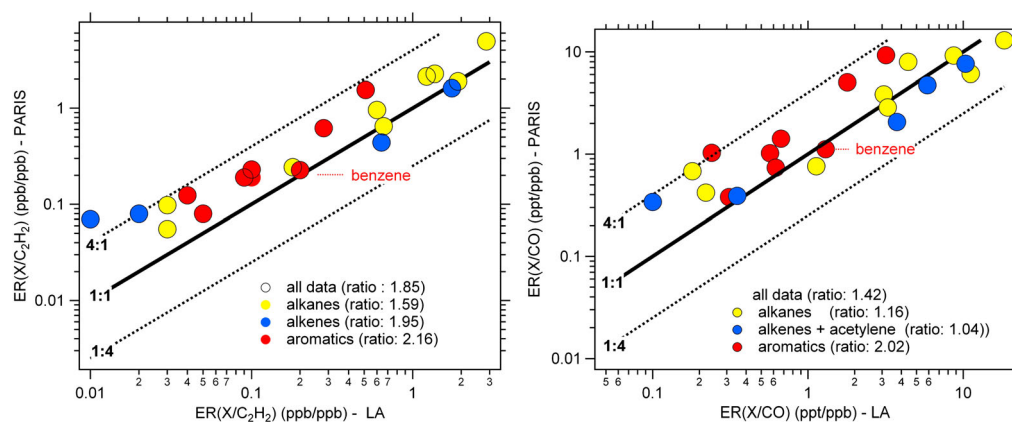
site in Paris is representative of the composition of Paris emissions, at least for toluene and C8 aromatics.

## 5. Composition of Urban VOC Emissions: Los Angeles Versus Paris

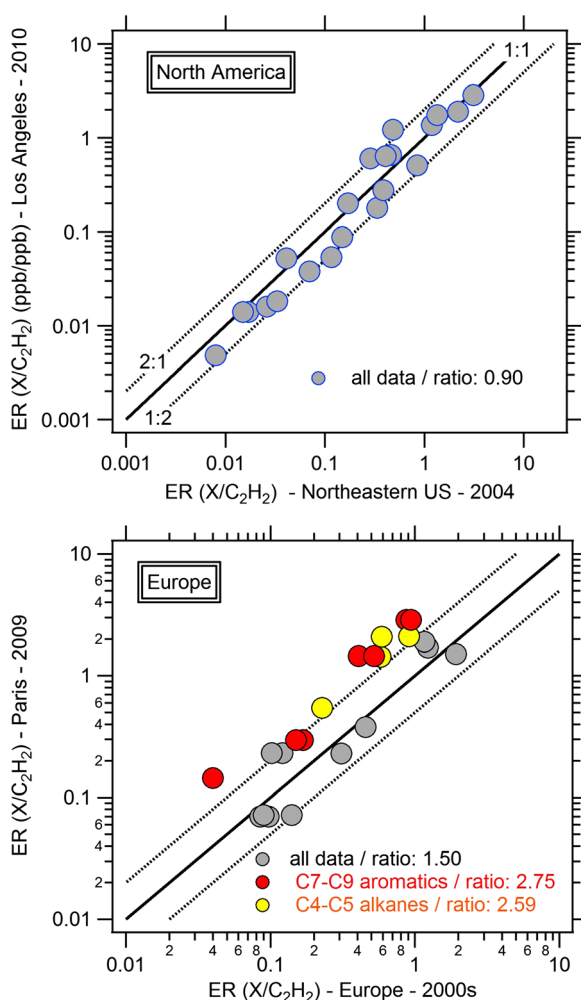
[29] The urban ER relative to acetylene and CO of major NMHC and OVOCs from the linear regression fit at ground sites are reported in Table 2 for Los Angeles and Paris and are quantitatively compared in Figure 7 for NMHC. The urban ERs of NMHC agree within a factor of 4 (Figure 7). The ratios of emission ratios between Paris and Los Angeles have been calculated, and their geometric means estimated as reported in Figure 7. Except for aromatics, the emission ratios all agree within a factor 2. Emission ratios of alkanes are higher in Paris by 35% in average. Within the aromatic class, only the benzene emission ratios are within a factor of 2 between Paris and Los Angeles. We calculated 10 kg VOC per capita per year in Paris versus 19 kg of VOC per capita per year in the South Coast Air Basin based on emissions numbers provided by local authorities and population statistics (AIRPARIF, 2005, and CARB, 2008, <http://www.arb.ca.gov/app/emsinv>). While the magnitude of VOC emissions from these inventories differs in both megacities, the relative composition appears fairly similar. In contrast, the urban ER of C7–C9 aromatics are about 2–3 times higher in Paris than in Los Angeles as seen in Figure 7.

