Is Traffic Still an Important Emitter of Monoaromatic Organic Compounds in European Urban Areas?

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22   **Abstract**

23   Trends of long-term observations and emission inventories suggest that traffic emissions will

24   no longer dominate the concentrations of mono-aromatic compounds (i.e. TEX - Toluene,

25   Xylenes and Ethylbenzene) in European urban areas. But the split limit between traffic and

26   other emission sector contributions such as solvent use remains tenuous. Here long-term

27   observations of an extensive set of hydrocarbons, including TEX, at traffic and urban

28   background sites in London, Paris and Strasbourg were combined to estimate the relative

29   importance of traffic emissions on TEX in every city. When analyzing the urban enhancement

30   emission ratios of TEX-to-benzene on a seasonal basis, two potential source signatures other

31   than traffic could be differentiated in all cities (1) summertime evaporation from fuel and/or

32   solvent and (2) wintertime domestic heating. However, traffic emissions still unambiguously

33   dominate the concentration levels of TEX in every city despite the reduction of their

34   emissions at exhaust pipe over the last two decades. Traffic explains between 60% and 96%

35   (at ±20%) of TEX levels while it is less clear for xylenes at some locations. Our results

36   provide a basis to evaluate regional emission inventories. The method is applicable at any

37   urban area where speciated hydrocarbon monitoring is available.

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39   Toc Art

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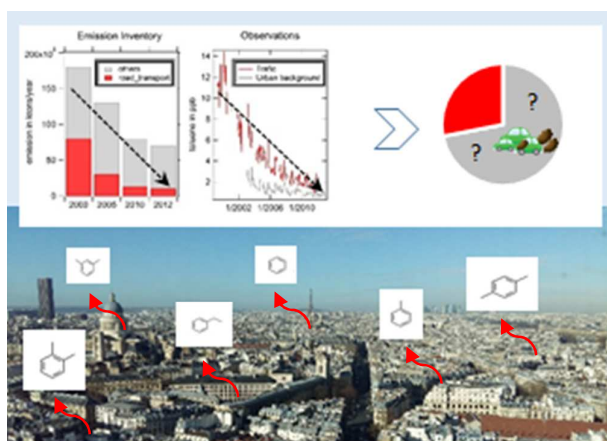
40   **Key points:**

41   • Emission inventories and multi-year trends of long-term observations raise the

42   question of the impact of traffic emissions on TEX concentration levels in European

43   urban areas

44   • One decade of hourly observations of hydrocarbons at traffic and urban stations in

45   Paris, London and Strasbourg is used to estimate the traffic fraction of TEX

46   concentrations

47   • The seasonal signature of TEX sources is rather due to seasonal changes in traffic

48   emission composition and additional wintertime domestic combustion for benzene

49   • It is demonstrated that traffic emissions still account for more than 60% of most TEX

50   concentrations regardless of the season while is less clear for xylenes at some urban

51   locations

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Introduction

BTEX (Benzene, Toluene, Ethylbenzene and (m+p) and o-Xylenes), a sub-group of Volatile Organic Compounds (VOC), still constitute a significant fraction of VOCs in urban atmospheres up to 47% in volume of total Non-Methane Hydrocarbons (NMHC) after C_2-C_9 alkanes[1; 2; 3; 4, 5]. BTEX are released into the atmosphere by either fossil fuel related emission sources (transport, storage and distribution of fossil fuels, industrial and residential combustion, processes) and solvent use[6]. For only benzene, which is known to be carcinogenic[7], the European air quality objective for health protection of 5 μg.m^{-3} (1.57 ppb STP) per year is still exceeded in the center of Paris close to major roadways[8]. Apart from their abundance and adverse health effects, BTEX have significant implications on atmospheric chemistry. Together with alkenes, they show the highest ozone-forming potential[9,10]. They have therefore been considered as key target compounds by ozone policy reduction measures, especially in urban areas where ozone is usually VOC-limited[11]. BTEX oxidation also contributes to the formation of Secondary Organic Aerosols (SOA). While high uncertainties persist on SOA yields depending on smog-chamber experimental conditions, BTEX show SOA yields as significant as the one of α-pinene, the most emitted and reactive biogenic precursor being currently the dominant SOA source at the global scale: yield values range from 1181 (benzene) to 1578 μg.m^{-3}.ppm^{-1} (xylenes), respectively[12,13] against 1826 μg.m^{-3}.ppm^{-1} for α-pinene[14]. Recent results have suggested that BTEX could explain 34% of SOA production in summer[15] in Paris megacity whereas such a contribution would be lower when taking into account a larger set of VOC of intermediate volatility (IVOC) in Los Angeles[16]. Like terpenes, oxidation of mono-aromatics would also lead to the rapid formation of highly oxygenated molecules as recently suggested by Molteni and coworkers[17].

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76   VOC emission reduction measures, such as emission reduction at vehicle exhaust pipe, have

77   successfully reduced their anthropogenic concentrations in cities like London[18], Paris and

78   other medium-sized cities in France[6], Los Angeles[19] and at rural stations [20,6]. The multi-year

79   trends of monthly average concentrations of toluene (Figure 1) and other aromatics (Figures

80   S1, S2, S3 in Supplement Information) at both urban background and traffic sites in three

81   European metropolitan areas (London, Paris and Strasbourg) support these findings.

82   Regardless of the city, all concentrations have consistently shown a clear decline at traffic

83   sites since 2000, especially in the first half of the decade. However, aromatic levels at urban

84   background sites have stayed almost constant since 2008 and concentrations at traffic sites

85   tend towards the urban background levels. This raises the question whether traffic emissions

86   still dominate TEX emissions. Up-to-date emission inventories in all three cities (see pie-

87   charts on the right hand panel of Figure 1 and Figures S1 to S3 in SI) show various features. It

88   should be noted that no local emission inventory is available for London megacity and the

89   emission distribution is adapted from the National Atmospheric Emission Inventory in UK

