Manuscript No. : acp-2019-74

Title: Composition and variability of gaseous organic pollution in the port megacity of Istanbul: source attribution, emission ratios and inventory evaluation.

Special Issue: *Chemistry and AeRosols Mediterranean Experiments (ChArMEx) (ACP/AMT inter-journal SI)*

Author(s): Baye T.P Thera et al.

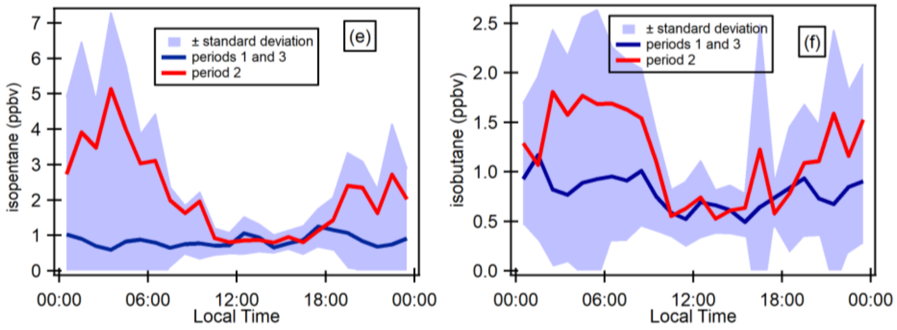
Dear editor,
We would like to thank the two reviewers for their helpful comments to improve the quality of the manuscript. We have reported below all the comments and have addressed them one by one. Our responses appear in blue.

Reviewer 1:

Comments:
According to the times series and diurnal figures (Fig 8 and9) all the extracted factors have more or less the same trend: they all increase after midnight until morning and then they all decrease with almost flat behavior during the rest of the day. This is not what is expected from a PMF analysis. It seems that the separation of the different sources is poor. If all the sources are always reaching the site all together at the same time from the same direction, then PMF is unable to separate them. What is the R^2 of the time series of the 5 factors between each other? How do the solutions do like in the case of 3 and 4 factors? I'm afraid that if the interpolation was done in periods with a lot of missing points in a row then the PMF results may be significantly altered. How do the solutions look like if you only use the real measurements without any interpolation?

Thera et al.: Reviewer 1 raises four critical points which are going to be discussed below.

(1) All the PMF factors except for the "mixed diurnal regional factor" have indeed more or less the same trend. Indeed, the PMF is sensitive to the variability of the species but by looking at the individual diurnal profiles of the factors (figure 6) the separation of the different sources is not poor. The previous representation of the factor diurnal profile could bring some confusion and the new figure 9 is more explicit. Except for the mixed diurnal regional factor, the PMF was able to distinctly separate the other factors. A relevant example is the one of pentanes and butanes for which representative diurnal profiles are reported in the figure below (figure a) extracted from the Figure 6 of the paper.



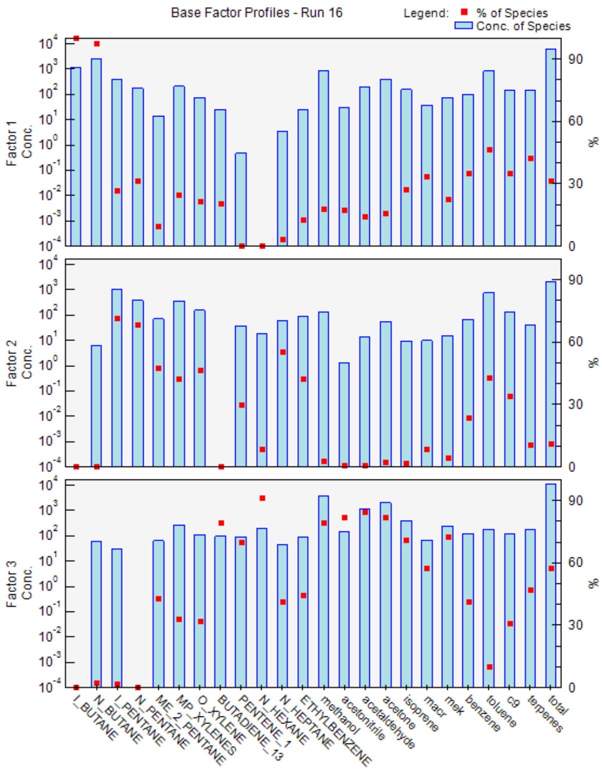
While their diurnal profiles almost show similar diurnal variability during periods 1 and 3 and 2, the PMF was able to isolate those compounds in two different and independent factors (factor 3 and 5) with an R^2 lower than 0.1 as discussed in section 3.3.2 and in the section below.