[30] The ERs of NMHC relative to acetylene in Los Angeles and Paris are compared with the ones previously published in other U.S. urban regions (northern East Coast during NEAQS experiment in 2004) and in Europe (northern France and London), respectively (Figure 8). Except for C7–C9 aromatics and C4–C5 alkanes in Paris, the ERs in Los Angeles and Paris agree within a factor of 2 with results from previous U.S. and European urban areas, respectively; the geometric mean of the ratios are within  $\pm 50\%$ . Again, Figure 8 highlights the enrichment of Paris air in C7–C9 aromatics and, to a lesser extent, butane and pentane isomers compared to other European urban areas. Differences in the (i) gasoline composition and in the (ii) vehicle fleet composition as two potential causes of such discrepancy are examined. *Gaimoz et al.* [2011] first showed that vehicle exhaust emissions mostly contribute to C7–C9 aromatic loads in Paris in 2007. The analysis of multiyear trends of C7–C9 aromatics/acetylene ratios also reveals that these ratios did not decrease from 2003 to 2012 in Paris (*Borbon et al.*, manuscript in preparation, 2013). This would suggest that C7–C9 aromatics and acetylene both come from traffic emissions with same efficiency of vehicle emission control systems. The potential effect of a solvent-use-related source will be therefore rejected for C7–C9 aromatics.

- Aromatics (benzene included) and C4–C5 alkanes are major constituents of gasoline. Their traffic emissions are made of an exhaust component, constituted by an unburned and burned gasoline fraction, and an evaporative component. In Europe, the standard in gasoline content is 1.0% vol for benzene and 35% vol for other aromatics (Directives 98/70/EC and 2003/17/EC). In California, these standards, known as the California

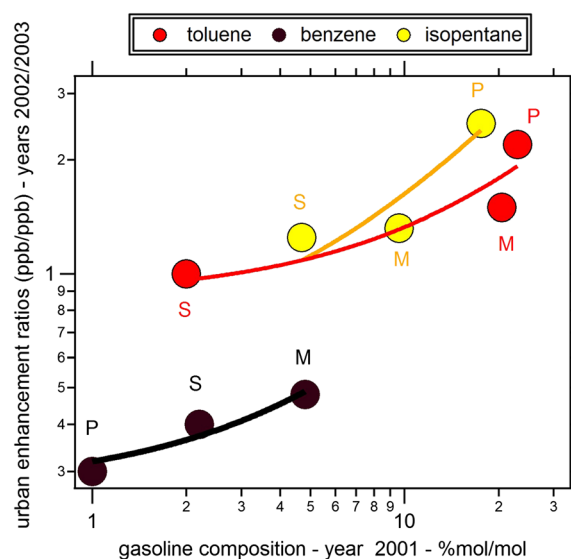


**Figure 7.** Comparison of NMHC emission ratios versus (left) acetylene and (right) CO between Paris and Los Angeles. The  $s$  and  $r^2$  terms are the respective values of slope and determination coefficient of a linear regression fit applied to each class of NMHC. The best fits are not shown.



**Figure 8.** Comparison of NMHC emission ratios relative to acetylene in Los Angeles and Paris to previous published studies in the United States [Warneke *et al.*, 2007] and Europe [Borbon *et al.*, 2003a, 2003b; Dollard *et al.*, 2007], respectively. The values of the ratio are given by the geometric mean of the ratios between Los Angeles and Paris and U.S. and European studies, respectively.

