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Is traffic still an important emitter of mono-aromatic organic compounds in European urban areas?

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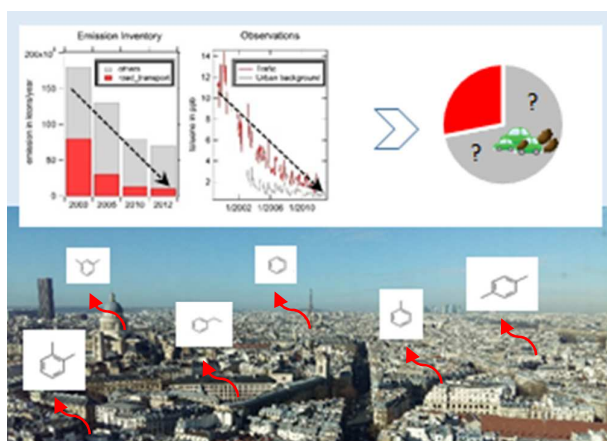
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22 Abstract

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 $\pm 20\%$) 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.



38

39

Toc Art

2

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

52

53 Introduction

54 BTEX (Benzene, Toluene, Ethylbenzene and (m+p) and o-Xylenes), a sub-group of Volatile
55 Organic Compounds (VOC), still constitute a significant fraction of VOCs in urban
56 atmospheres up to 47% in volume of total Non-Methane Hydrocarbons (NMHC) after C₂-
57 C₉ alkanes^{1; 2; 3; 4, 5}. BTEX are released into the atmosphere by either fossil fuel related
58 emission sources (transport, storage and distribution of fossil fuels, industrial and residential
59 combustion, processes) and solvent use⁶. For only benzene, which is known to be
60 carcinogenic⁷, the European air quality objective for health protection of 5 $\mu\text{g}\cdot\text{m}^{-3}$ (1.57 ppb
61 STP) per year is still exceeded in the center of Paris close to major roadways⁸. Apart from
62 their abundance and adverse health effects, BTEX have significant implications on
63 atmospheric chemistry. Together with alkenes, they show the highest ozone-forming
64 potential^{9,10}. They have therefore been considered as key target compounds by ozone policy
65 reduction measures, especially in urban areas where ozone is usually VOC-limited¹¹. BTEX
66 oxidation also contributes to the formation of Secondary Organic Aerosols (SOA). While high
67 uncertainties persist on SOA yields depending on smog-chamber experimental conditions,
68 BTEX show SOA yields as significant as the one of α -pinene, the most emitted and reactive
69 biogenic precursor being currently the dominant SOA source at the global scale: yield values
70 range from 1181 (benzene) to 1578 $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppm}^{-1}$ (xylenes), respectively^{12,13} against
71 1826 $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppm}^{-1}$ for α -pinene¹⁴. Recent results have suggested that BTEX could explain
72 34% of SOA production in summer¹⁵ in Paris megacity whereas such a contribution would be
73 lower when taking into account a larger set of VOC of intermediate volatility (IVOC) in Los
74 Angeles¹⁶. Like terpenes, oxidation of mono-aromatics would also lead to the rapid formation
75 of highly oxygenated molecules as recently suggested by Molteni and coworkers¹⁷.

76 VOC emission reduction measures, such as emission reduction at vehicle exhaust pipe, have
77 successfully reduced their anthropogenic concentrations in cities like London¹⁸, Paris and
78 other medium-sized cities in France⁶, Los Angeles¹⁹ 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

101 uncertainties up to a factor of 4²¹ 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.

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 project²⁸. 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 $5 \mu\text{g}\cdot\text{m}^{-3}$ 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).

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 magnitude³⁰. 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-workers²⁸.

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 ($ER = \Delta[TEX]/\Delta[\text{benzene}]$) 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

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 magnitude³¹. 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

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-2010³⁰ 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 center³⁰.

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**

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

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

226 where $[\text{tracer}]_{\text{traffic}}$ is the concentration of a traffic tracer subtracted by its regional background
227 concentration ($[\text{tracer}]_{\text{bckgd}}$) which could be significant for longer-lived compounds like
228 benzene²⁸ and $\text{ER}_{\text{traffic}}$ 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 benzene²⁸. 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).

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.

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 ($ER_{\text{traffic}} \times [\text{tracer}]$) and background ($[\text{TEX}]_{\text{bkgd}}$) 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

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 $\pm 13\text{-}24\%$ 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 subtracting 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

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-workers²⁸
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

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 $39\% \pm 13\%$ of
355 Motor Vehicle Exhaust and $38\% \pm 17\%$ to Solvent Use to toluene concentrations while our
356 study allocates $79\% \pm 19\%$ to traffic emissions on an annual basis. For C_8 -aromatics, PMF
357 allocates $39\% \pm 16\%$ to Solvent Use and $36\% \pm 13\%$ to MVE against $72\% \pm 24\%$ 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

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.

