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Volatile and intermediate volatility organic compounds in suburban Paris: variability, origin and importance for SOA formation

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Supplementary material S1: Determination of hexadecane partition coefficient Kp.

The gas-phase partitioning constant of a compound i, $K_{p,i}$, is defined as (Pankow, 1994):

$$K_{p,i} = \frac{f_{om}\,760\,RT}{MW_{om}\zeta_i p^{\circ}_{L,i}10^6}$$

With f_{om} the fraction of total aerosol mass that is organic matter, R the gas constant (8.2×10^{-5} m^{-3} atm mol^{-1} K^{-1}), T the ambient temperature (K), MW_{om} the average molecular weight of organic matter in the aerosol (g mol^{-1}), ζ_i the activity coefficient of the compound i, $p^{\circ}_{L,i}$ the liquid vapor pressure of compound i (Torr).

Table S1 presents the different parameters needed for the determination of $K_{p,hexadecane}$ from the SIRTA measurements. Concerning $p^{\circ}_{L,i}$, we determined it from the vapor pressure available in the Reaxys database (http://www.elsevier.com/online-tools/reaxys); we corrected it for temperature using Clausius-Clapeyron relationship (Williams et al., 2010). MW_{om} has not been determined for the MEGAPOLI experiments. Williams et al. (2010) have determined a value of 200 g mol^{-1} from ambient measurements of the particulate matter at the University of California, Riverside (USA). Their sampling site is located near an important highway (Docherty et al., 2011). Hence, the influence of traffic and more generally of the local emission sources is certainly more important at Riverside than at SIRTA. Even though the composition of the organic matter might be different between the two sampling sites, we used the same value (200 g mol^{-1}) in our calculations. Indeed, it appears to be a good estimate, especially since, in summer, f_{om} at Riverside (41%) (Williams et al., 2010) is similar than f_{om} at SIRTA (48.9%). As for $\zeta_{hexadecane}$, it is somewhere around 6: Chandramouli et al. (2003) have determined from models a mean activity coefficient of 6.5 (±3.6) for heptadecane in particles emitted from catalyzed and uncatalyzed gasoline engine exhaust. For this reason, we have set $\zeta_{hexadecane} = 6$.

$K_{p,hexadecane}$ is found to be 2.16×10^{-4} and 8.61×10^{-4} in summer and in winter, respectively.

Table S1. Parameters used for the determination of the gas-phase partitioning constant $K_{p,hexadecane}$.

	Summer experiment	Winter Experiment
f_{om} (%)	48.9	36.0
Mean T (K)	291.5	275.1
MW_{om} (g mol^{-1})	200	200
$p^{\circ}_{L,i}$ (Torr)	3.43×10^{-4}	5.97×10^{-5}
ζ_i	6	6

Supplementary material S2: Experimental conditions for the determination of the VOC emission factors (EF) by Fontaine (2000).

Fontaine determined I/VOC EF by studying the emission at the exhaust of 15 cars with different motorization (light-duty diesel vehicles, catalyst and non-catalyst gasoline vehicles), imitating mean urban driving conditions (MVEG cycle), which are representative of the European driving cycle. The measurements at the exhaust of the cars have been performed with a motor's temperature comprised between 20°C and 30°C, in order to work under similar conditions and to limit the influence of the ambient temperature on the EF. So the EF determined by Fontaine does not include cold start. However, this experimental condition, and so the non-inclusion of the cold start in our approach, should not have a significant influence on our results since we used these EF for the MEGAPOLI summer campaign, where the average ambient temperature was equal to 16.8 (± 3.0)°C. Since EF have been determined for cars with different motorization, the ER (emission ratio) for the different compounds were determined by taking into account the composition of the vehicle fleet (CCFA, 2009), as exposed in the main text (Eq. (1)).

Supplementary material S3: Representativeness of the VOC emission ratio determined from Fontaine's work (2000).

With the ER determined from Fontaine's work (2000), we used those determined in Paris (at LHVP) during the MEGAPOLI summertime campaign (Borbon et al., 2013), the latter being representative of urban areas (Borbon et al., 2013). Figure S1 represents the correlations of pairs of VOCs measured in winter in Paris in 2003 or in 2009/2010. The ER from Fontaine's work (2000) is also represented in the figure. Figure S1 exhibits good agreement between the data from Fontaine's study (2000) and those obtained from measurements in 2003 and 2009/2010. One can see that the urban ER are within the uncertainty range of the vehicle ER from Fontaine (2000). Then, this result allows us to use Fontaine's ER when they are not available from Borbon et al. (2013). Moreover, slopes of the VOCs pairs correlations appear similar between 2003 and 2009/2010: the relative composition of vehicle exhaust did not change significantly (≤ 30%) over the last decade. This last result indicates that the change in the fuel compositions in France/in Paris has not led to a significant change in the VOCs emission ratios within 7 years. On the basis of these results, we consider that the ER determined by Fontaine (2000) are similar to those determined in Paris (at LHVP) during the MEGAPOLI summertime campaign (Borbon et al., 2013) and are also representative of urban areas.