90   (NAEI) for the year 2000 (D. Derwent and S. Beevers' personal communication). For toluene,

91   the road-transport sector accounts for half of its emissions in London and Paris and only 10%

92   in Strasbourg. For xylenes (Figures S1 and S2), the road-transport contribution drops down to

93   4%-33% except for o-xylene in London (57%). The solvent use and/or residential sector

94   appear as the other major source explaining between 28% and 56% of toluene emissions and

95   44 to 77% especially for xylenes. Only ethylbenzene would be still largely emitted by the

96   road-transport sector (44 – 68 %) (see Figure S3). Regional emission inventories for two

97   European cities, Paris and Zurich in 2005, also pointed to the use of solvents from all source

98   categories as the new dominant source of total VOCs at the urban scale. Finally, the

99   homogeneity of aromatic multi-year trends depicted in observations is not reflected in

100 regional emission inventories. However emission inventories for VOCs still show high

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101 uncertainties up to a factor of 4 [21] and observations provide useful constraints for their

102 evaluation[22; 23 24; 21;25]. Source-receptor models like PMF (Positive Matrix Factorization)

103 usually point to the contribution of various sources to total measured VOC ambient levels[26; 27;

104 24]. BTEX usually show significant contributions in the source profiles of vehicle exhaust,

105 solvent use-related activities and wood combustion for benzene[26, 27, 24, 28]. Mathematics

106 supporting source-receptor models directly imply an estimation of source/factor contributions

107 to total measured VOC concentrations rather than individual species. Towards the complexity

108 of TEX emission sources, there is still no consensus on the importance of BTEX source and

109 for traffic in particular. Moreover, the seasonality of emission changes has been poorly

110 studied for BTEX.

111 In this study, we combine long-term and continuous *in-situ* measurements of NMHC,

112 including BTEX, carried out in European urban areas by air quality monitoring network

113 programs over the past decade to investigate the importance of traffic emissions on mono-

114 aromatic levels at the urban scale. Due to its stringent regulation in fossil fuel and solvent

115 formulation compared to other mono-aromatic compounds, benzene will be treated here as a

116 combustion source tracer rather than a target species for the quantification of traffic

117 contribution. This study provides a scientific basis to evaluate the accuracy of regional

118 emission inventories.

119 **Experimental**

120 Data analysis mostly relies on continuous hourly observations of a large set of NMHC,

121 including BTEX, performed by European air quality networks in the megacities of London

122 (UK by DEFRA), Paris (France by AIRPARIF) and Strasbourg (Eastern France by ASPA).

123 The chosen period for data analysis covers the years 2008 to 2013. Special care was put on

124 data quality checks. The description of quality assurance tests is provided in Boynard et al.

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125   (2014)[2] and Waked et al. (2016) [6] for French data and Dollard et al. (2007)[29] for UK data. The

126   purpose here is to evaluate the importance of traffic emissions relative to other anthropogenic

127   emissions. Data analysis has therefore combined observations collected at both traffic and

128   urban background sites in each city to provide perspectives from contrasted urban situations

129   non-influenced by industrial emissions. Traffic sites represent those locations under the direct

130   influence of nearby traffic emissions, usually a roadway tolerating traffic greater than 10,000

131   vehicles per day. Urban background sites are under the influence of multi-emitters, at a

132   distance of major traffic lanes of 40 m on average and are more likely representative of the

133   urban mixing of all anthropogenic emissions. Details on the database are reported in Table 1.

134   A description of the sites, meteorology and analytical devices is provided in the Supplement

135   Information (pages S5-S6). Note that the Paris data has been completed by tunnel

136   measurements performed during the PREQUALIF project [28]. The number of missing data is

137   usually lower than 25% over the six-year period.

138   **Results and discussion**

139   *Concentration levels of BTEX*

140   Average concentration levels of mono-aromatics including benzene in the three metropolitan

141   areas are reported in Table S1 (2nd to 5th column) in the Supplement Information for the year

142   2011. BTEX concentration levels range between 0.03 ppb (ethylbenzene at Strasbourg Ouest

143   and 1,74 ppb (toluene at Paris-Auteuil), i.e. two orders of magnitude. Concentration levels are

144   2 to 4 times higher at the traffic sites compared to urban background sites. Concentrations of

145   benzene are quite similar between the three cities at ±0.040 ppb at traffic sites and ±0.070 ppb

146   at urban background sites. This is consistent with its stringent regulation policy at European

147   level to achieve the air quality standard of 5 $\mu g.m^{-3}$ per year by, for instance, limiting its

148   presence at 1% vol. in fuels (Directives 98/70/EC replace by 2009/30/EC and 2003/17/EC).

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149   On the opposite, the sum of BTEX load is higher in Paris by 1.4 at traffic sites to 2.4 at urban

150   background sites while concentration levels in London and Strasbourg are surprisingly quite

151   comparable. However, the atmospheric composition in BTEX is very similar between near-

152   traffic and urban background atmospheres. Together with (m+p)-xylenes, toluene (which is

153   the dominant species among BTEX) explains 70% of BTEX load. This suggests that BTEX

154   concentrations are driven by emissions with a non-visible effect of photochemical processing

155   at the background sites. For the latter we would have expected an enrichment of air mass

156   composition in longer-lived mono-aromatics like benzene given that BTEX reactivity towards

157   OH radical spans one order of magnitude[30]. For benzene, a domestic heating source is highly

158   suspected, especially in Strasbourg (see following sections) and as recently shown by Baudic

159   and co-workers[28].

