This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

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

Journal:	<i>Environmental Science & Technology</i>
Manuscript ID	es-2017-01408s.R2
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	BORBON, Agnès; CNRS, Laboratoire de Météorologie Physique LaMP/CNRS Boynard, Anne; LATMOS Site de Paris Salameh, Therese; IMT Lille Douai Baudic, Alexia; AIRPARIF Gros, Valerie; Institut Pierre Simon Laplace Gauduin, Julie; AIRPARIF Perrussel, Olivier; AIRPARIF Pallares, Cyril; ATMOS ALSACE

SCHOLARONE™
Manuscripts

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

Agnès Borbon^{1*}, Anne Boynard², Thérèse Salameh^{3†}, Alexia Baudic^{4,5}, Valérie Gros⁴,
Julie Gauduin⁵, Olivier Perrussel⁵, Cyril Pallares⁶

1. Université Clermont Auvergne, CNRS, LaMP, F-63000 Clermont-Ferrand, France
2. LATMOS/IPSL, UPMC Univ. Paris 06 Sorbonne Universités, UVSQ, CNRS, Paris, France
3. Laboratoire Inter-Universitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, Créteil, France
4. Laboratoire des Sciences du Climat et de l'Environnement (LSCE), UMR CNRS 8212, Commissariat à l'Energie Atomique et aux énergies alternatives, Université Versailles Saint-Quentin, Institut Pierre-Simon Laplace, Gif sur Yvette, France.
5. AIRPARIF, Association Agréée de Surveillance de la Qualité de l'Air en Île-de-France, 75004 Paris, France
6. Agence de surveillance de la qualité de l'air (ASPA), F-67300, Schiltigheim, France

[†]now at : IMT Lille Douai, Univ. Lille, SAGE - Département Sciences de l'Atmosphère et Génie de l'Environnement, 59000 Lille, France

* corresponding author a.borbon@opgc.univ-bpclermont.fr

Abstract

Trends of long-term observations and emission inventories suggest that traffic emissions will no longer dominate the concentrations of mono-aromatic compounds (i.e. TEX - Toluene, Xylenes and Ethylbenzene) in European urban areas. But the split limit between traffic and other emission sector contributions such as solvent use remains tenuous. Here long-term observations of an extensive set of hydrocarbons, including TEX, at traffic and urban background sites in London, Paris and Strasbourg were combined to estimate the relative importance of traffic emissions on TEX in every city. When analyzing the urban enhancement emission ratios of TEX-to-benzene on a seasonal basis, two potential source signatures other than traffic could be differentiated in all cities (1) summertime evaporation from fuel and/or solvent and (2) wintertime domestic heating. However, traffic emissions still unambiguously dominate the concentration levels of TEX in every city despite the reduction of their emissions at exhaust pipe over the last two decades. Traffic explains between 60% and 96% (at $\pm 20\%$) of TEX levels while it is less clear for xylenes at some locations. Our results provide a basis to evaluate regional emission inventories. The method is applicable at any urban area where speciated hydrocarbon monitoring is available.

Toc Art

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 $\mu\text{g.m}^{-3}$ (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 $\mu\text{g.m}^{-3}.\text{ppm}^{-1}$ (xylenes), respectively^{12,13} against
71 1826 $\mu\text{g.m}^{-3}.\text{ppm}^{-1}$ 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.

VOC emission reduction measures, such as emission reduction at vehicle exhaust pipe, have successfully reduced their anthropogenic concentrations in cities like London¹⁸, Paris and other medium-sized cities in France⁶, Los Angeles¹⁹ and at rural stations^{20,6}. The multi-year trends of monthly average concentrations of toluene (Figure 1) and other aromatics (Figures S1, S2, S3 in Supplement Information) at both urban background and traffic sites in three European metropolitan areas (London, Paris and Strasbourg) support these findings. Regardless of the city, all concentrations have consistently shown a clear decline at traffic sites since 2000, especially in the first half of the decade. However, aromatic levels at urban background sites have stayed almost constant since 2008 and concentrations at traffic sites tend towards the urban background levels. This raises the question whether traffic emissions still dominate TEX emissions. Up-to-date emission inventories in all three cities (see pie-charts on the right hand panel of Figure 1 and Figures S1 to S3 in SI) show various features. It should be noted that no local emission inventory is available for London megacity and the emission distribution is adapted from the National Atmospheric Emission Inventory in UK (NAEI) for the year 2000 (D. Derwent and S. Beevers' personal communication). For toluene, the road-transport sector accounts for half of its emissions in London and Paris and only 10% in Strasbourg. For xylenes (Figures S1 and S2), the road-transport contribution drops down to 4%-33% except for o-xylene in London (57%). The solvent use and/or residential sector appear as the other major source explaining between 28% and 56% of toluene emissions and 44 to 77% especially for xylenes. Only ethylbenzene would be still largely emitted by the road-transport sector (44 – 68 %) (see Figure S3). Regional emission inventories for two European cities, Paris and Zurich in 2005, also pointed to the use of solvents from all source categories as the new dominant source of total VOCs at the urban scale. Finally, the homogeneity of aromatic multi-year trends depicted in observations is not reflected in regional emission inventories. However emission inventories for VOCs still show high