Reformulated Gasoline Phase 3 Standards, are more restrictive: the benzene content is 0.8% vol, while the total aromatic content is 22% vol. While the standard adopted for benzene is the same, some differences can be expected for individual compounds between EU countries. The urban enhancement ratios of benzene, toluene, and isopentane to acetylene in three French urban areas (Paris, Marseille, and Strasbourg) in the framework of the national NMHC monitoring program (see section 2.1) are reported in Figure 9 as a function of the gasoline composition distributed in 2001 and reported by Borbon *et al.* [2003b]. Butanes were left out as they have other urban emission sources as well as alkenes that are combustion products. Only ambient data collected at morning traffic rush hours were selected for the summer of 2002 and 2003. A high spatial variability in the fuel composition (in % vol.) was found for aromatics (toluene) and C2–C5 alkanes



**Figure 9.** VOC/acetylene enhancement ratios in French urban areas (P, Paris; S, Strasbourg; M, Marseille) as a function of distributed gasoline composition. The lines are the best linear regression fits.

(isopentane). In France, the gasoline used across the nation comes from different refineries. Toluene has the highest aromatic content observed in Paris and regional differences in composition could be as large as an order of magnitude in 2001. It is also seen that the VOC composition of urban air for unburned gasoline is dependent on the composition of the gasoline. These regional differences could explain the differences observed in the emission ratios between Paris and Los Angeles in 2009 and 2010 if fuel composition has not significantly changed since then. The similarity between emission ratios in Paris in 2009 (Table 2) and 2002/2003 (Figure 9) would support such hypothesis.

- ii. The use of powered two wheelers (PTW) for commuting as an alternative to the use of private passenger cars is increasing in large congested urban centers. In Paris, for the year 2008, powered two wheelers represented 4% of the number of displacement modes, which is 2 times higher than the other French urban centers, and represents 23% of the mileage by the PTW running fleet in France [*Ministère de l'Écologie, du Développement durable, des Transports et du Logement*, 2008]. Due partly to a delayed control on emissions at PTW exhaust in the EU compared to passenger car exhaust, the emissions per km of CO, NO<sub>x</sub>, and NMHC from modern two-stroke mopeds are much higher than gasoline and diesel cars; for NMHC, it can be a factor 10 to 150 higher and even more when considering individual species because of significant unburned fuel fractions in two-stroke motors [*Prati and Costagliola*, 2009]. A significant contribution of PTW to overall road transport emissions can be expected in the Paris area according to the regional emission inventory: 35% of the VOC emissions by road transport sector would be explained by this category (AIRPARIF, 2005). Two studies have recently reported on a detailed chemical characterization of hydrocarbon emissions from modern two-stroke mopeds complying with the pre-Euro, Euro1, and Euro2 regulations in Europe [*Adam et al.*, 2010; *Montero et al.*, 2010]. The dominating hydrocarbons in the fingerprints belong to the fuel unburned fraction. In general, results show a larger fraction of unburned alkanes rather than aromatics. However, the hydrocarbon emission fingerprints show a large variability depending on gasoline composition and vehicle age. The results in Figure 9 suggest that the urban emission ratios in Paris will depend on the strength of the aromatic fraction in the gasoline formulation. Based on our limited evidence, the importance of the PTW sources to aromatic emissions in Paris cannot be excluded.

[31] Previous studies [*Warneke et al.*, 2007; *Baker et al.*, 2008] have shown that urban VOC emissions in the United States had similar composition. While our results confirm and extend these previous findings, they also bring new insights. By combining the information from Figures 7 and 8, our results suggest that the composition of alkanes, alkenes, acetylene, and benzene emissions is similar in northern mid-latitude urban areas. However, regional characteristics in fuel composition could affect the emission composition of C7–C9 aromatics as seen in the Paris

megacity. Moreover, the relative composition of NMHC urban emissions appears not to be affected by the higher proportion of diesel-powered vehicles in Europe, and France in particular. In accordance, the composition of NMHC emissions in LA was found to be the same between weekdays and weekends, when diesel traffic is reduced by 40 to 80% in the whole basin [*Pollack et al.*, 2012, and reference therein]. As a consequence, emissions from gasoline-powered vehicles appear to be the dominant source of C2–C9 hydrocarbons, as well as CO, in northern mid-latitude urban areas, as already demonstrated by *Gentner et al.* [2009] for California.