160   *Seasonal source signature on TEX*

161   The magnitude of TEX concentrations is affected by the proximity of emission sources, the

162   extent of photochemical processes and boundary layer conditions. To minimize those effects,

163   we use the TEX-to-benzene enhancement emission ratio (ER = Δ[TEX]/Δ[benzene]) at urban

164   background sites to identify the TEX source signature on a seasonal basis in order to index

165   seasonal changes in urban enhancement ratios to potential changes in the nature and intensity

166   of their sources. The TEX-to-benzene enhancement ratio equals the slope of a linear 2-sided

167   fit of a TEX-to-benzene correlation plot. An illustration of summertime (July) and wintertime

168   (January) scatterplots is provided in Figure 2a over the six-year period at the urban

169   background sites. Urban enhancement ER of toluene-to-benzene representative of traffic,

170   domestic wood combustion and gasoline evaporation emissions are also reported to provide a

171   comparison basis, which is rather qualitative than quantitative regarding the numerous factors

172   modifying the emission composition. These three emission categories have been usually

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173   identified as TEX major sources in urban areas[21; 24; 28]. The determination of the reported

174   values of ER is described in the Supplement Information (pages S7-S8). Emissions from

175   solvent use cannot be excluded but representative ER relative to benzene can hardly be

176   determined. The main reason is due to the diversity of solvents. Speciated emission profiles

177   usually show great variability with, for instance, toluene-to-benzene ratios spanning two

178   orders of magnitude[31]. Moreover, benzene, due to its toxic and carcinogen nature, has been

179   strongly limited in solvent formulations. Current standards in Europe have established limits

180   in benzene at 0.1% in cleaning products.

181   Remarkably, scatterplots show similar multiform patterns in all urban areas (Figure 2a). The

182   scatterplots lie within a domain delimited by the evaporative source ER in its upper part and

183   the domestic wood combustion ER in its lower part. Within these limits, the wintertime and

184   summertime scatterplots roughly split along the traffic ER line, suggesting the additional

185   influence of sources during both seasons despite expected seasonal changes in the

186   composition of traffic emission. In summer, the scatterplot equals (Strasbourg) or is above the

187   traffic ER line (Paris and London) and tends to the one of evaporative emissions. This would

188   suggest the presence of fugitive evaporative processes in addition to traffic. In winter, the

189   scatterplot lies between the traffic ER in its upper part and the domestic wood combustion ER

190   in its lower part. This would suggest an additional source of wood combustion for benzene[27,

191   28]. Note that the observed multiform patterns are rather driven by the seasonal variability of

192   benzene mixing ratios than the ones of toluene especially in Strasbourg, a city submitted to

193   well-marked continental climatic conditions. For Strasbourg this is consistent with the

194   emission inventory (Figure 1). Note also that the multiform pattern is temperature-dependent

195   as seen in Paris and Strasbourg when color-coded with temperature (Figure S4 in Supplement

196   Information). Toluene mixing ratios stay rather constant between both seasons. One cannot

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197   exclude that the correlation slope can be affected by photochemical processing for most

198   reactive VOCs[21,22] especially in summer. When applying the nighttime and daytime filters

199   values following Borbon et al. (2013)[30], no significant difference is depicted suggesting that

200   emissions mainly control TEX concentrations (not shown here). It is consistent with

201   observations during MEGAPOLI-2010 [30] in Paris. The effect of photochemistry on TEX

202   concentrations was only visible in the Paris plume explored by the French ATR-42 aircraft

203   during the MEGAPOLI campaign in the summer 2009 at a distance above 50 km, at least,

204   from the urban center[30].

205   The correlation slopes have been determined on a monthly basis at traffic and urban

206   background sites. The toluene-to-benzene ERs are reported in Figure 2b for Paris and

207   Strasbourg. As expected, a clear seasonal variability is depicted on ER time series with a

208   higher variability at urban background sites. However, both cities show an opposite pattern. In

209   Paris, ERs are similar in winter and the urban background ER significantly increases in

210   summer compared to the traffic ER. In Strasbourg, the summertime ERs are similar while the

211   urban background ER decreases compared to the traffic ER in winter. Such temporal and

212   spatial variability also suggests the potential gaining importance of summertime sources other

213   than traffic as in Paris (evaporation) and the potential gaining importance of wintertime

214   sources other than traffic as in Strasbourg (residential wood combustion).

215   Finally, seasonal scatterplots of TEX mixing ratios versus benzene mixing ratios and time

216   series of TEX-to-benzene ER suggest a seasonal change in traffic emission composition and

217   the potential influence of sources other than traffic to BTEX concentrations. The importance

218   of these additional source contributions is going to be evaluated in the next section.

219   **Contribution of traffic emissions to TEX concentrations**

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220   The method consists in estimating the fraction of each TEX originating from traffic emissions

221   at the urban background sites which are representative of the urban emission mixing. This

222   fraction is calculated by dividing the TEX concentration originating from traffic emissions to

223   the measured concentration. The TEX concentration originating from traffic emissions

224   ($[TEX]_{traffic}$) is expressed as follows:

225        $$[TEX]_{traffic} = ([tracer]_{traffic} - [tracer]_{bckgd}) \times ER_{traffic} \qquad \text{(equation 1)}$$

226   where $[tracer]_{traffic}$ is the concentration of a traffic tracer subtracted by its regional background

227   concentration ($[tracer]_{bckgd}$) which could be significant for longer-lived compounds like

228   benzene[28] and $ER_{traffic}$ is the urban enhancement emission ratio from traffic between TEX and

229   the traffic tracer. This equation is derived from the one developed by Borbon et al. (2003)[21].