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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.

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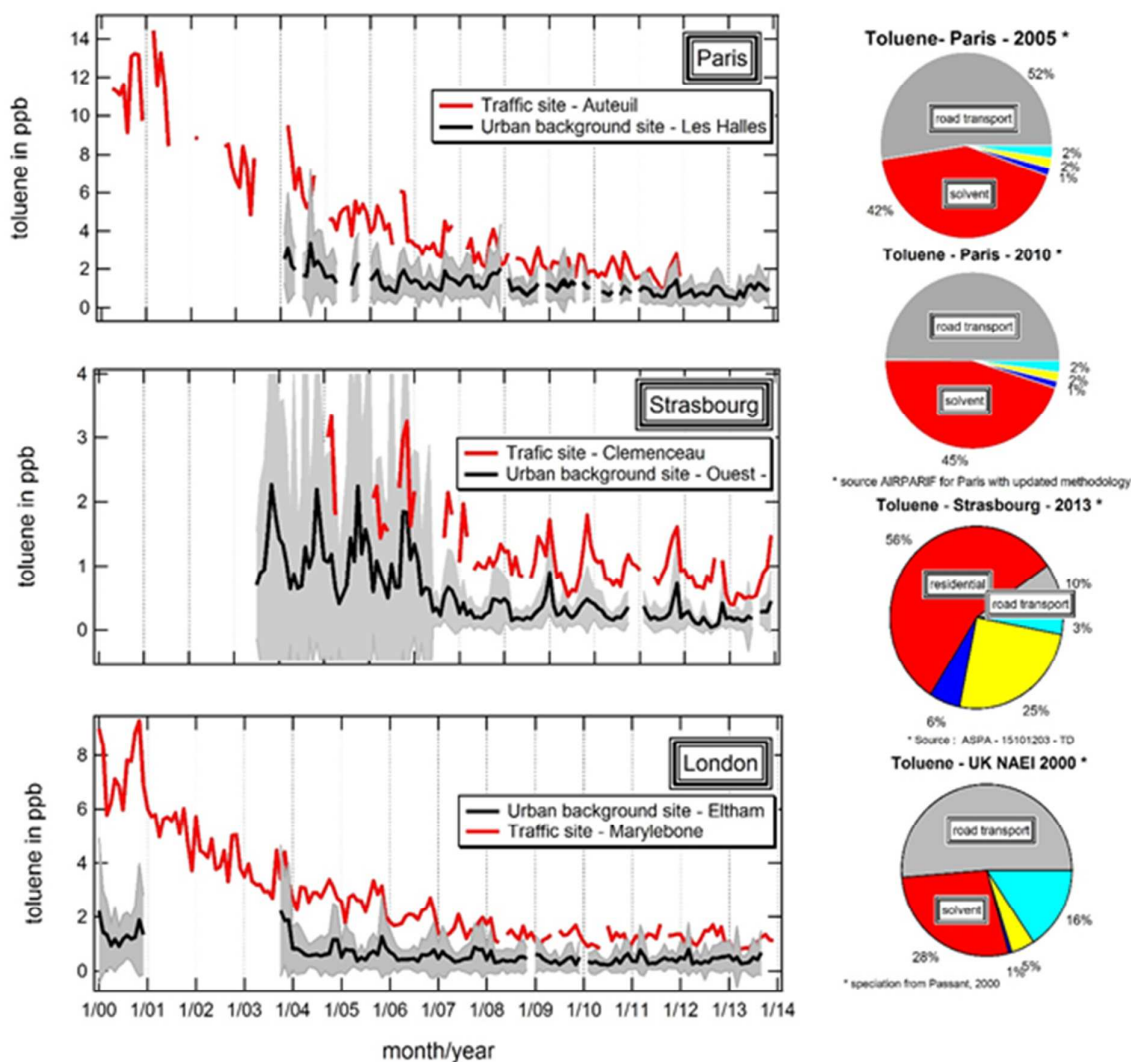
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Figures and Tables