uncertainties up to a factor of 4²¹ and observations provide useful constraints for their evaluation^{22; 23 24; 21;25}. Source-receptor models like PMF (Positive Matrix Factorization) usually point to the contribution of various sources to total measured VOC ambient levels^{26; 27; 24}. BTEX usually show significant contributions in the source profiles of vehicle exhaust, solvent use-related activities and wood combustion for benzene^{26, 27, 24, 28}. Mathematics supporting source-receptor models directly imply an estimation of source/factor contributions to total measured VOC concentrations rather than individual species. Towards the complexity of TEX emission sources, there is still no consensus on the importance of BTEX source and for traffic in particular. Moreover, the seasonality of emission changes has been poorly studied for BTEX.

In this study, we combine long-term and continuous *in-situ* measurements of NMHC, including BTEX, carried out in European urban areas by air quality monitoring network programs over the past decade to investigate the importance of traffic emissions on mono-aromatic levels at the urban scale. Due to its stringent regulation in fossil fuel and solvent formulation compared to other mono-aromatic compounds, benzene will be treated here as a combustion source tracer rather than a target species for the quantification of traffic contribution. This study provides a scientific basis to evaluate the accuracy of regional emission inventories.

Experimental

Data analysis mostly relies on continuous hourly observations of a large set of NMHC, including BTEX, performed by European air quality networks in the megacities of London (UK by DEFRA), Paris (France by AIRPARIF) and Strasbourg (Eastern France by ASPA). The chosen period for data analysis covers the years 2008 to 2013. Special care was put on data quality checks. The description of quality assurance tests is provided in Boynard et al.

(2014)² and Waked et al. (2016)⁶ for French data and Dollard et al. (2007)²⁹ for UK data. The purpose here is to evaluate the importance of traffic emissions relative to other anthropogenic emissions. Data analysis has therefore combined observations collected at both traffic and urban background sites in each city to provide perspectives from contrasted urban situations non-influenced by industrial emissions. Traffic sites represent those locations under the direct influence of nearby traffic emissions, usually a roadway tolerating traffic greater than 10,000 vehicles per day. Urban background sites are under the influence of multi-emitters, at a distance of major traffic lanes of 40 m on average and are more likely representative of the urban mixing of all anthropogenic emissions. Details on the database are reported in Table 1. A description of the sites, meteorology and analytical devices is provided in the Supplement Information (pages S5-S6). Note that the Paris data has been completed by tunnel measurements performed during the PREQUALIF project²⁸. The number of missing data is usually lower than 25% over the six-year period.

Results and discussion

Concentration levels of BTEX

Average concentration levels of mono-aromatics including benzene in the three metropolitan areas are reported in Table S1 (2nd to 5th column) in the Supplement Information for the year 2011. BTEX concentration levels range between 0.03 ppb (ethylbenzene at Strasbourg Ouest and 1,74 ppb (toluene at Paris-Auteuil), i.e. two orders of magnitude. Concentration levels are 2 to 4 times higher at the traffic sites compared to urban background sites. Concentrations of benzene are quite similar between the three cities at ± 0.040 ppb at traffic sites and ± 0.070 ppb at urban background sites. This is consistent with its stringent regulation policy at European level to achieve the air quality standard of $5 \mu\text{g}\cdot\text{m}^{-3}$ per year by, for instance, limiting its presence at 1% vol. in fuels (Directives 98/70/EC replace by 2009/30/EC and 2003/17/EC).