230   Acetylene has been commonly used as a traffic exhaust tracer[21, 32]. However, a non-exhaust

231   combustion source cannot be excluded especially during the winter season regarding domestic

232   heating as for benzene [28]. In past studies, acetylene and ethylene have already shown

233   significant contributions in the *wood burning* factor solution calculated by PMF [27, 28]. To take

234   into account potential additional sources to traffic and seasonal changes in their relative

235   importance, five hydrocarbon tracers have been selected in order to derive an uncertainty of

236   the TEX traffic fraction. These tracers include: four combustion products/tracers (ethylene,

237   propene, acetylene and benzene) for which a wintertime domestic heating combustion source

238   cannot be excluded and an unburned-fuel VOC (isopentane) for which a gasoline evaporation

239   source has been demonstrated in summer[21, 3]. In addition, source attributions for the five

240   tracers by the AIRPARIF (Paris) and NAEI (UK) emission inventories are reported in the

241   Supplement information (figure S8).

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242 $ER_{traffic}$ is determined from the slope of a two-sided linear regression fit between TEX at

243 traffic rush hours and the tracer measured at the traffic sites. For Paris, the determination of

244 $ER_{traffic}$ for TEX combines ERs relative to benzene at the traffic site (Auteuil) and ER of

245 benzene relative to other tracers from the Prequalif tunnel experiment (see 6th column of

246 Table S1). While the $ER_{traffic}$ from the PREQUALIF experiment was only determined during

247 the fall period (September-October 2012), it is representative of the average of expected

248 monthly ERs, the maxima and minima usually being observed in summer and winter (see

249 discussion below). While the contribution at the traffic site of additional sources can be

250 neglected, some seasonal changes in vehicle fuel composition can be expected as a result of

251 seasonal changes in fuel composition regulation and temperature-dependent evaporative

252 emissions. $ER_{traffic}$ was therefore determined on a monthly basis. $ER_{traffic}$ relative to the five

253 tracers values are reported in Table S1 at the three traffic sites. The monthly variability of

254 $ER_{traffic}$ is significant showing minimum and maximum values in winter and summer,

255 respectively. Minimum values from near-traffic measurements found in the literature are also

256 reported for comparison. All TEX are highly correlated with the five tracers at the traffic sites

257 with an R^2 higher than 0.80 and a narrow distribution along the regression slope as an

258 evidence of the traffic origin for TEX (see the example in figure S7 for toluene versus

259 benzene at traffic sites). Values of TEX-to-benzene ER are in the same range among the three

260 cities. It should be noted that ER in Paris and London are in the upper range compared to

261 Strasbourg (only toluene-to-benzene ER reported) and other ER derived from tunnel

262 measurements in Europe. This enrichment has been first pointed out by Borbon et al. (2013)

263 and would be due to two-wheeler powered vehicles (Salameh et al., to be submitted in 2017).

264 Note that the ER relative to benzene is quite similar and the greatest variability is usually

265 observed for toluene and (m+p)-xylenes. Values of ER of TEX relative to other tracers are

266 also consistent between Paris and London.

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267   [tracer]$_{bckgd}$ is determined on an hourly basis and is derived from a linear interpolation of

268   minimum concentrations observed over a 4-day period between 2008 and 2013. The method

269   was validated by comparing the time series of interpolated background concentrations to the

270   ones observed at European rural sites in the frame of the EMEP monitoring network and

271   extracted from the EBAS database (http://ebas.nilu.no). VOC data collected twice a week is

272   available from 2008 to 2013 during a 4-hour sampling by canisters. For France, two rural sites

273   have been selected: La Tardière (LT, Western France) and Peyrusse-Vieille (PV, Southern

274   France)[20]. As an example, a comparison is provided on Figures S5 and S6 in the Supplement

275   Information for the five tracers for Paris and Strasbourg. Except for some periods when local

276   influences at the rural areas cannot be excluded, especially under a continental influence and

277   analytical uncertainties, the time series of interpolated urban background minimum

278   concentrations are consistent with the ones at rural background sites. Median ratios between

279   calculated backgrounds and the ones at Peyrusse-Vieille and La Tardière equal 1.25 and 0.76,

280   respectively.

281   In Figure 3, we have compared the average mixing ratios derived from the traffic

282   (ER$_{trafic}$×[tracer]) and background ([TEX]$_{bkgd}$) terms to the observed mixing ratios in the case

283   of toluene at the three urban background sites. TEX background concentration was determined

284   following the 4-day minima interpolation method described previously for the five tracers. The

285   summertime average contributions of traffic, background and non-traffic terms are illustrated

286   by pie charts and the values of annual traffic contributions to measured concentrations are

287   reported below.

288   Regardless of the location, toluene concentrations show the typical seasonal variability of

289   anthropogenic VOC with maximum concentrations in winter and minimum concentrations in

290   summer. On an annual basis and regardless of the location, traffic emissions unambiguously

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291   dominate toluene mixing ratios by explaining more than 70% of the observed concentrations.

292   Given the use of five tracers, the standard deviation of traffic fraction was estimated to be

293   within a ± 13-24 % range. The background contribution is significant with an annual average

294   of 7% in Strasbourg, 16% in London and 20% in Paris. Contrary to other mono-aromatics, a

295   high background level was found for toluene in Paris exceeding by almost 0.40 ppb the rural

296   ones. We suspect the background concentration being overestimated by our method. We

297   cannot exclude that the estimated background include a non-traffic source term. However,

298   when substracting the background term, traffic emissions explains more than 90% of toluene

299   concentrations. In summer, the traffic contribution remains higher than 58% (Paris, 2013) and

300   higher than 78% without accounting for the background term. This is not significantly different

301   from the annual contribution. The expected additional contribution of summertime evaporative

302   sources (like gasoline evaporation from Figure 2) is not depicted. Firstly, our apportionment

303   method (see equation 1) takes into account the seasonal variability of traffic emission

304   composition by the determination and the use of monthly ER values (Table S1). Secondly, this

305   suggests that the shape of the scatterplots reported in Figure 2a is driven rather by the seasonal

306   change of traffic emission composition and additional non-traffic sources in winter like

307   domestic combustion for the tracers. It should be noted that the sum of the traffic and

308   background terms in winter is usually higher than observed concentrations, indicating that

309   combustion sources other than traffic contribute to the tracer mixing ratios. The strongest

310   evidence is seen at the continental background site of Strasbourg. When only considering

311   isopentane as a traffic tracer in winter in Strasbourg, the traffic contribution falls by 20%

312   compared to the one by combustion tracers but remains above a 50%-contribution (not shown

313   here). However, our results suggest that the traffic source contribution has decreased by 31%

314   in Paris over the last six years. This trend is not depicted in Strasbourg and London. Further

315   analysis for the years following 2013 should be performed to confirm this trend. On an annual

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316   basis, these results are consistent with emission inventories in the megacities of Paris and

317   London (Figure 1) even if the observed traffic contribution is higher. For Strasbourg, the

318   emission inventory only allocates 10% of toluene emissions to traffic (Figure 1) which would

319   be largely underestimated as suggested by our results.