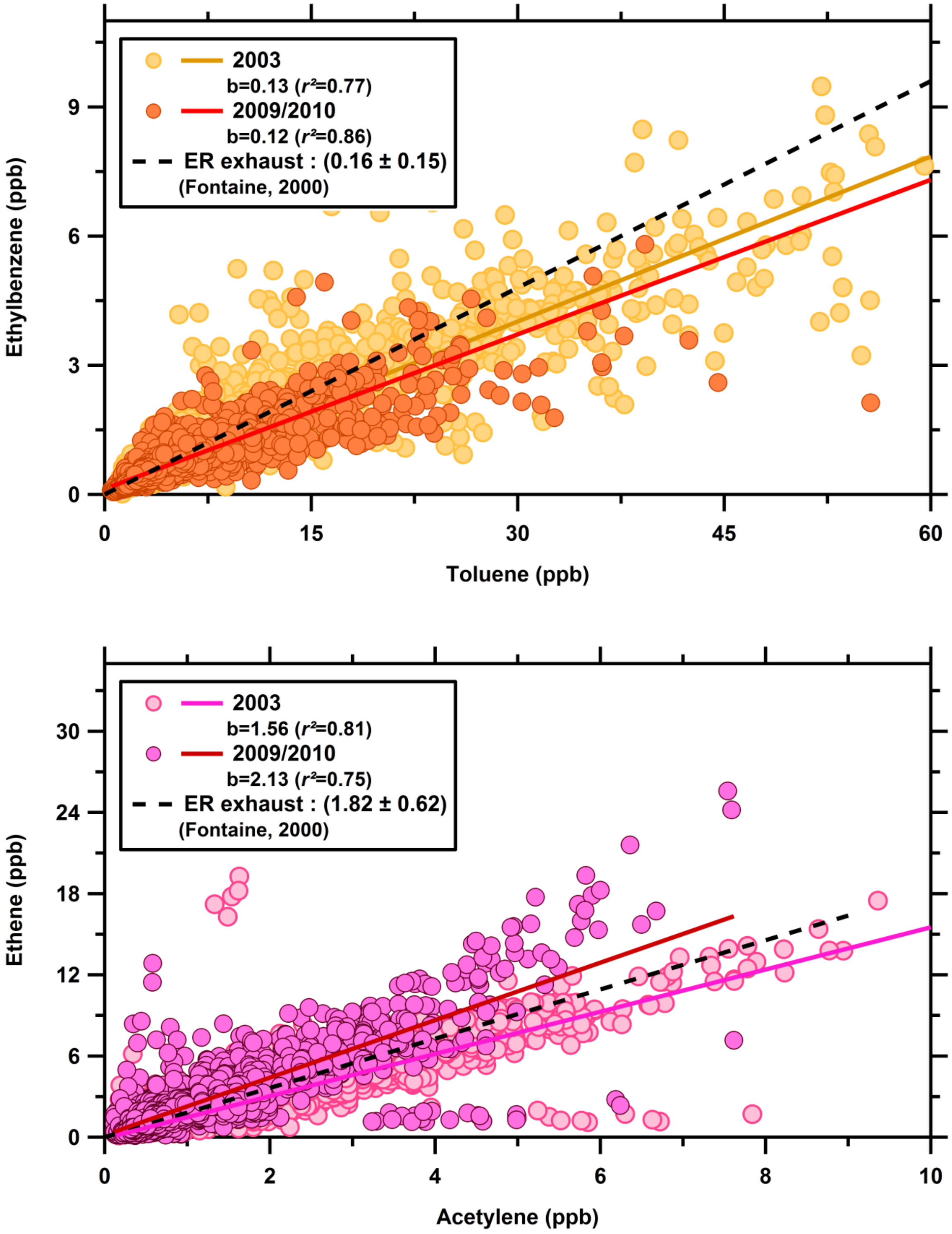

Figure S1. Correlations of some anthropogenic VOC pairs from the Air Quality Network in Paris in 2003 and 2009/2010 (urban background site in the centre of Paris). The black dashed lines are the lower and upper limits of the vehicle exhaust emission ratio from Fontaine (2000).

As for the IVOCs, little information on the emission factors or emission ratios is available in the literature. Fraser et al. (1998), Schauer et al. (2002) and more recently Gentner et al. (2013) determined emission factor of various VOCs and IVOCs at the exhaust of gasoline light-duty cars. However, these results did not seem appropriate to our study since they have been determined under the Federal Test Procedure (FTP) urban driving cycle (Schauer et al., 2002) or real American driving conditions (Fraser et al., 1998; Gentner et al., 2013) and, then, are representative rather of the American fleet of vehicles than of the French one. Hence, ER determined from Fontaine's EF (Fontaine, 2000) appear to be the best estimates for the C_{12}-C_{16} alkanes.