On the opposite, the sum of BTEX load is higher in Paris by 1.4 at traffic sites to 2.4 at urban background sites while concentration levels in London and Strasbourg are surprisingly quite comparable. However, the atmospheric composition in BTEX is very similar between near-traffic and urban background atmospheres. Together with (m+p)-xylenes, toluene (which is the dominant species among BTEX) explains 70% of BTEX load. This suggests that BTEX concentrations are driven by emissions with a non-visible effect of photochemical processing at the background sites. For the latter we would have expected an enrichment of air mass composition in longer-lived mono-aromatics like benzene given that BTEX reactivity towards OH radical spans one order of magnitude³⁰. For benzene, a domestic heating source is highly suspected, especially in Strasbourg (see following sections) and as recently shown by Baudic and co-workers²⁸.

Seasonal source signature on TEX

The magnitude of TEX concentrations is affected by the proximity of emission sources, the extent of photochemical processes and boundary layer conditions. To minimize those effects, we use the TEX-to-benzene enhancement emission ratio ($ER = \Delta[TEX]/\Delta[benzene]$) at urban background sites to identify the TEX source signature on a seasonal basis in order to index seasonal changes in urban enhancement ratios to potential changes in the nature and intensity of their sources. The TEX-to-benzene enhancement ratio equals the slope of a linear 2-sided fit of a TEX-to-benzene correlation plot. An illustration of summertime (July) and wintertime (January) scatterplots is provided in Figure 2a over the six-year period at the urban background sites. Urban enhancement ER of toluene-to-benzene representative of traffic, domestic wood combustion and gasoline evaporation emissions are also reported to provide a comparison basis, which is rather qualitative than quantitative regarding the numerous factors modifying the emission composition. These three emission categories have been usually

identified as TEX major sources in urban areas^{21; 24; 28}. The determination of the reported values of ER is described in the Supplement Information (pages S7-S8). Emissions from solvent use cannot be excluded but representative ER relative to benzene can hardly be determined. The main reason is due to the diversity of solvents. Speciated emission profiles usually show great variability with, for instance, toluene-to-benzene ratios spanning two orders of magnitude³¹. Moreover, benzene, due to its toxic and carcinogen nature, has been strongly limited in solvent formulations. Current standards in Europe have established limits in benzene at 0.1% in cleaning products.

Remarkably, scatterplots show similar multiform patterns in all urban areas (Figure 2a). The scatterplots lie within a domain delimited by the evaporative source ER in its upper part and the domestic wood combustion ER in its lower part. Within these limits, the wintertime and summertime scatterplots roughly split along the traffic ER line, suggesting the additional influence of sources during both seasons despite expected seasonal changes in the composition of traffic emission. In summer, the scatterplot equals (Strasbourg) or is above the traffic ER line (Paris and London) and tends to the one of evaporative emissions. This would suggest the presence of fugitive evaporative processes in addition to traffic. In winter, the scatterplot lies between the traffic ER in its upper part and the domestic wood combustion ER in its lower part. This would suggest an additional source of wood combustion for benzene^{27, 28}. Note that the observed multiform patterns are rather driven by the seasonal variability of benzene mixing ratios than the ones of toluene especially in Strasbourg, a city submitted to well-marked continental climatic conditions. For Strasbourg this is consistent with the emission inventory (Figure 1). Note also that the multiform pattern is temperature-dependent as seen in Paris and Strasbourg when color-coded with temperature (Figure S4 in Supplement Information). Toluene mixing ratios stay rather constant between both seasons. One cannot

exclude that the correlation slope can be affected by photochemical processing for most reactive VOCs^{21,22} especially in summer. When applying the nighttime and daytime filters values following Borbon et al. (2013)³⁰, no significant difference is depicted suggesting that emissions mainly control TEX concentrations (not shown here). It is consistent with observations during MEGAPOLI-2010³⁰ in Paris. The effect of photochemistry on TEX concentrations was only visible in the Paris plume explored by the French ATR-42 aircraft during the MEGAPOLI campaign in the summer 2009 at a distance above 50 km, at least, from the urban center³⁰.

The correlation slopes have been determined on a monthly basis at traffic and urban background sites. The toluene-to-benzene ERs are reported in Figure 2b for Paris and Strasbourg. As expected, a clear seasonal variability is depicted on ER time series with a higher variability at urban background sites. However, both cities show an opposite pattern. In Paris, ERs are similar in winter and the urban background ER significantly increases in summer compared to the traffic ER. In Strasbourg, the summertime ERs are similar while the urban background ER decreases compared to the traffic ER in winter. Such temporal and spatial variability also suggests the potential gaining importance of summertime sources other than traffic as in Paris (evaporation) and the potential gaining importance of wintertime sources other than traffic as in Strasbourg (residential wood combustion).