320   Annual values and summertime pie charts of the traffic contribution are compiled for all other

321   mono-aromatic compounds in Table 2. The values of summertime traffic contribution are

322   usually within the standard deviation of the annual ones. While the split limit between traffic

323   and non-traffic contribution is more tenuous for $>C_7$-aromatics (e.g. (m+p)-xylenes in

324   Strasbourg), traffic emissions would still dominate the concentrations of $>C_7$-aromatics. The

325   summertime (and annual) contribution of traffic is usually higher than 60% and up to 96% over

326   the last six years in the three cities. One exception is the 2013-contribution with a 43%-value

327   to o-xylene concentrations in London and a 46%-contribution for (m+p)-xylenes in Strasbourg

328   in 2009. In London, the summertime traffic contribution to o-xylene concentrations has

329   decreased from 86% to 43%. The decreasing trend for (m+p)-xylenes in London is surprisingly

330   not as clear as for o-xylene. This finding is consistent with the observed change at Eltham in

331   the o-xylene-to-(m+p)-xylenes when looking at the shape of the scatterplot (not shown here)

332   Further analysis should be performed after 2013 to confirm. These results are qualitatively

333   consistent with emission inventories for ethylbenzene but usually disagree for xylenes in the

334   French cities of Paris and Strasbourg, for which the solvent use dominates by far their

335   emissions (Figure 1).

336   In Paris, the traffic contribution for the year 2010 is compared to the one extracted from a PMF

337   source-receptor study by Baudic et al.[28] for the same reference year. Baudic and co-workers[28]

338   performed a PMF analysis on a one-year hourly VOC dataset, including the NMHC data used

339   here. They found an optimized solution of 6 factors, including a Motor Vehicle Exhaust, an

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340   Evaporative Sources and a Solvent Use factor. The Evaporative Source factor is related to

341   gasoline evaporation as well as other fossil fuel storage and distribution activities. The

342   contribution of BTEX to this factor being less than 1% , the following discussion will only

343   focus on the two other factors. From the fraction of each TEX in the factor profiles and the

344   modelled concentration of each factor, the modelled contribution of the Motor Vehicle Exhaust

345   (MVE) Factor was calculated to TEX concentrations predicted by the PMF model. This

346   comparison should be interpreted with caution since (i) the MVE contribution is calculated on

347   TEX predicted concentrations (ii) PMF source profiles are assumed to be constant during the

348   whole year in the PMF calculation (iii) assumptions regarding factor identification. For the

349   latter, factor identification is consolidated by comparing to near-source measurement profiles

350   and independent source tracer such as BC_{ff} (Black Carbon from fossil fuel combustion) for the

351   MVE factor. Regarding item (i), note that observed concentrations are 30% higher than the

352   ones predicted by the PMF 6-factor solutions for toluene and higher than 20% for C_8-

353   aromatics. Regarding item (ii) ER calculations have shown a clear seasonal variability

354   implying that traffic emission profiles change during the year. PMF allocates 39%±13% of

355   Motor Vehicle Exhaust and 38%±17% to Solvent Use to toluene concentrations while our

356   study allocates 79%±19% to traffic emissions on an annual basis. For C_8-aromatics, PMF

357   allocates 39%±16% to Solvent Use and 36%±13% to MVE against 72%±24% to traffic

358   emissions in our study. While traffic emissions include both exhaust and gasoline evaporative

359   losses in our study, the approach developed here shows a higher contribution of traffic source

360   to aromatic emissions for all $\geq C_7$ aromatics than the one suggested by the PMF. Given the

361   limitations of such a comparison (see above), it is expected that the factor-of-two difference of

362   traffic is the upper limit and should be lower and within the uncertainties of both approaches.

363   Except the study by Baudic (2016), there is almost no recent study reporting on VOC source

364   apportionment in European urban areas for a direct comparison. As VOC emission regulation

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365   is decided at European level, we expect our results to be extrapolated to other tertiary

366   metropolitan areas in Europe which have the same anthropogenic activity pattern. However, at

367   lower latitude cities like the ones on the Mediterranean border, higher ambient temperature

368   should favor the contribution of evaporative losses.

379   **Supplement Information Available**. Time series of TEX concentrations in the three cities.

380   Source contributions to TEX emissions from emission inventories. Description of the sites

381   and analytical devices for VOC measurements. Determination of the toluene-to-benzene ER

382   representative of traffic, wood combustion and gasoline evaporation emissions. Time series of

383   hydrocarbon tracer concentrations at urban and rural sites for background determination.

384   BTEX average concentrations at traffic and urban background sites and $ER_{traffic}$ used in source

385   apportionment calculation. Correlation plots for the determination of $ER_{traffic}$. Source

386   contributions to tracer emissions.