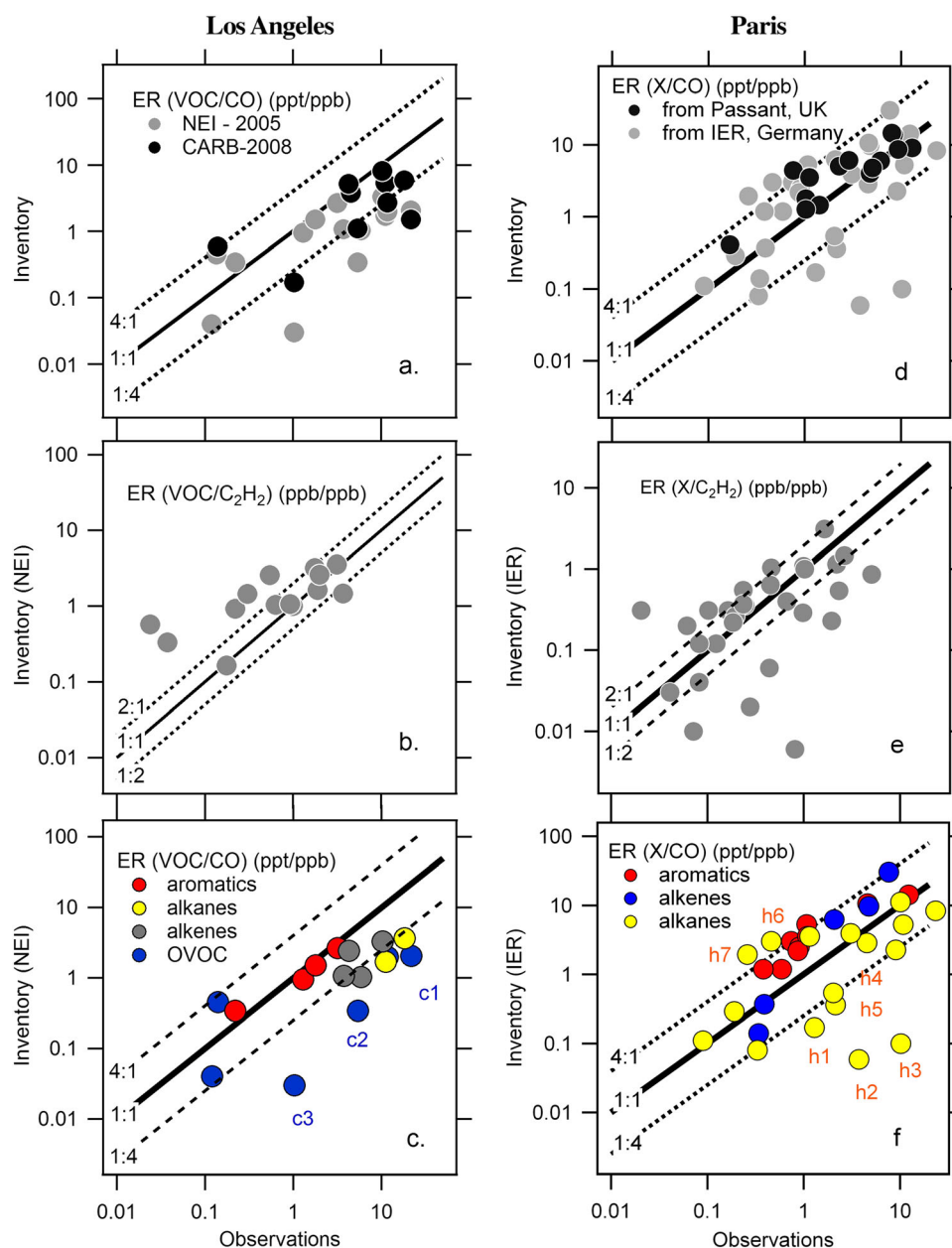
## 6. Evaluation of the Emission Inventories in Los Angeles and Paris