Supplementary material S4: Assumptions in the different SOA estimation approaches.

- The SOA yields: The SOA yields used here are the most recent yields available in the literature, and the most adapted to the MEGAPOLI campaign conditions. They are those determined from chamber studies by Seinfeld and Pandis (1998) for the C_4-C_6 alkanes. Those of toluene, benzene and m,p-xylene were determined by Ng et al. (2007). However, the toluene SOA yield determined by Ng et al. (2007) was also used for ethylbenzene, as Odum et al. (1997) demonstrated that the yield of SOA formed from the photooxidation of the two compounds were similar. For the same reason, the o-xylene SOA yield has been taken equal to the m,p-xylenes SOA yield. These yields have been determined according to the NO_x concentrations, given that the concentrations of NO_x strongly influence the yields. Indeed, experiments performed under high-NO_x conditions (100's of ppb) lead to lower aromatic SOA yield than under low-NO_x conditions ($[NO_x]<1$ ppb) (Song et al., 2005; Ng et al., 2007). During the MEGAPOLI summer campaign the average concentration of NO_x was equal to 7 ppb. Thus, yields of the aromatic compounds determined under low-NO_x conditions were used here, since these conditions are the closest to those encountered during the MEGAPOLI summer campaign. As for the C_9-C_{16} alkanes, the SOA formation was mainly investigated only under high-NO_x conditions (Lim and Ziemann, 2005, 2009; Jordan et al., 2008; Presto et al., 2010). However, according to Loza et al. (2014) the n-alkanes SOA yields determined under high-NO_x conditions are higher than at low-NO_x conditions. Presto et al. (2010) investigated the SOA formation of the C_{12}-C_{16} n-alkanes under high-NOx concentrations and at different organic mass concentrations (C_{OA}): $1\ \mu g\ m^{-3} < C_{OA} < 50\ \mu g\ m^{-3}$. COA is another parameter of the chamber experiments known to highly influence the SOA yields. During the MEGAPOLI campaign, on average $C_{OA}=2\ \mu g\ m^{-3}$ at SIRTA. But $C_{OA}=40\ \mu g\ m^{-3}$ in the chamber for the determination f the aromatic SOA yields (Ng et al., 2007). Hence, both C_{12}-C_{16} n-alkanes IVOCs particulate yields at $C_{OA}=2\ \mu g\ m^{-3}$ and $C_{OA}=40\ \mu g\ m^{-3}$ are used in the SOA estimation from the integrated approach, so the contribution of the aromatics and of the IVOCs to SOA formation can be fairly compared. The values obtained by Lim and Ziemann (2009) for the C_9-C_{11} n-alkanes were applied in this work, However, the later yields were determined under high C_{OA} (up to $1\ 600\ \mu g\ m^{-3}$) which implies an overestimation of the SOA formation at SIRTA from the corresponding precursors.

- The VOC-to-CO emission ratios: emission ratio of C_{11}-C_{16} alkanes were determined from Fontaine's work (2000), following Eq. (S1):

$$\frac{VOC_i}{CO} = {\frac{VOC_i}{nonane}}_{Fontaine} \times {\frac{Nonane}{CO}}_{Borbon} \qquad \text{(S1)}$$

with $\frac{VOC_i}{CO}$ the VOC_i emission ratio to CO, ${\frac{VOC_i}{nonane}}_{Fontaine}$ the VOC_i emission ratio to nonane determined from Fontaine's work (2000), and ${\frac{nonane}{CO}}_{Borbon}$ the nonane emission ratio to CO determined by Borbon et al. (2013).

- [OH]*Δt: in this product, Δt is taken to be equal to the photochemical age and can be expressed by Eq. (S2) (Warneke et al., 2007):

$$\Delta t = \frac{1}{OH\ (k_{VOC_1} - k_{VOC_2})} \times \ ln{\frac{VOC_1}{VOC_2}}_{t=0} - \ ln{\frac{VOC_1}{VOC_2}}_{t} \qquad \text{(S2)}$$

with $k_{VOC,i}$ the rate constants of VOC_i with OH.