Finally, seasonal scatterplots of TEX mixing ratios versus benzene mixing ratios and time series of TEX-to-benzene ER suggest a seasonal change in traffic emission composition and the potential influence of sources other than traffic to BTEX concentrations. The importance of these additional source contributions is going to be evaluated in the next section.

Contribution of traffic emissions to TEX concentrations

The method consists in estimating the fraction of each TEX originating from traffic emissions at the urban background sites which are representative of the urban emission mixing. This fraction is calculated by dividing the TEX concentration originating from traffic emissions to the measured concentration. The TEX concentration originating from traffic emissions ($[\text{TEX}]_{\text{traffic}}$) is expressed as follows:

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

where $[\text{tracer}]_{\text{traffic}}$ is the concentration of a traffic tracer subtracted by its regional background concentration ($[\text{tracer}]_{\text{bckgd}}$) which could be significant for longer-lived compounds like benzene²⁸ and $\text{ER}_{\text{traffic}}$ is the urban enhancement emission ratio from traffic between TEX and the traffic tracer. This equation is derived from the one developed by Borbon et al. (2003)²¹.

Acetylene has been commonly used as a traffic exhaust tracer^{21, 32}. However, a non-exhaust combustion source cannot be excluded especially during the winter season regarding domestic heating as for benzene²⁸. In past studies, acetylene and ethylene have already shown significant contributions in the *wood burning* factor solution calculated by PMF^{27, 28}. To take into account potential additional sources to traffic and seasonal changes in their relative importance, five hydrocarbon tracers have been selected in order to derive an uncertainty of the TEX traffic fraction. These tracers include: four combustion products/tracers (ethylene, propene, acetylene and benzene) for which a wintertime domestic heating combustion source cannot be excluded and an unburned-fuel VOC (isopentane) for which a gasoline evaporation source has been demonstrated in summer^{21, 3}. In addition, source attributions for the five tracers by the AIRPARIF (Paris) and NAEI (UK) emission inventories are reported in the Supplement information (figure S8).

ER_{traffic} is determined from the slope of a two-sided linear regression fit between TEX at traffic rush hours and the tracer measured at the traffic sites. For Paris, the determination of ER_{traffic} for TEX combines ERs relative to benzene at the traffic site (Auteuil) and ER of benzene relative to other tracers from the Prequalif tunnel experiment (see 6th column of Table S1). While the ER_{traffic} from the PREQUALIF experiment was only determined during the fall period (September-October 2012), it is representative of the average of expected monthly ERs, the maxima and minima usually being observed in summer and winter (see discussion below). While the contribution at the traffic site of additional sources can be neglected, some seasonal changes in vehicle fuel composition can be expected as a result of seasonal changes in fuel composition regulation and temperature-dependent evaporative emissions. ER_{traffic} was therefore determined on a monthly basis. ER_{traffic} relative to the five tracers values are reported in Table S1 at the three traffic sites. The monthly variability of ER_{traffic} is significant showing minimum and maximum values in winter and summer, respectively. Minimum values from near-traffic measurements found in the literature are also reported for comparison. All TEX are highly correlated with the five tracers at the traffic sites with an R^2 higher than 0.80 and a narrow distribution along the regression slope as an evidence of the traffic origin for TEX (see the example in figure S7 for toluene versus benzene at traffic sites). Values of TEX-to-benzene ER are in the same range among the three cities. It should be noted that ER in Paris and London are in the upper range compared to Strasbourg (only toluene-to-benzene ER reported) and other ER derived from tunnel measurements in Europe. This enrichment has been first pointed out by Borbon et al. (2013) and would be due to two-wheeler powered vehicles (Salameh et al., to be submitted in 2017). Note that the ER relative to benzene is quite similar and the greatest variability is usually observed for toluene and (m+p)-xylenes. Values of ER of TEX relative to other tracers are also consistent between Paris and London.

[tracer]_{bkgd} is determined on an hourly basis and is derived from a linear interpolation of minimum concentrations observed over a 4-day period between 2008 and 2013. The method was validated by comparing the time series of interpolated background concentrations to the ones observed at European rural sites in the frame of the EMEP monitoring network and extracted from the EBAS database (<http://ebas.nilu.no>). VOC data collected twice a week is available from 2008 to 2013 during a 4-hour sampling by canisters. For France, two rural sites have been selected: La Tardière (LT, Western France) and Peyrusse-Vieille (PV, Southern France)²⁰. As an example, a comparison is provided on Figures S5 and S6 in the Supplement Information for the five tracers for Paris and Strasbourg. Except for some periods when local influences at the rural areas cannot be excluded, especially under a continental influence and analytical uncertainties, the time series of interpolated urban background minimum concentrations are consistent with the ones at rural background sites. Median ratios between calculated backgrounds and the ones at Peyrusse-Vieille and La Tardière equal 1.25 and 0.76, respectively.