387

388   **References**

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532 <u>Figures and Tables</u>

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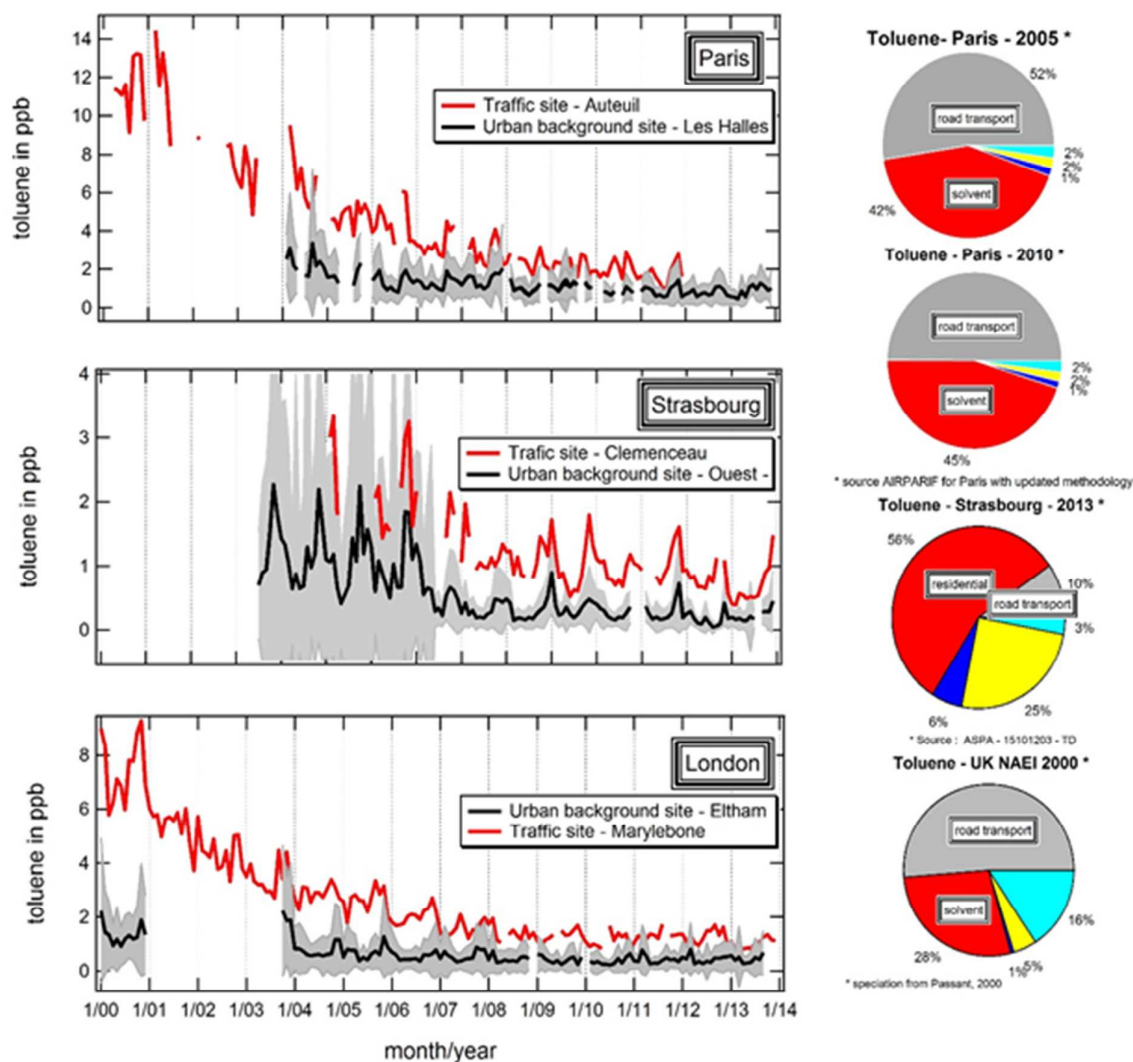
537 Figure 1 : Time series of toluene monthly mean concentrations in Paris, Strasbourg and
538 London at traffic and urban background sites since 2000 (left panel). The grey shaded area
539 corresponds to the standard deviation of the monthly mean concentrations at the background
540 sites. Associated apportioned emissions of toluene extracted from local emission inventories
541 are reported on right panel (grey: road transport ; red: solvent use or residential for
542 Strasbourg; dark blue: extraction and distribution of fossil fuel; yellow: non-industrial
543 combustion and industrial activities for Strasbourg; light blue: other activities.