### 6.1. Comparison With the Observed Emission Ratios

[32] The comparison is based on the national (NEI) and regional (CARB) emission database in Los Angeles and the AIRPARIF inventory in Paris disaggregated by the two European reference VOC specifications from the UK [*Passant*, 2002] and Germany [*Theloke and Friedrich*, 2007]. For the purpose of the comparison, the gridded VOC emissions from the inventories have been integrated for all available species and CO in both a small and larger domain in both megacities (see Figure S3 in the supporting information). The ratios between emissions of different species were found to be relatively independent of domain size indicating a relatively homogeneous distribution of sources. The on-road category in the U.S. inventories is equivalent to SNAP 7 source category in the European nomenclature. The average contribution of the on-road sources to the total VOC anthropogenic emissions is 30% in Los Angeles and 16% in Paris. Higher contributions come from area sources and mobile non-road sources for the U.S. inventories. In particular, the solvent use sector (SNAP 6) in Paris would explain at least 50% of VOC emissions. After summing up all source categories for individual VOCs, the urban emission ratios relative to CO and acetylene (not shown here) are compared. Lumping of the species in the inventory is the main limitation to the comparison. A detailed list of the individual species that could be compared is provided in the supporting information (Table S2).

[33] The urban emission ratios relative to CO agree within a factor of 4 in both megacities (Figures 10a and 10d). In Los Angeles, the inventory ERs generally fall below the 1:1 line, whereas in Paris, the inventory ERs are generally above the 1:1 line. When comparing the emission ratios relative to acetylene (Figures 10b and 10e) and calculating the geometric mean of the ratio of emission ratios, the differences between inventories and observations are reduced by a factor of 2 for most of the compounds. One possible explanation is that the emissions of CO are overestimated by the NEI 2005 in Los Angeles as shown by *Brioude et al.* [2011] while they are underestimated by AIRPARIF in Paris by a factor of 2. In Los Angeles, the emissions of CO by the non-road mobile source category (two- and four-stroke lawn and garden equipment) would be overestimated.

[34] The VOC speciation is another source of discrepancy. Figures 10c and 10f report the emission ratios relative to CO color coded by the VOC groups. The largest discrepancies



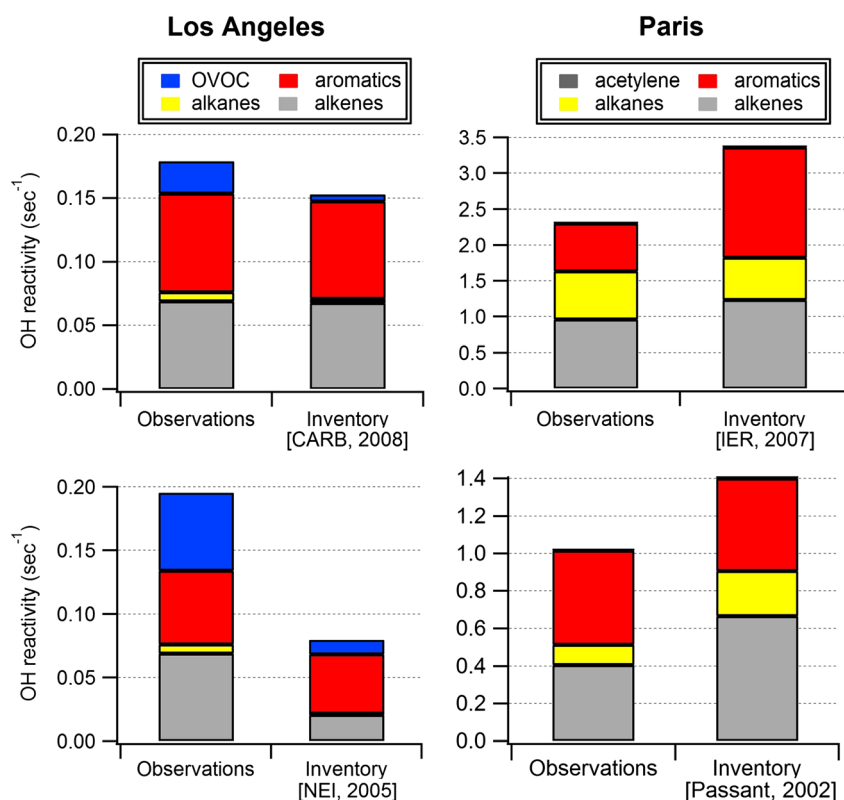
**Figure 10.** Comparison of the measured emission ratio relative to (a, c, d, f) CO and (b, e) acetylene to the ones in the anthropogenic VOC emission database currently used in Los Angeles and Paris (see text for details). Abbreviations are as follows: c1, methanol; c2, acetaldehyde; c3, benzaldehyde; h1, 2-methylpentane; h2, 2,3-dimethylpentane; h3, methylcyclohexane; h4, n-heptane; h5, 3-methylhexane; h6, n-nonane; h7, n-decane.