In Figure 3, we have compared the average mixing ratios derived from the traffic ($ER_{\text{traffic}} \times [\text{tracer}]$) and background ($[\text{TEX}]_{\text{bkgd}}$) terms to the observed mixing ratios in the case of toluene at the three urban background sites. TEX background concentration was determined following the 4-day minima interpolation method described previously for the five tracers. The summertime average contributions of traffic, background and non-traffic terms are illustrated by pie charts and the values of annual traffic contributions to measured concentrations are reported below.

Regardless of the location, toluene concentrations show the typical seasonal variability of anthropogenic VOC with maximum concentrations in winter and minimum concentrations in summer. On an annual basis and regardless of the location, traffic emissions unambiguously

dominate toluene mixing ratios by explaining more than 70% of the observed concentrations. Given the use of five tracers, the standard deviation of traffic fraction was estimated to be within a ± 13 -24 % range. The background contribution is significant with an annual average of 7% in Strasbourg, 16% in London and 20% in Paris. Contrary to other mono-aromatics, a high background level was found for toluene in Paris exceeding by almost 0.40 ppb the rural ones. We suspect the background concentration being overestimated by our method. We cannot exclude that the estimated background include a non-traffic source term. However, when subtracting the background term, traffic emissions explains more than 90% of toluene concentrations. In summer, the traffic contribution remains higher than 58% (Paris, 2013) and higher than 78% without accounting for the background term. This is not significantly different from the annual contribution. The expected additional contribution of summertime evaporative sources (like gasoline evaporation from Figure 2) is not depicted. Firstly, our apportionment method (see equation 1) takes into account the seasonal variability of traffic emission composition by the determination and the use of monthly ER values (Table S1). Secondly, this suggests that the shape of the scatterplots reported in Figure 2a is driven rather by the seasonal change of traffic emission composition and additional non-traffic sources in winter like domestic combustion for the tracers. It should be noted that the sum of the traffic and background terms in winter is usually higher than observed concentrations, indicating that combustion sources other than traffic contribute to the tracer mixing ratios. The strongest evidence is seen at the continental background site of Strasbourg. When only considering isopentane as a traffic tracer in winter in Strasbourg, the traffic contribution falls by 20% compared to the one by combustion tracers but remains above a 50%-contribution (not shown here). However, our results suggest that the traffic source contribution has decreased by 31% in Paris over the last six years. This trend is not depicted in Strasbourg and London. Further analysis for the years following 2013 should be performed to confirm this trend. On an annual

basis, these results are consistent with emission inventories in the megacities of Paris and London (Figure 1) even if the observed traffic contribution is higher. For Strasbourg, the emission inventory only allocates 10% of toluene emissions to traffic (Figure 1) which would be largely underestimated as suggested by our results.

Annual values and summertime pie charts of the traffic contribution are compiled for all other mono-aromatic compounds in Table 2. The values of summertime traffic contribution are usually within the standard deviation of the annual ones. While the split limit between traffic and non-traffic contribution is more tenuous for $>C_7$ -aromatics (e.g. (m+p)-xylenes in Strasbourg), traffic emissions would still dominate the concentrations of $>C_7$ -aromatics. The summertime (and annual) contribution of traffic is usually higher than 60% and up to 96% over the last six years in the three cities. One exception is the 2013-contribution with a 43%-value to o-xylene concentrations in London and a 46%-contribution for (m+p)-xylenes in Strasbourg in 2009. In London, the summertime traffic contribution to o-xylene concentrations has decreased from 86% to 43%. The decreasing trend for (m+p)-xylenes in London is surprisingly not as clear as for o-xylene. This finding is consistent with the observed change at Eltham in the o-xylene-to-(m+p)-xylenes when looking at the shape of the scatterplot (not shown here) Further analysis should be performed after 2013 to confirm. These results are qualitatively consistent with emission inventories for ethylbenzene but usually disagree for xylenes in the French cities of Paris and Strasbourg, for which the solvent use dominates by far their emissions (Figure 1).

