

1 **Supplementary material to**

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3 **Volatile and Intermediate-Volatility Organic Compounds in**  
4 **sub-urban Paris: variability, origin and importance for SOA**  
5 **formation**

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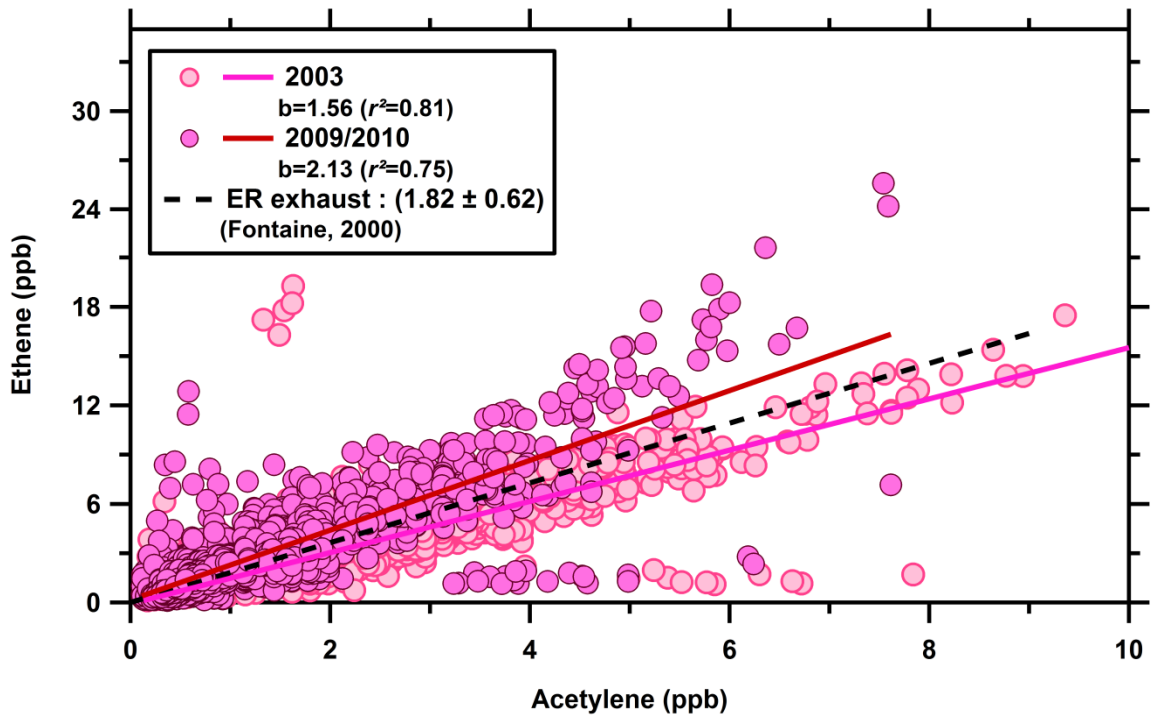
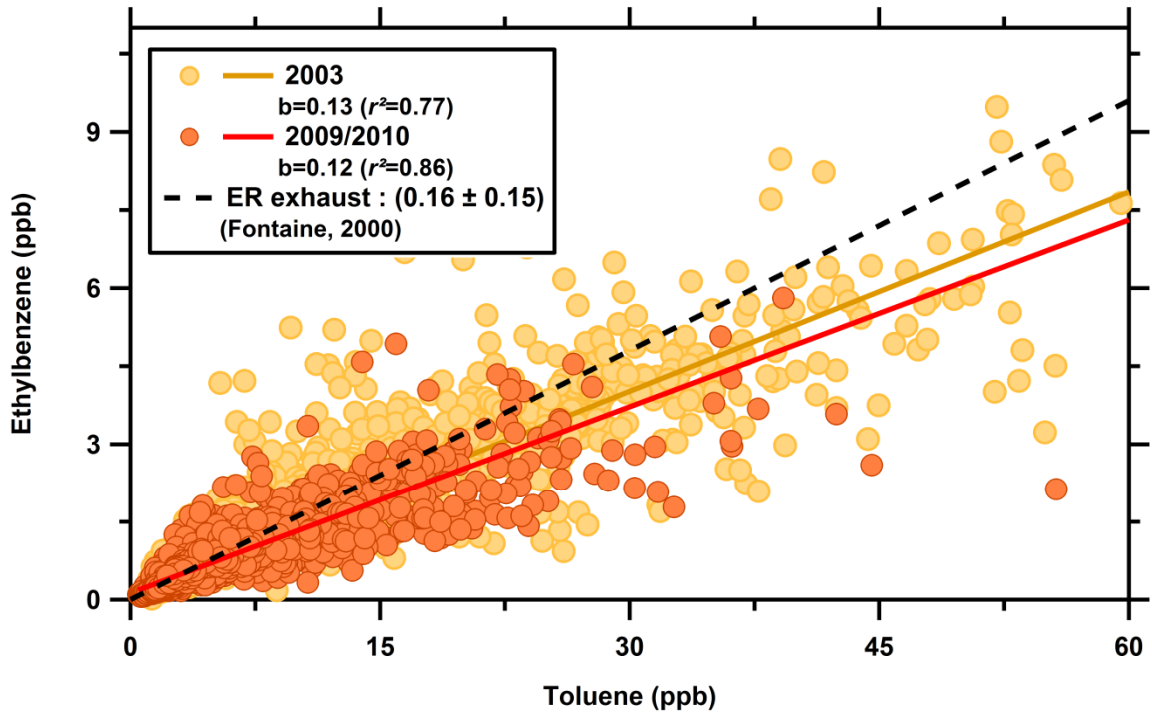
34 **Supplementary material S1: Experimental conditions for the determination of the VOC**  
35 **emission factors (EF) by Fontaine (2000).**