are observed for oxygenated VOCs and alkanes. It should be noted that branched alkanes are largely underestimated, while n-nonane and n-decane are overestimated in Paris. These results are consistent with previous studies by *Warneke et al.* [2007] and *Vautard et al.* [2003]. In Paris, the sensitivity of the emission ratio values from the inventory to different source scenarios was also tested. In addition to the standard inventory, two special scenarios were considered in the inventory for the emission ratio calculation: one scenario only considering road transport source and one without solvent use source scenario. The values of alkene emission ratios do not change in either scenario as they mainly come

from traffic emissions. Some values of the emission ratios of alkanes and aromatics changed between the scenarios but with no clear evidence of a reduction of differences with either special scenario. This shows that the causes of discrepancies between inventory and observations come from the estimated amount of emissions per source category as well as the VOC speciation used.

## 6.2. Implication for Chemistry

[35] Two metrics are used to test how well the emission database reproduces the potential of sampled air masses to form ozone and SOA: OH reactivity and the SOA formation



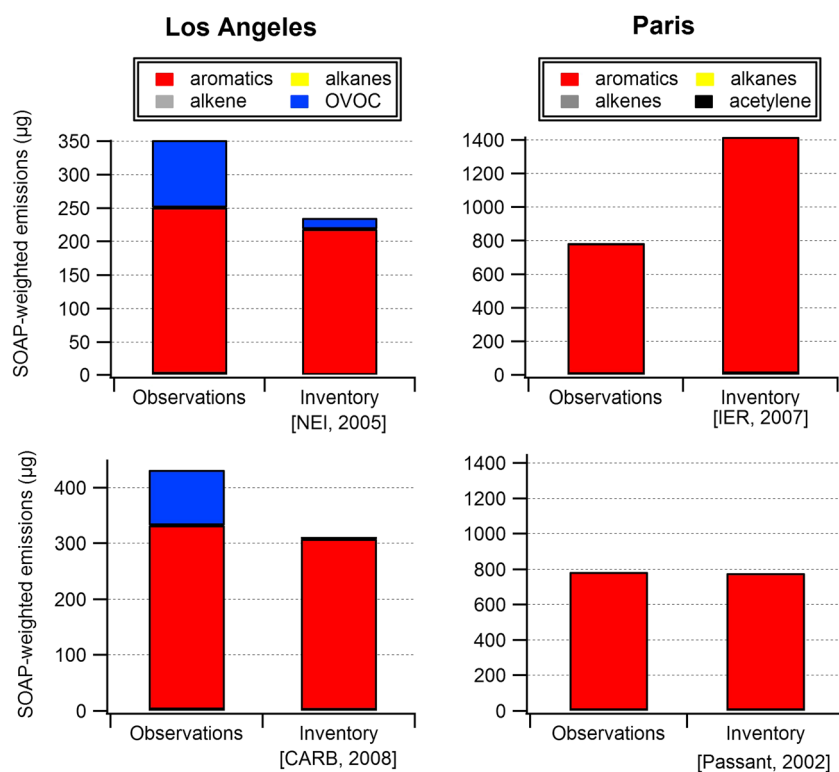
**Figure 11.** Sum of VOC reactivity with OH calculated from the emission ratios of anthropogenic VOCs and a CO enhancement of 100 ppb in Los Angeles and Paris. Observed reactivity (left-hand bars) is compared with the different emission database reactivities (right-hand bars) for both megacities. The number and nature of the VOC used in the comparison are different depending on the speciation available in each emission inventory.