In Paris, the traffic contribution for the year 2010 is compared to the one extracted from a PMF source-receptor study by Baudic et al.²⁸ for the same reference year. Baudic and co-workers²⁸ performed a PMF analysis on a one-year hourly VOC dataset, including the NMHC data used 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

is decided at European level, we expect our results to be extrapolated to other tertiary metropolitan areas in Europe which have the same anthropogenic activity pattern. However, at lower latitude cities like the ones on the Mediterranean border, higher ambient temperature should favor the contribution of evaporative losses.

Acknowledgements

Nadine Locoge, Stéphane Sauvage and Antoine Waked from IMT Lille Douai (France) were very helpful for consolidating VOC observations from AASQA and EMEP stations. Stéphane Bonneau and Alexandre Probellet at AIRPARIF and ASPA, respectively, were efficient in providing the NMHC and BTEX original data from the AASQA. The authors would like to thank Roy Harrison, Dick Derwent and Sean Beevers (Kings College) for the information they provided on the status of VOC emission inventories for the UK and London. Thérèse Salameh benefitted from an Ile de France – R2DS postdoctoral grant (2015-2016) and Anne Boynard benefitted from a financial support from CNES. The authors would like to thank Cathy Clerbaux for allowing the preparation of the present work.

Supplement Information Available. Time series of TEX concentrations in the three cities. Source contributions to TEX emissions from emission inventories. Description of the sites and analytical devices for VOC measurements. Determination of the toluene-to-benzene ER representative of traffic, wood combustion and gasoline evaporation emissions. Time series of hydrocarbon tracer concentrations at urban and rural sites for background determination. BTEX average concentrations at traffic and urban background sites and ER_{traffic} used in source apportionment calculation. Correlation plots for the determination of ER_{traffic} . Source contributions to tracer emissions.

References

- [1] Gros, V., Gaimoz, C., Herrmann, F., Custer, T., Williams, J., Bonsang, B., Sauvage, S., Locoge, N., D'Argouges, O., Sarda-Estève, R., Sciare, J., Volatile organic compounds sources in Paris in spring 2007. Part I: qualitative analysis, *Environ. Chem.*, **2011**, Vol. 8, N°1, pp 74-90
- [2] Boynard, A., Borbon, A., Leonardis, T., Barletta, B., Meinardi, S., Blake, D.R., Locoge, N., Spatial and seasonal variability of measured anthropogenic non-methane hydrocarbons in urban atmospheres : Implication on emission ratios. *Atmos. Environ.*, **2014**, 82, pp.258-267. [10.1016/j.atmosenv.2013.09.039](https://doi.org/10.1016/j.atmosenv.2013.09.039)
- [3] Salameh, T., Sauvage, S., Afif, C., Borbon A., Leonardis, T., Brioude, J., Waked, A., Locoge, N., Exploring the seasonal NMHC distribution in an urban area of the Middle East during ECOCEM campaigns: very high loadings dominated by local emissions and dynamics, *Environ. Chem.*, **2015**, 12(3), 316-328, <http://dx.doi.org/10.1071/EN14154>.
- [4] Dominutti P.A., Nogueira, T., Borbon, A., de Fatima Andrade, M., Fornaro, A., One-year of NMHCs hourly observations in São Paulo megacity: meteorological and traffic emissions effects in a large ethanol burning context, *Atmos. Environ.*, **2016**, 142, 371-382, <http://dx.doi.org/10.1016/j.atmosenv.2016.08.008>.
- [5] Wang, G., Cheng, S., Wei, W., Zhou, Y., Yao, S., Zhang, H., Characteristics and source apportionment of VOCs in the suburban area of Beijing, China, *Air. Poll. Res.* **2016**, 7(4), 711-724, <http://dx.doi.org/10.1016/j.apr.2016.03.006>.
- [6] Waked, A., Sauvage, S., Borbon, A., Gauduin, J., Pallares, C., Vagnot, MP., Léonardis, T., Locoge, N., Multi-year levels and trends of non-methane hydrocarbon concentrations observed in ambient air in France, *Atmos. Environ.*, **2016**, 263-275, 141, <https://doi.org/10.1016/j.atmosenv.2016.06.059>.
- [7] Cocheo, V., Sacco, P., Boaretto, C., De Saeger, E., Perez Ballesta, P., Skov, H., Goelen, E., Gonzalez, N., Baeza Caracena, A., Urban benzene and population exposure, *Nature Brief Communication*, **2000**, vol. 404,
- [8] AIRPARIF, Air quality annual report *Surveillance et information sur la qualité de l'air en Ile de France en 2015*, April 2016, 93 pages, http://www.airparif.asso.fr/_pdf/publications/bilan-2015.pdf
- [9] Carter W.P.L., Development of ozone reactivity scales for volatile organic compounds. *Journal of Air and Waste Management Association*, **1994**, 44, pp. 881-899.
- [10] Carter W.P.L., Updated Maximum Incremental Reactivity scale for regulatory applications, Air Pollution Ressource Center and College of Engineering, Center for Environmental Research and Technology, University of California, Preliminary Report, **1998**, Contract n° 95-308, Riverside, USA, 73 p.