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

49

50 **Supplementary material S2: Representativeness of the VOC emission ratio determined**  
51 **from Fontaine's work (2000).**

52 With the ER determined from Fontaine's work (2000), we used those determined in Paris (at  
53 LHVP) during the MEGAPOLI summertime campaign (Borbon et al., 2013), the latter being  
54 representative of urban areas (Borbon et al., 2013). Figure S1 represents the correlations of  
55 pairs of VOCs measured in winter in Paris in 2003 or in 2009/2010. The ER from Fontaine's  
56 work (2000) is also represented on the figure. Figure S1 exhibits good agreement between the  
57 data from Fontaine's study (2000) and those obtained from measurements in 2003 and  
58 2009/2010. One can see that the urban ER are within the uncertainty range of the vehicle ER  
59 from Fontaine (2000). Then, this result allows us to use Fontaine's ER when they are not  
60 available from Borbon et al. (2013). Moreover, slopes of the VOCs pairs correlations appear  
61 similar between 2003 and 2009/2010: the relative composition of vehicle exhaust did not  
62 change significantly over the last decade at  $\pm 30\%$ . This last result indicates that the change in  
63 the fuel compositions in France/in Paris has not led to a significant change in the VOCs  
64 emission ratios within 7 years. On the basis of these results, we consider that the ER  
65 determined by Fontaine (2000) are similar to those determined in Paris (at LHVP) during the  
66 MEGAPOLI summertime campaign (Borbon et al., 2013) and are also representative of urban  
67 areas.



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69

70 Figure S1. Correlations of some anthropogenic VOC pairs from the Air Quality Network in  
 71 Paris in 2003 and 2009/2010 (urban background site in the centre of Paris). The black dashed  
 72 lines are the lower and upper limits of the vehicle exhaust emission ratio from Fontaine  
 73 (2000).