potential (SOAP). The OH reactivity of a compound is calculated by multiplying its concentration with the OH rate coefficient [Atkinson and Arey, 2003]. While the number of individual VOCs used in the comparison is limited (see Table S2 in the supporting information), they span 2 orders of magnitude of OH rate coefficients.

[36] The propensity of the air mass VOC load to form SOA relies on the secondary organic aerosol potential (SOAP) recently developed by Derwent *et al.* [2010]. The SOAP is derived from a photochemical trajectory model using the Master Chemical Mechanism for a typical urban air mass in Europe. The concept of SOAP reflects the ability of each organic compound to form SOA on an equal mass emitted basis relative to toluene set to 100. The SOAP-weighted mass emission of a compound is calculated by multiplying its concentration (in  $\mu\text{g m}^{-3}$ ) by its SOAP value reported by Derwent *et al.* [2010] for 113 organic compounds. As a class, the aromatics exhibit the greatest propensity to form SOA preceding intermediate volatility organics (undecane and dodecane) and monoterpenes (pinenes). The total OH reactivity and the weighted SOAP from the measured and inventory emission ratios relative to CO are reported in Figures 11 and 12, respectively, for Los Angeles and Paris. Both metrics are calculated for a 100 ppb enhancement of CO and a corresponding VOC increase at the time of emission. The compounds used for each comparison is limited by the compounds extracted from the inventory as listed in Table S2 in the supporting information.

[37] Despite the large discrepancies between the individual emission ratios (see section 6.1), the overall OH reactivity of the measured VOCs and the reactivity of the same compounds in the regional emission database per molecule of CO emitted agree within 15% to 40% in Los Angeles and Paris, respectively (Figure 11). However, the national NEI inventory underestimates by almost 70% the total OH reactivity per molecule of CO emitted in Los Angeles. Given the respective overestimation and underestimation of CO emissions in Los Angeles by the NEI and in Paris, respectively (Figure 10), these differences would be half reduced, which would bring the OH reactivity from inventories into good agreement with observations, especially for the NEI in Los Angeles. At present, the use of the CARB emission database in air quality models is expected to be more accurate for the prediction of ozone in the Los Angeles basin. It should be recognized that the OH reactivity comparison is calculated for fresh emissions; as these emissions age, the short-lived aromatics and alkenes are depleted, and the OH reactivity will become dominated by alkanes and secondary OVOC that increase with aging. While biogenic VOCs are not under the scope of our analysis, their contribution to total OH reactivity at midday derived from the product of their individual concentrations with their OH rate coefficient suggests that they only contribute to 2% of the total OH reactivity.

[38] The relative contribution of each class of VOC is in fairly good agreement between observations and inventories



**Figure 12.** Same as Figure 11, except for weighted SOAP.

except for oxygenated VOC in the NEI. Alkanes play a minor role (30% maximum) in total OH reactivity, at the time of emissions, in both megacities. Despite large discrepancies in the emission ratios, they have a lower reactivity toward OH. Aromatics and alkenes dominate the NMHC total OH reactivity, explaining more than 50% together. Observed anthropogenic OVOC contribute at least 30% to the total OH reactivity at the time of emissions but are strongly underestimated by the inventories.