- [11] Deguillaume, L., Beekmann, M., Derognat, C., Uncertainty evaluation of ozone production and its sensitivity to emission changes over the Ile-de-France region during summer periods, *J. Geophys. Res. Atmos.*, **2008**, 113, 1–13, doi: 10.1029/2007JD009081.
- [12] Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Flagan, R. C. and Seinfeld, J. H.: The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor, *Science*, **1997**, 276(5309), 96–99, doi:10.1126/science.276.5309.96.
- [13] Ng, N. L., Kroll, J. H., Chan, A. W. H., Chabra, P. S., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, *Atmos. Chem. Phys.*, **2007**, 7(14), 3909–3922, doi:10.5194/acp-7-3909-2007.
- [14] Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C. and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, *J. Geophys. Res.*, **2006**, 111(D17), D17305, doi:10.1029/2006JD007050.
- [15] Ait-Helal, W., Borbon, A., Sauvage, S., de Gouw, J. A., Colomb, A., Gros, V., Freutel, F., Crippa, M., Afif, C., Baltensperger, U., Beekmann, M., Doussin, J.-F., Durand-Jolibois, R., I. Fronval, , N. Grand, N., Leonardis, T., Lopez, M., Michoud, V., Miet, K., Perrier, S., Prévôt, A. S. H., Schneider, J., Siour, G., Zapf, P., and Locoge, N., Volatile and intermediate volatility organic compounds in suburban Paris: variability, origin and importance for SOA formation, *Atmos. Chem. Phys.*, **2014**, 14, 10439–10464, doi:10.5194/acp-14-10439-2014
- [16] Zhao, Y., Hennigan, C. J., May, A. A., Tkacik, D. S., de Gouw, J. A., Gilman, J. B., Kuster, W., Borbon, A., and Robinson, A.L., Intermediate-volatility organic compounds: a large source of secondary organic aerosol, *Env. Sc. Tech.*, **2014**, 48(23) Pages: 13743-13750, DOI: 10.1021/es5035188.
- [17] Molteni, U., Bianchi, F., Klein, F., El Haddad, I., Frege, C., Rossi, MJ., Dommen, J., Baltensperger, U., Formation of highly oxygenated organic molecules from aromatic compounds. *Atmos. Chem. Phys. Discuss.*, **2016**, doi: 10.5194/acp-2016-1126, under review.
- [18] von Schneidmesser, E., Monks, P. S. and Plass-Duelmer, C., Global comparison of VOC and CO observations in urban areas, *Atmos. Environ.*, **2010**, 44(39), 5053–5064, doi:10.1016/j.atmosenv.2010.09.010.
- [19] Warneke, C., de Gouw, J.A., Holloway, J.S., Peischl, J., Ryerson, T.B., Atlas, E., Blake, D., Trainer, M., Parrish, D.D., Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions, *J. Geophys. Res. Atmospheres*, **2012**, 117, D00V17, doi:10.1029/2012JD017899
- [20] Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P., Galloo, J.C., Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas, *Atmos. Environ.*, 2009, 43, 2430–2441.