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a)
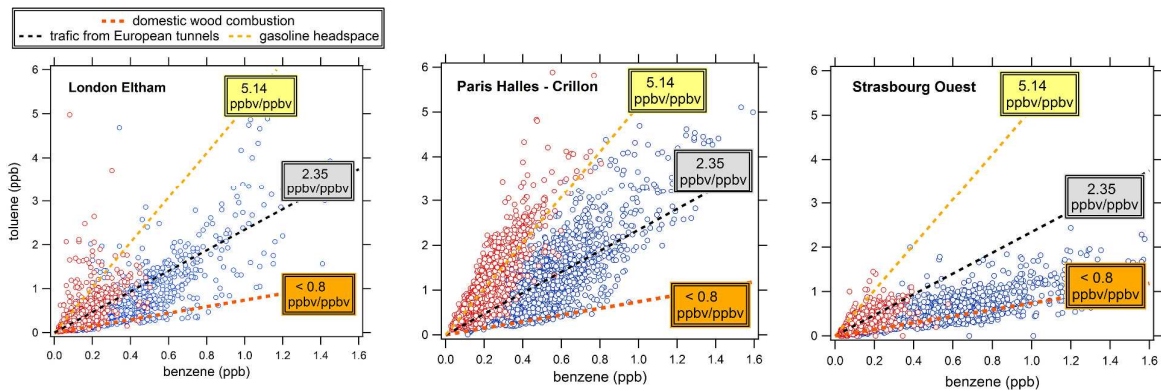
547   b)
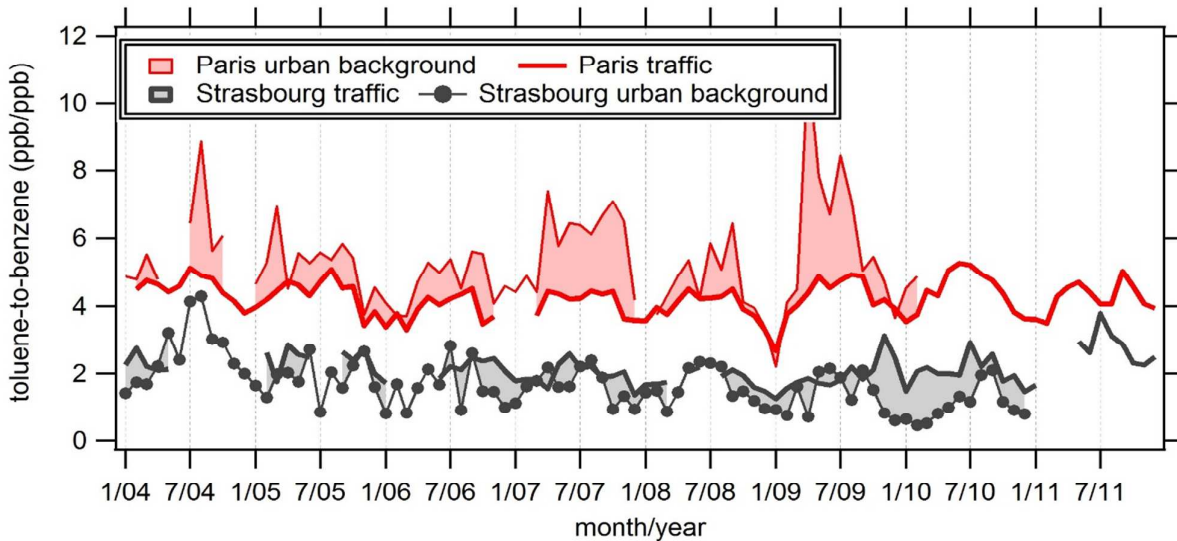
548   Figure 2: (a) Scatterplots of toluene versus benzene concentrations in January (blue) and July
549   (red) months at London, Paris and Strasbourg urban background sites (2008-2013). Dotted
550   lines are average toluene-to-benzene ERs representative of traffic (Aït-Helal et al., 2015),
551   domestic wood combustion (Gaeggeller et al. 2008; Evtyugina et al., 2014; Baudic et al.,
552   2016) and gasoline evaporation emissions (Salameh et al., 2017). (b) Time series of monthly
553   toluene-to-benzene urban enchancement ratios (ER) derived from the slopes of correlation
554   plots for Paris and Strasbourg at traffic and urban background sites

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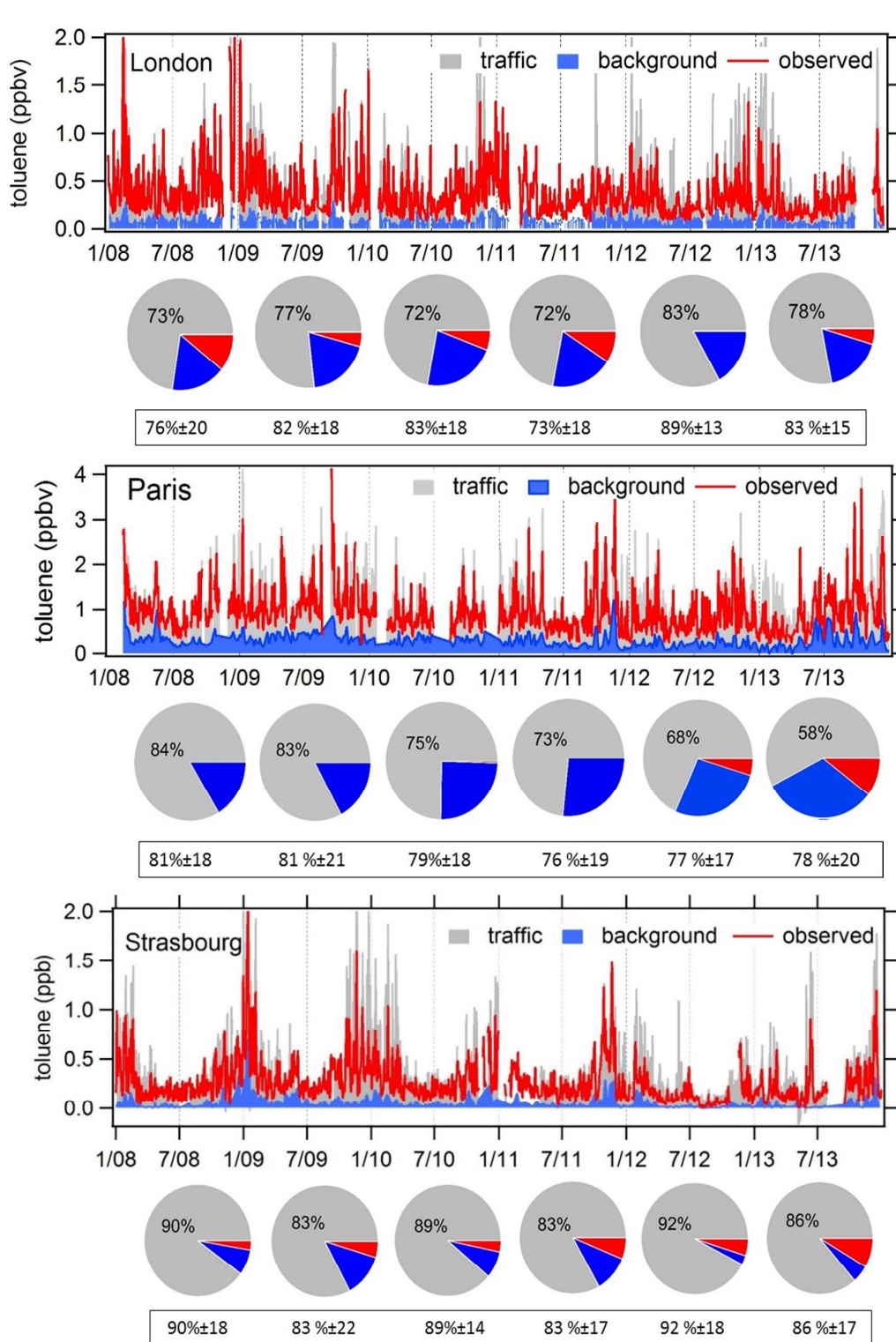
Figure 3 : Time series of toluene concentration terms in Paris, Strasbourg and London between 2008 and 2013. Data are smoothed a 30-day basis. Below time series, pie charts represent the average summertime (JJA) percent contribution of the traffic term (in grey),