(2) The best number of factor for the PMF run has been selected rigorously as described in section 2.4.3 of the paper. It is based on common statistical criteria such as Q (residual sum of squares), IM (maximum individual Column mean), IS (maximum individual column standard deviation) as defined by Lee and al. (1999) and R^2 (indicator of the degree of correlation between predicted and observed concentrations). Q, IM, IS and R^2 were then plotted against the number of factors (from 2 to 12) in order to extract the optimal numbers of factors. Moreover we made sure that the factors were not dependent between each other. In the table below, we have reported the R^2 of the time series of the chosen 5 factors between each other. R^2 does not exceed 0.28. There is therefore no significant correlation between the factors which means that the factors are independent. A discussion on R^2 values between the five factors have been added in the paper in lines 267-269.

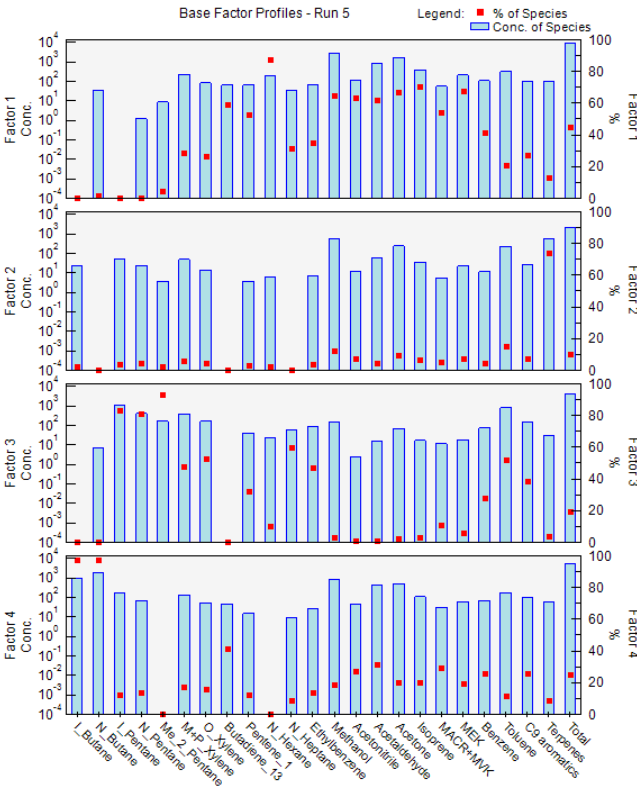
	Toluene	Biogenic terpenes	Natural gas evaporation	Mixed diurnal regional emissions	Road transport
Toluene	x	0.0590	0.1050	0.0015	0.2630
Biogenic terpenes	x	x	0.2822	0.0265	0.0185
Natural gas evaporation	x	x	x	0,0003	0.0499
Mixed diurnal regional emissions	x	x	x	x	0.0650
Road transport	x	x	x	x	x

(3) The solution with 3 and 4 factors is discussed. The solution of 3 factors does not enable to separate properly the species (see figure below): factor 1 is composed mainly of pentanes and aromatics compounds, factor 2 of butanes and some aromatic compounds and factor 3 of a mixed of all compounds except for butanes and pentanes. Terpenes was distributed between all the three factors.). The total correlation between reconstructed and measured VOC is poor for a PMF run for a solution of 3 factors (R^2=0.78) and species like butanes are poorly reconstructed (R^2= 0.1).