74

75 As for the IVOCs, very few information on the emission factors or emission ratios is available  
76 in the literature. Only Schauer et al. (2002) determined emission factor of various VOCs and  
77 IVOCs at the exhaust of gasoline light-duty cars. However, these results did not seem  
78 appropriate to our study since (i) they have been determined under the Federal Test Procedure  
79 (FTP) urban driving cycle and, then, are representative rather of the American fleet of  
80 vehicles than of the French one, (ii) the experiments were performed using American oil, and  
81 (iii) the study is barely more recent than Fontaine's work. For all these reasons, ER  
82 determined from Fontaine's EF (Fontaine, 2000) appear to be the best estimates for the C<sub>12</sub>-  
83 C<sub>16</sub> alkanes.

84 **Supplementary material S3: Assumptions in the different SOA estimation approaches.**

85 - The SOA yields: The SOA yields used here are the most recent yields available in the  
86 literature, and the most adapted to the MEGAPOLI campaign conditions. They are those  
87 determined from chamber studies by Seinfeld and Pandis (1998) for the C<sub>4</sub>-C<sub>6</sub> alkanes. Those  
88 of toluene, benzene and m,p-xylene were determined by Ng et al. (2007). However, the  
89 toluene SOA yield determined by Ng et al. (2007) was also used for ethylbenzene, as Odum et  
90 al. (1997) demonstrated that the yield of SOA formed from the photooxidation of the two  
91 compounds were similar. For the same reason, the o-xylene SOA yield has been taken equal  
92 to the m,p-xylenes SOA yield. These yields have been determined according to the NO<sub>x</sub>  
93 concentrations, given that the concentrations of NO<sub>x</sub> strongly influence the yields. Indeed,  
94 experiments performed under high-NO<sub>x</sub> conditions (100's of ppb) lead to lower SOA yield  
95 than under low-NO<sub>x</sub> conditions ([NO<sub>x</sub>] < 1 ppb) (Song et al., 2005; Ng et al., 2007). During the  
96 MEGAPOLI summer campaign the average concentration of NO<sub>x</sub> was equal to 7 ppb. Thus,  
97 yields of the aromatic compounds determined under low-NO<sub>x</sub> conditions were used here,  
98 since these conditions are the closest to those encountered during the MEGAPOLI summer  
99 campaign. As for the C<sub>9</sub>-C<sub>16</sub> alkanes, the SOA formation was mainly investigated only under  
100 high-NO<sub>x</sub> conditions (Lim and Ziemann, 2005, 2009; Jordan et al., 2008). The values  
101 obtained by Lim and Ziemann (2009) were applied in this work, since they provide yields for  
102 all the n-alkanes of intermediate volatility studied here. However, according to their studies,  
103 the use of the SOA yields determined under high-NO<sub>x</sub> conditions implies an underestimation  
104 of the SOA formation at SIRTAs from the corresponding precursors.

105

106 - The VOC-to-CO emission ratios: emission ratio of C<sub>11</sub>-C<sub>16</sub> alkanes were determined from  
107 Fontaine's work (2000), following Eq. (S1):

$$\frac{VOC_i}{CO} = \left( \frac{VOC_i}{nonane} \right)_{Fontaine} \times \left( \frac{Nonane}{CO} \right)_{Borbon} \quad (S1)$$

108 with  $\frac{VOC_i}{CO}$  the VOC<sub>i</sub> emission ratio to CO,  $\left( \frac{VOC_i}{nonane} \right)_{Fontaine}$  the VOC<sub>i</sub> emission ratio to  
109 nonane determined from Fontaine's work (2000), and  $\left( \frac{nonane}{CO} \right)_{Borbon}$  the nonane emission  
110 ratio to CO determined by Borbon et al. (2013).