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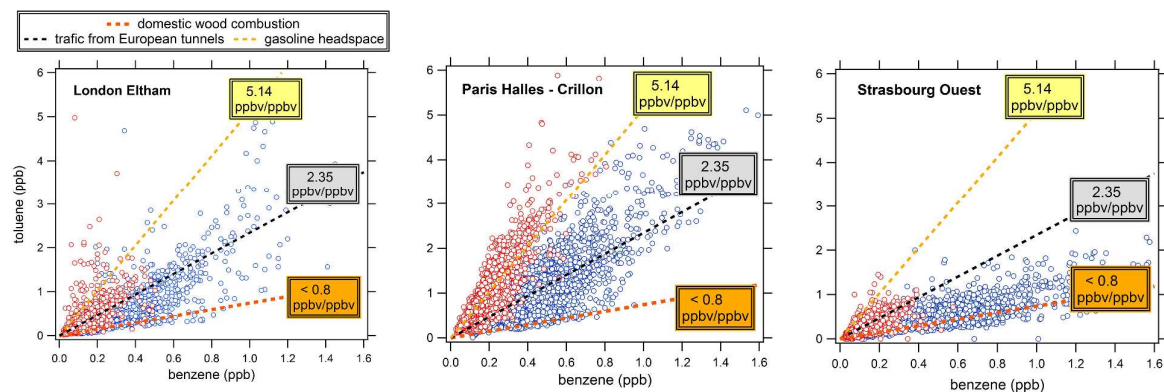
537 Figure 1 : Time series of toluene monthly mean concentrations in Paris, Strasbourg and
 538 London at traffic and urban background sites since 2000 (left panel). The grey shaded area
 539 corresponds to the standard deviation of the monthly mean concentrations at the background
 540 sites. Associated 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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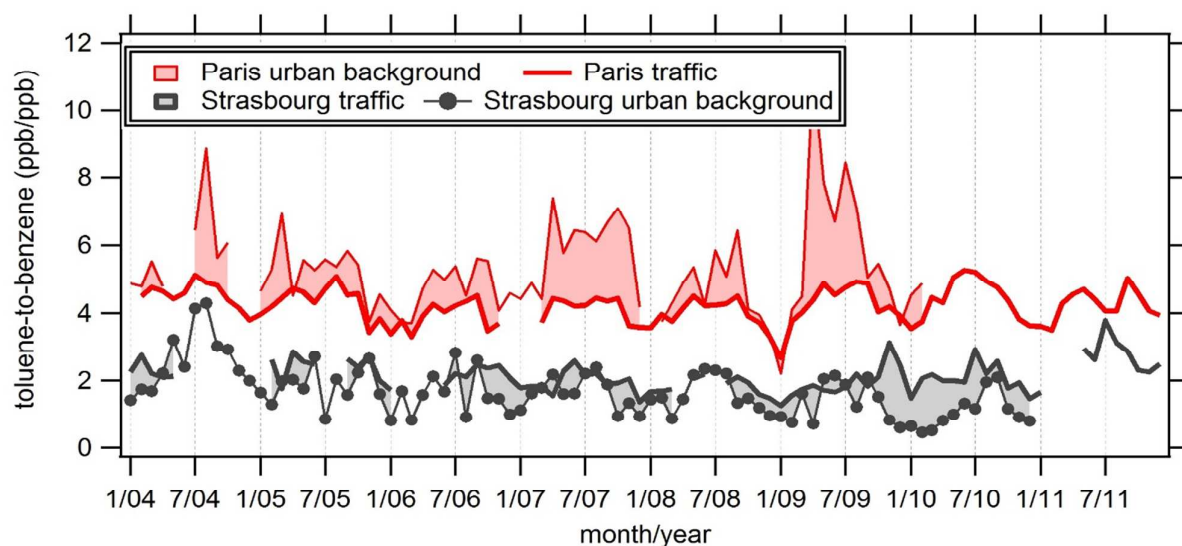
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548 Figure 2: (a) Scatterplots of toluene versus benzene concentrations in January (blue)
 549 (red) months at London, Paris and Strasbourg urban background sites (2008-2013). Dotted
 550 lines are average toluene-to-benzene ERs representative of traffic (Ait-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 enhancement ratios (ER) derived from the slopes of correlation
 554 plots for Paris and Strasbourg at traffic and urban background sites