3 factor solution

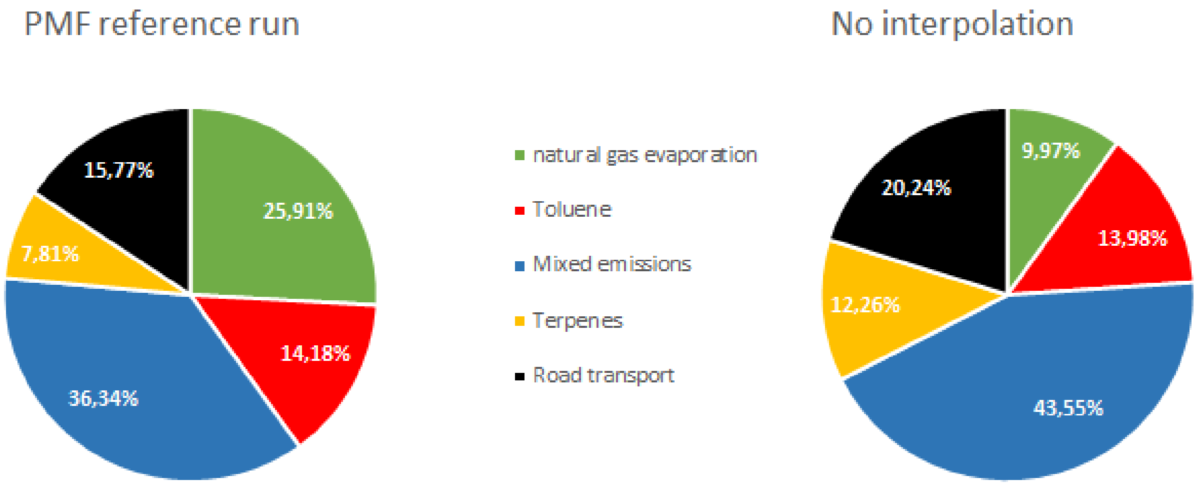


4 factor solution



In the case of 4 factors; we have the same factors as for the solution with 5 factors except for toluene (see figure below): mixed diurnal regional factors (factor 1), terpenes (factor 2), road transport (factor 3) and natural gas evaporation (factor 4). However, Toluene is better reconstructed by the PMF with the 5 factors solution ($R^2 = 0.95$) than the 4-factors solution ($R^2 = 0.74$). Furthermore, the sensitivity tests, the PMF output uncertainties methods, and the f-peak enable us to choose the 5 factor as the optimal solution.

(4) There was one period during which there were no measurements by the GC-FID: from 09/24 at 23:48 to 09/25 at 10:18.This period corresponds to 10h and 30 minutes of missing points. However the PMF in this experiment designed as the reference run was carried out by removing this period as discussed in section 2.4.4. Note that the PMF cannot be run with any missing points; As a consequence either we will interpolate or we will replace the missing data by the median value which is more likely to alterate the results since the latter smoothes the variability. We run the PMF by replacing missing data by the median instead of interpolating. The same number and nature of factors have been found while some differences are found in factor's contribution like the ones for Natural Gas Evaporation (26% against 10%). . Comparison between both run is reported below.



However, the reference run is still the best solution since the R^2_{total} of the observed vs modelled by the PMF is 0.97 for the PMF reference run against 0.90 for the PMF run with no interpolation. There were only 65 % of the species that were well reconstructed by the PMF ($R^2 \geq 0.5$) with the run with no interpolation against 83 % for the PMF reference run. Furthermore, butanes were poorly reconstructed by the PMF with the solution with no interpolation ($R^2 = 0.19$) while these species were well reconstructed by the PMF reference run($R^2 > 0.90$). A discussion on this test has been added in the sensitivity test section (2.4.5) and in Table 2.

General comments

1. Abstract: The abstract is too long. It should be shorter and more condense in a way that the reader gets only the important information. It should be more educational and provide the translation of the results.

   Thera et al.: The abstract has been shorten and condense by highlighting only important information as you suggested.