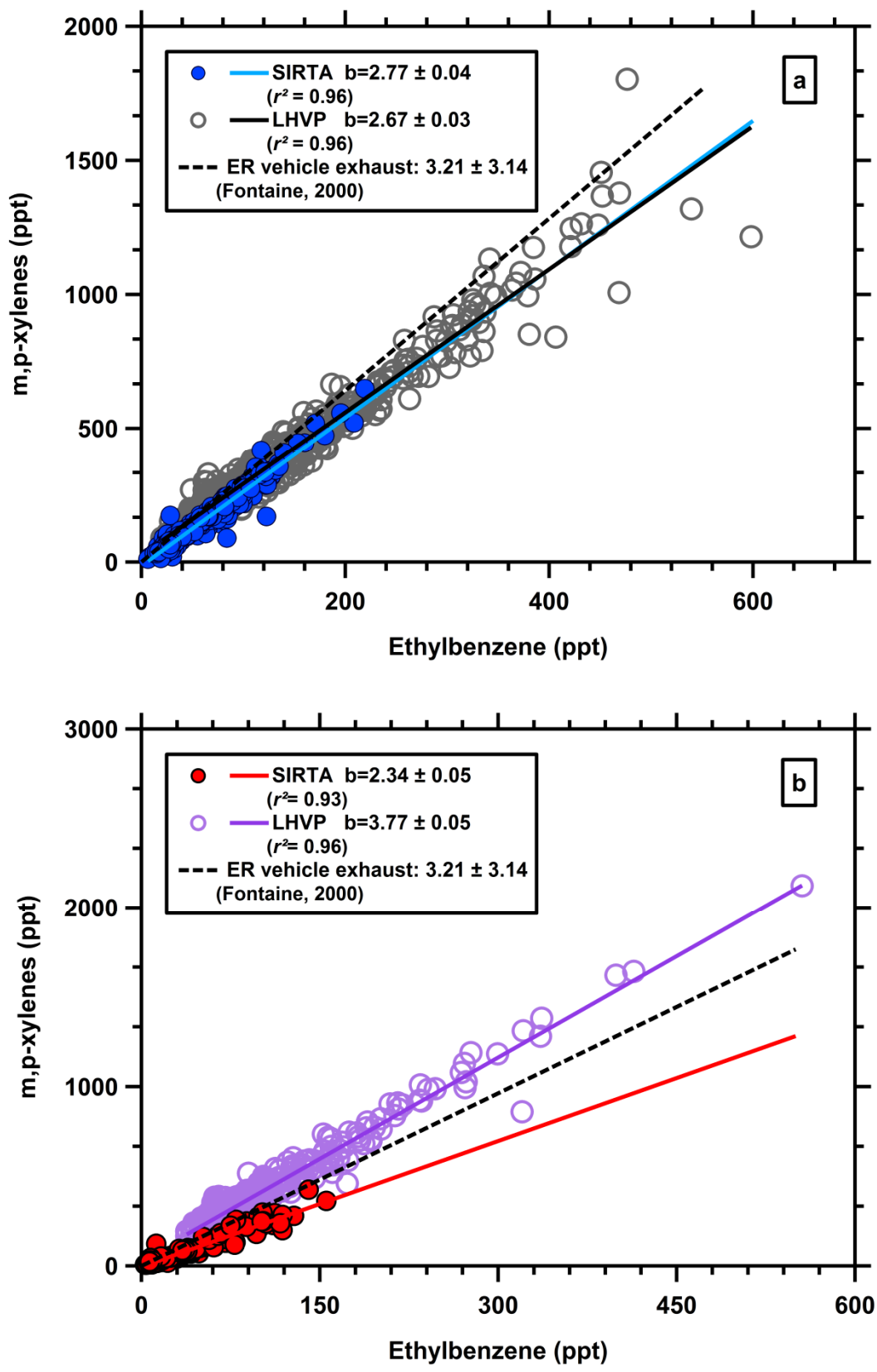
111 -  $[OH]*\Delta t$ : in this product,  $\Delta t$  is taken to be equal to the photochemical age and can be  
112 expressed by Eq. (S2) (Warneke et al., 2007):

$$\Delta t = \frac{1}{[OH](k_{VOC_1} - k_{VOC_2})} \times \left[ \ln \frac{[VOC_1]}{[VOC_2]} \Bigg|_{t=0} - \ln \frac{[VOC_1]}{[VOC_2]} \Bigg|_t \right] \quad (S2)$$

113 with  $k_{VOC_i}$  the rate constants of  $VOC_i$  with OH.

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

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



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