- [21] Borbon A., H. Fontaine, N. Locoge, M. Veillerot, J.C. Galloo, Developing receptor-oriented methods for non-methane hydrocarbon characterisation in urban air. Part II: source apportionment, *Atmos. Environ.*, **2003**, 37 4065–4076.
- [22] Warneke, C S., McKeen, A., de Gouw, J.A., Goldan, P.D., Kuster, W. C., Holloway, J.S., Williams, E.J., Lerner, B. M, Parrish, D. D., Trainer, M., Fehsenfeld, F.C., Kato, S., Atlas, E. L., Baker, A., and Blake, D. R., Determination of urban volatile organic compound emission ratios and comparison with an emissions database. *J. Geophys. Res.*, **2007**, 112, D10S47. <http://dx.doi.org/10.1029/2006JD007930>.
- [23] Coll, I., Rousseau, C., Barletta, B., Meinardi, S., and Blake, D.R., Evaluation of an urban NMHC emission inventory by measurements and impact on CTM results, *Atmos. Env.*, **2010**, 44(31), 3843-3855.
- [24] Gaimoz, C., Sauvage, S., Gros, V., Herrmann, F., Williams, J., Locoge, N., Perrussel, O., Bonsang, B., d'Argouges, O., Sarda-Estève, R., Sciare, J., 2011. Volatile Organic Compounds Sources in Paris in Spring 2007. Part II: Source Apportionment Using Positive Matrix Factorisation. *Environ. Chem.*, **2011**, 8, no. 1, 91–103.
- [25] Salameh, T., Borbon, A., Afif, C., Sauvage, S., Leonardis, T., Gaimoz, C., and Locoge, N.: Composition of gaseous organic carbon during ECOCEM in Beirut, Lebanon: new observational constraints for VOC anthropogenic emission evaluation in the Middle East, *Atmos. Chem. Phys.*, **2017**, 17, 193-209, doi:10.5194/acp-17-193-2017, 2017.
- [26] Niedojadlo, A., Becker, K. H., Kurtenbach, R., Wiesen, P., The contribution of traffic and solvent use to the total NMVOC emission in a German city derived from measurements and CMB modelling, *Atmos. Environ.*, **2007**, 41, 7108. doi:10.1016/J.ATMOSENV.
- [27] Lanz, V. A., Hueglin, C., Buchmann, B., Hill, M., Locher, R., Staehelin, J. and Reimann, S.: Receptor modeling of C2–C7 hydrocarbon sources at an urban background site in Zurich, Switzerland: changes between 1993–1994 and 2005–2006, *Atmos. Chem. Phys.*, **2008**, 8(9), 2313–2332, doi:10.5194/acp-8-2313-2008.
- [28] Baudic, A., Gros, V., Sauvage, S., Locoge, N., Sanchez, O., Sarda-Estève, R., Kalogridis, C., Petit, J.-E., Bonnaire, N., Baisnée, D., Favez, O., Albinet, A., Sciare, J., and Bonsang, B.: Seasonal variability and source apportionment of volatile organic compounds (VOCs) in the Paris megacity (France), *Atmos. Chem. Phys.*, 2016, 16, 11961-11989, doi:10.5194/acp-16-11961-2016
- [29] Dollard, G. J., Dumitrean, P., Telling, S., Dixon, J. and Derwent, R. G., Observed trends in ambient concentrations of C2–C8 hydrocarbons in the United Kingdom over the period from 1993 to 2004, *Atmos. Environ.*, **2007**, 41, 2559–2569.
- [30] Borbon, A., Gilman, J.B., Kuster, W. C., Grand, N., Chevaillier, S., Colomb, A., Dolgorouky, C., Gros, V., Lopez, M., Sarda-Estève, R., Holloway, J., Stutz, J., Perrussel, O., Petetin, H., McKeen, S., Beekmann, M., Warneke, C., Parrish, D.D., and de Gouw, J., Emission ratios of anthropogenic VOC in northern mid-latitude megacities: observations vs.

- 521 emission inventories in Los Angeles and Paris. *J. Geophys. Res.*, **2013**, vol. 118, 2041–2057,
522 doi:10.1002/jgrd.50059
523
- 524 [31] Yuan, B., Shao, M., Lu, S., Wang, B., Source profiles of volatile organic compounds
525 associated with solvent use in Beijing, China, *Atmos. Environ.*, **2010**, 44, 1919-1926.
526
- 527 [32] Salameh, T., Afif, C., Sauvage, S., Borbon, A., and Locoge, N.: Speciation of Non-
528 Methane Hydrocarbons (NMHC) from anthropogenic sources in Beirut, Lebanon, *Environ.*
529 *Sci. Pollut. Res.*, **2014**, 21, 10867–10877, doi:10.1007/s11356-014-2978-5.
530
531

Figures and Tables

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

546

a)

547

b)

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

556

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.
607

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

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

Table 1: VOC data used for this study

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%	Waked et al., 2016 Baudic et al., 2016
	Les Halles - Crillon	Urban	48.86N 2.34 E	AIRPARIF	2008 - 2013	6%	
	Guy Moquet tunnel	Tunnel	48.01N 2.65E	PREQUALIF experiment	Sept-Oct. 2012	2%	
Strasbourg	Clémenceau	Traffic	48.35N 7.44E	ASPA	2008 - 2013	3%	Boynard et al., 2014
	Strasbourg Ouest	Urban	48.36N 7.42E	ASPA	2008 - 2013	16%	