2. Introduction: The authors use quite old literature (15-20 years old). They should enrich/replace/add more recent citations. In addition in lines 84-92. where the authors describe other VOCs studies in cities in the eastern Mediterranean. and in lines 116-118. where the authors refer to previous VOC PMF analysis. they have ignored an important study in Athens and Patras (Greece) by Kaltsonoudis et al. (2016): Temporal variability and sources of VOCs in urban areas of the eastern Mediterranean (ACP). where online VOCs were measured and PMF analysis was performed following a very alike concept with the present paper. The author should provide a comparison with respect to the results of Kaltsonoudis et al. (2016) as Athens is one of the important Mediterranean cities.

Thera et al: The introduction has been enriched with more recent citation. The work of Kaltsonoudis et al. (2016) has been added in Lines 79 in addition to the other VOC studies made in the cities of the eastern Mediterranean as well as in lines 112 where previous PMF studies were made**.**

Specific comments:

3. Lines 152-153: Why did the authors use Teflon tubing instead of silcosteel or stainless steel tubing for VOC sampling? Teflon has a memory effect which could affect the measurements. What were the losses of certain VOCs in this 3m Teflon line?

Thera et al: Silco-treated steel or heated stainless steel lines are the ones recommended for hydrocarbon sampling while Teflon-PFA (perfluoroalcoxy) is the one recommended for the sampling of oxygenated VOCs. See ACTRIS http://fp7.actris.eu/Portals/97/deliverables/PU/WP4_D4.4_M24.pdf. A compromise needed to be found for the PTR-MS which encompasses hydrocarbons like aromatics and oxygenated VOCs (OVOC) like acetone. We decided to use Teflon-PFA. The good consistency at ±20% between PTRMS, AIRMOVOC, canisters and tubes reported in Figure S2 suggests that the Teflon-PFA is well adapted.

4. Lines 234-235: Which data set of isoprene. benzene. toluene and C8 aromatics concentration were used in the PMF? Those taken by the PTRMS or those by GC-FID or was the average of these 2 instruments? Please explain.

Thera et al.: The data set of isoprene, benzene, toluene and C8-aromatics concentration used in the PMF are those taken by the PTRMS. One of the reason is that there were only two missing points with PTRMS data which is better for running the PMF model. The text have been modified for more clarity in lines 230: *[…] Alkanes and alkenes were measured by the GCFID while benzene. toluene, isoprene, C8- aromatic, carbonyls, alcohol, nitrile and terpenes were the ones measured by the PTRMS. For benzene. toluene and C8 aromatics the PTR-MS data were selected for the PMF run because of the smallest number of missing data […]*

5. Line 241: Linear interpolation is accepted if there is one or two missing points between two measurements. If the missing points correspond to several hours between two measurements, then the interpolation does not necessary represents the real ambient concentrations. In this meantime the concentration could have changed a lot and an interpolation could lead in fake results. So, the criterium of using or not interpolation is not the total missing points (in your case 40%) but where there points are located/ distributed between the measured points (how long a missing a period 1 hour? 5 hours? 10 hours? Please clarify that.

Thera et al.: This comment also refers to the first one. The longest period (10h and 30 min) with missing data occurred from the night of 09/24 to the morning of 09/25 for compounds measured by the GC-FID. The PMF reference run was performed by removing this period.

Depending on the compound, the missing point period can last up to 10 continuous hours like methyl-2-pentane and one full day for m+p-xylenes. We could have replaced the missing points either by the median or by interpolation. This is the reason why we only did interpolation with species that have less than 40 % of missing data. The missing data are homogeneously distributed between all the periods. We found it more accurate to replace the missing data by the interpolation which take into account previous concentration rather than by a median. Moreover, the test with or without interpolation show that even with using the median, the PMF is less performant (see previous discussion in the first answer (4)).

6. Lines 321- 330: This part is not clear to me. What is the "one VOC fingerprint" and the "other VOC fingerprint"? What is the goal of this paragraph?