As reported by (Nelson and Quigley, 1983; Roberts et al., 1984; Parrish et al., 1998; Monod et al., 2001; Warneke et al., 2007), the calculation of the photochemical age is usually based on the ratio of two aromatic compounds of same origin with different rate coefficients towards OH. The photochemical age of the plumes sampled at SIRTA is assessed here by considering the LHVP VOCs ratio as the ratio at *t*=0, since LHVP is an urban background site surrounded by the aromatic compounds sources. Figure S2 illustrates the correlations between m,p-xylenes and ethylbenzene obtained at SIRTA and LHVP in winter and in summer (Fig. S2a and Fig. S2b, respectively). These compounds, of different reactivity, exhibit good correlations at each site regardless of the season (r^2>0.93), underlying their common emission sources. In winter, the m,p-xylenes/ethylbenzene ratios obtained at SIRTA and at LHVP agree within 4% whereas, in summer, the ratio is 38% lower at SIRTA. The lower summertime emission ratio at SIRTA indicates that m,p-xylenes are photochemically faster depleted than ethylbenzene, as could be expected from their rate coefficient with OH. Besides, it complies with LHVP considered as an emission site.

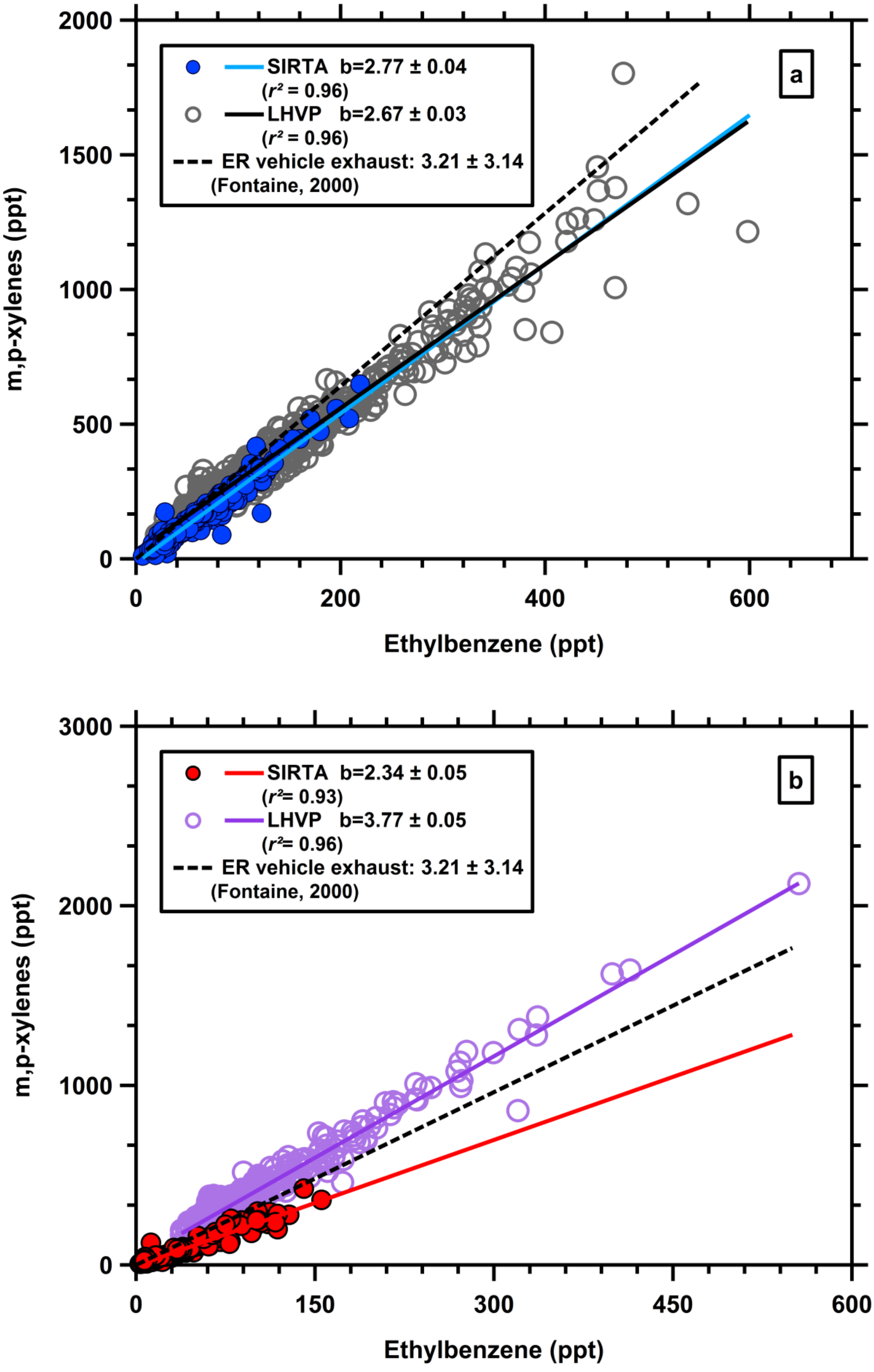

Figure S2. Scatterplots between m,p-xylene and ethylbenzene mixing ratios in sub-urban Paris (SIRTA) and urban Paris (LHVP) in winter (a) and summer (b).

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