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605   background term (in blue) and non-traffic term (in red) to toluene concentrations. Framed
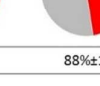606   numbers are the annual average contribution of traffic and its standard deviation.
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608   Table 2:
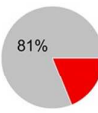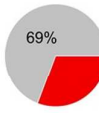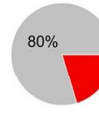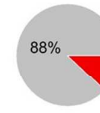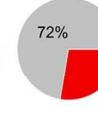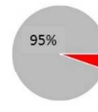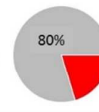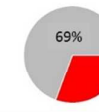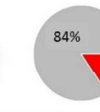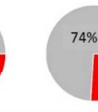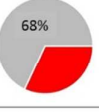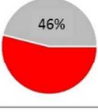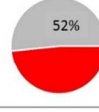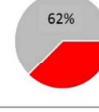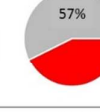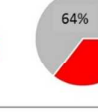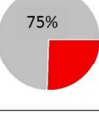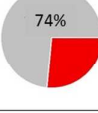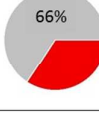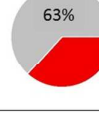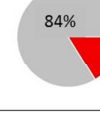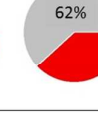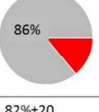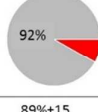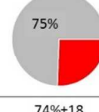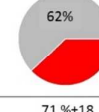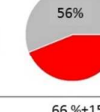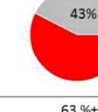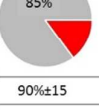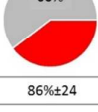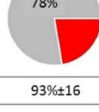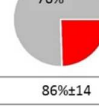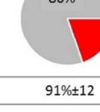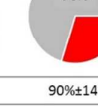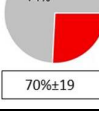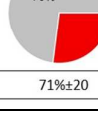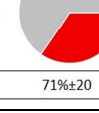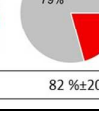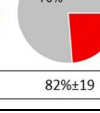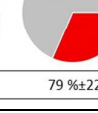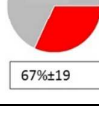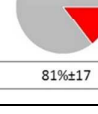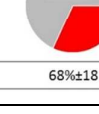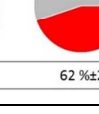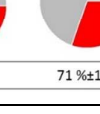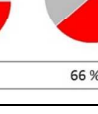
Aromatics	Cities	2008	2009	2010	2011	2012	2013
(m+p)-xylenes	Paris	81%	81%	69%	80%	88%	72%
		79%±16	78%±16	77%±15	83 %±18	93 %±9	87 %±9
	London	89%	95%	80%	69%	84%	74%
		84%±19	89%±17	79%±19	76 %±17	84 %±13	79 %±14
	Strasbourg	68%	46%	52%	62%	57%	64%
		72%±26	71%±27	71%±27	71 %±24	75 %±25	81%±27
o-xylene	Paris	75%	74%	66%	63%	84%	62%
		83%±21	77%±22	67%±24	73 %±23	82%±18	77 %±21
	London	86%	92%	75%	62%	56%	43%
		82%±20	89%±15	74%±18	71 %±18	66 %±15	63 %±20
	Strasbourg	85%	60%	78%	76%	80%	70%
		90%±15	86%±24	93%±16	86%±14	91%±12	90%±14
ethylbenzene	Paris	74%	73%	65%	79%	76%	68%
		70%±19	71%±20	71%±20	82 %±20	82%±19	79 %±22
	London	68%	86%	68%	55%	70%	61%
		67%±19	81%±17	68%±18	62 %±20	71 %±13	66 %±13
	Strasbourg	83%	62%	72%	71%	77%	75%
		89%±15	85%±21	90%±18	84%±17	88%±14	92%±13

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609   Table 2: Mean contribution in % of traffic emissions (in grey) to (m+p)-xylenes, o-xylene and
610   ethylbenzene concentrations in summer (JJA) in Paris, London and Strasbourg between 2008
611   and 2013. Non-traffic contribution (in red) includes the background. Framed numbers
612   represent the annual mean contribution of traffic emissions

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615   Table 1: VOC data used for this study

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Location	Site	Type	Coord.	Network	Period	% missing data	Reference
London	Marylebone Road	Traffic	51.52 N, -0.1546 W	Hydrocarbon Automatic Network	2008 - 2013	23%	Dollard et al., 2007
	Eltham	Urban	51.45 N, 0.071 E	Hydrocarbon Automatic Network	2008 - 2013	19%	Dollard et al., 2007
Paris	Auteuil	Traffic	48.85N 2.25E	AIRPARIF	2008 - 2011	24%	
	Les Halles - Crillon	Urban	48.86N 2.34 E	AIRPARIF	2008 - 2013	6%	Waked et al., 2016
	Guy Moquet tunnel	Tunnel	48.01N 2.65E	PREQUALIF experiment	Sept-Oct. 2012	2%	Baudic et al., 2016
Strasbourg	Clémenceau	Traffic	48.35N 7.44E	ASPA	2008 - 2013	3%	
	Strasbourg Ouest	Urban	48.36N 7.42E	ASPA	2008 - 2013	16%	Boynard et al., 2014

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