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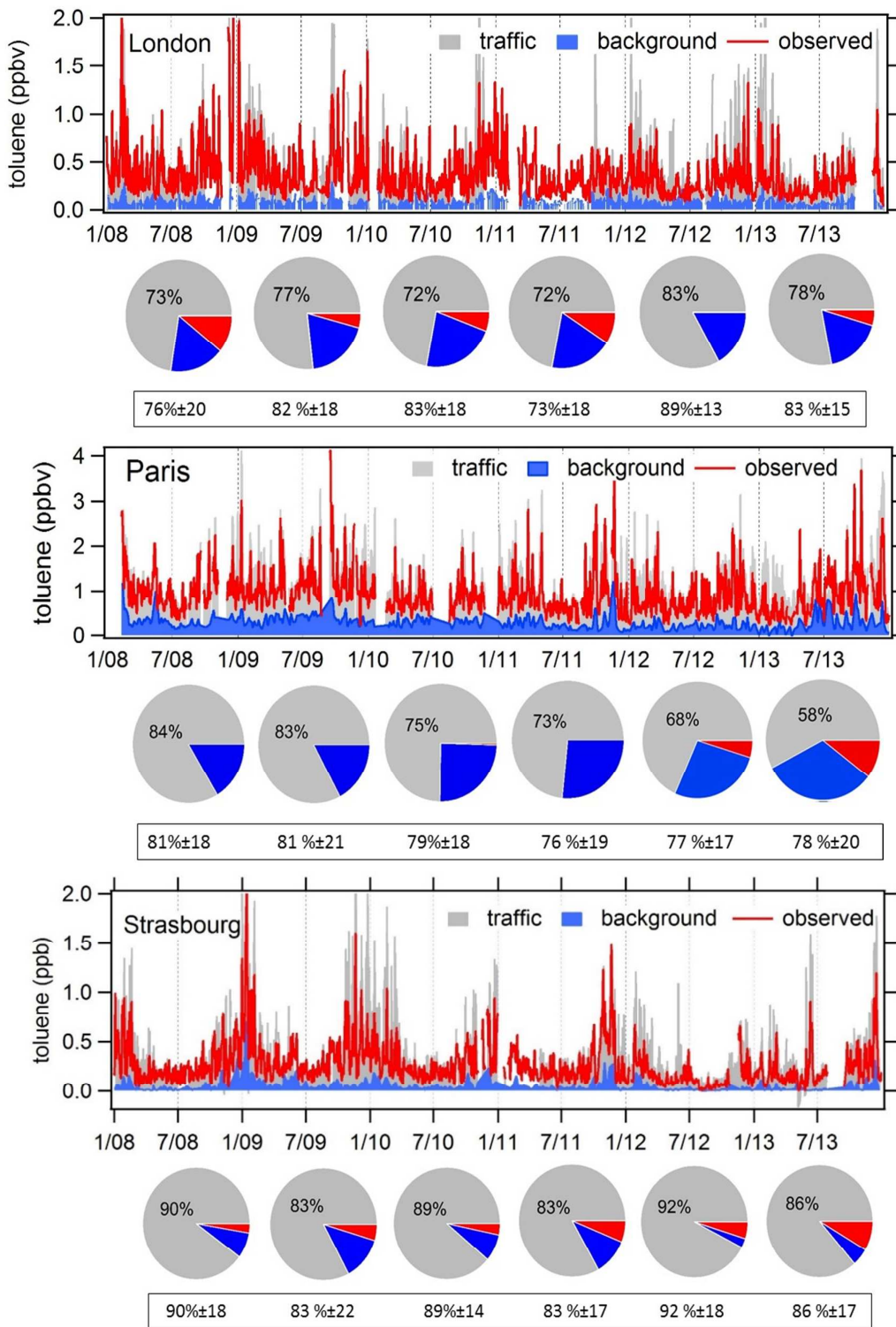


Figure 3 : Time series of toluene concentration terms in Paris, Strasbourg and London between 2008 and 2013. Data are smoothed a 30-day basis. Below time series, pie charts represent the average summertime (JJA) percent contribution of the traffic term (in grey),

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	 79%±16	 78%±16	 77%±15	 83%±18	 93%±9	 87%±9
	London	 84%±19	 89%±17	 79%±19	 76%±17	 84%±13	 79%±14
	Strasbourg	 72%±26	 71%±27	 71%±27	 71%±24	 75%±25	 81%±27
o-xylene	Paris	 83%±21	 77%±22	 67%±24	 73%±23	 82%±18	 77%±21
	London	 82%±20	 89%±15	 74%±18	 71%±18	 66%±15	 63%±20
	Strasbourg	 90%±15	 86%±24	 93%±16	 86%±14	 91%±12	 90%±14
ethylbenzene	Paris	 70%±19	 71%±20	 71%±20	 82%±20	 82%±19	 79%±22
	London	 67%±19	 81%±17	 68%±18	 62%±20	 71%±13	 66%±13
	Strasbourg	 89%±15	 85%±21	 90%±18	 84%±17	 88%±14	 92%±13

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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