[39] The propensity of urban anthropogenic VOC emissions to form SOA shows good agreement at  $\pm 30\%$  except for the IER inventory in Paris (Figure 12). The IER inventory overestimates SOAP by almost 70%. Aromatics show the highest SOAPs [Derwent *et al.*, 2010] and large emission ratios (Table 2). Therefore, the observed SOAP-weighted anthropogenic emission is dominated by aromatic emissions. The ability of an emission database to correctly represent the SOAPs from anthropogenic precursors is then dependent on the aromatic emission ratios and Figure 4f has shown the overestimation of aromatic emission ratios by the IER. Anthropogenic OVOC can also explain 30% of the SOAP-weighted anthropogenic emissions in Los Angeles. The propensity of OVOC to form SOA is mainly driven by benzaldehyde in Los Angeles. Benzaldehyde has a SOAP 2 times higher than that of toluene, and its emission ratio relative to CO is underestimated by a factor of 10 by the NEI and CARB inventories. Recent work has shown that intermediate volatility and semi-volatility organic compounds, either emitted directly or from the evaporation of organic particles, may be important for SOA formation [Robinson *et al.*, 2007; de Gouw *et al.*, 2011]. These

compounds ( $>C_{12}$ ) are not considered in this analysis. In suburban Paris, the contribution of the oxidation of observed  $C_{11}$ – $C_{16}$  alkanes to SOA formation represents half of the contribution from aromatics (Ait-Helal *et al.*, manuscript in preparation, 2013). While some consistency is found between observations and inventories in this work, it should be kept in mind that SOA formation in urban areas is typically more efficient than can be explained from the VOCs included in this analysis [de Gouw *et al.*, 2005; Volkamer *et al.*, 2006]. However, biogenic VOC precursors are not expected to significantly contribute to SOA formation in the LA plume [Bahreini *et al.*, 2012].

## 7. Conclusion

[40] Detailed data sets for VOC were recently collected during the CalNex and MEGAPOLI campaigns in Los Angeles and Paris, respectively, at ground sites and on board an aircraft. A set of no-chemistry conditions was defined to estimate the emission ratios of VOC relative to CO and acetylene. The plume composition downwind of downtown Los Angeles and Paris is affected by chemistry during the first hours after emissions. Linear regression fits using temporal and spatial filters and the photochemical age method adapted from de Gouw *et al.* [2005] were applied to estimate the emission ratios of VOCs. Emission ratios from both methods show agreement generally within  $\pm 20\%$ .

[41] The emission ratios of NMHC between both megacities compare generally within a factor of 2 except for  $C_7$ – $C_9$  aromatics. The  $C_7$ – $C_9$  fraction of aromatics is about 3 times higher in Paris, even compared with other European



urban areas. Our results suggest that the emissions of gasoline-powered vehicles dominate the composition of NMHC in northern mid-latitude urban areas. However, regional characteristics could affect the composition of their emissions: the gasoline composition in aromatics is suspected as one possible reason that aromatics are higher in Paris, although the higher proportion of powered two-wheel vehicles could also play a role.

[42] Emission ratios extracted from four anthropogenic VOC emission reference databases were compared with the observed emission ratios. Large discrepancies between observed emissions ratios and those calculated from the inventories of up to a factor of 4 or more were revealed. VOCs emitted not only by road transport but also by area sources generally show the largest differences (alkanes and oxygenated VOCs). A bias in CO emissions was also depicted in both megacities. Nevertheless, when only considering anthropogenic VOC emissions, the regional inventories are able to well simulate within  $\pm 40\%$  the formation of ozone and SOA per molecule of inert tracer emitted at urban scale when using the total OH reactivity metric and the SOA potential metric. In particular, for Los Angeles, the use of the CARB emission database in air quality models is expected to be the most accurate for the prediction of ozone across the basin.

[43] Finally, our results show that traffic emissions dominate the composition of urban anthropogenic NMHC emissions, which does not agree with emission inventories.

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