Thera et al.: the term "fingerprint" was replaced by "composition" to make it clearer and some sentences have been modified. The objective of the comparison between the different composition is to show what type of source signature can be depicted at the Besiktas supersite (lines 325-358*):[…] Therefore, the analysis only focuses on VOC relative composition. The relative composition divided into major VOC chemical groups at each sites by sorbent tubes and canisters is reported on Figure 3a and 3b. respectively. The composition is variable across the megacity for the aliphatic fraction of high and intermediate volatility hydrocarbons (C2-C16). As expected. the composition of the 29/09 12:05 sample at the Besiktas site is like the ones derived from the nearby roadway side measurements highlighting the influence of road transport emissions at the supersite. Interestingly. the VOC composition of the three samples from sorbent tubes at the Besiktas site are different from the ones at the nearby roadway side with a higher proportion of IVOC. The other VOC composition of the 26/09 10:31 sample by canister is rather similar to the one from the seashore sample in Galata (29/09 16:12 sample). In the same way the VOC composition of the samples at the supersite derived from tubes are rather like the Besiktas seashore one ; for both of them. the proportion of IVOC is significant (from 15 % to 40 % in weight). While light VOC are expected to be of minor importance when considering ship emissions. the higher presence of heavier organics is however expected as observed for alkanes by Xiao et al. (2018) in ship exhaust at berth. The VOC composition comparison would thus suggest not only the impact of road traffic emissions on their composition but also the potential impact of local ship traffic emissions. Finally the composition at Besiktas is not affected by Residential emissions which are enriched in light C2-C3 alkanes (canisters) or aromatics (canisters) […]*

7. Lines 331-387 (Section 3.2.2): This section is not well organized. For example. The authors discuss the diurnal profiles of NOx in the lines 338-339 and they go back again to NOx diurnal cycle in lines 371-375. The CO and VOC diurnal patterns are also repeated. Please first discuss the time series and then the diurnal profiles.

Thera et al.: This section has been reorganized as you suggested in lines 360-441: *[…]The variability of VOC concentrations is driven by several factors: emissions (anthropogenic or biogenic), photochemical reactions (especially with the OH radical during the day and ozone and nitrates at night for alkenes) and the dynamic of the atmosphere (including dilution due to the height of the boundary layer) (Filella and Peñuelas, 2006). The time series of inorganic trace gases (NOx and CO) and some VOC representing the diversity of sources and reactivity are reported in Figure 5. The meteorological periods 1, 2 and 3 described in the previous section 3.1 are also indicated. Because NOx at the super site were only measured from 09/25 to 09/30, data from the air quality station in Besiktas were used (see Figure 1). One should note that the time series of NOx at the supersite and at the Besiktas station are consistent.*

Time series of NOx and CO show high concentrations but a different pattern regardless of the origin of air masses. While a daily cycle of NOx is depicted, CO does not show any clear pattern. The NO2/NOx ratio fluctuates between 0.34 to 0.93 with an average and median value of 0.53 and 0.55, respectively. These values are very high compared to what is usually found in the literature (Grice et al., 2009; Kousoulidou et al., 2008; Keuken et al., 2012) which are mostly low and below 0.50. However higher values of NO2/NOx ratio can be found in diesel passenger cars (Grice et al., 2009. Vestreng et al., 2009) and vans (Kousoulidou et al., 2008). This ratio would reflect the impact of the combustion of heavy fuels in the megacity. After road transport, cargo shipping is a second highest contributor to NOx levels according to the local/regional inventory (Markakis et al., 2012).

Anthropogenic VOC time series (benzene, isopentane and isobutane) exhibit a high frequency variability but usually show higher concentrations during the night especially during period 2. One cause are the very low wind speeds at night especially during period 2 (Figure 3), which would reinforce the accumulation of pollutants. Under marine influence (periods 1 and 3), VOC concentrations are the lowest, especially during period 3, which is characterized by rainy days (September 27th and 28th), high wind speed and colder temperatures (Figure 5). These conditions favor atmospheric dispersion. During transition periods and under continental influence (period 2), VOC concentrations exhibit a strong day-by-day variability with episodic nocturnal peaks especially on September 25th and 26th. While these peaks are not always concomitant between VOC and are not associated with any increase in NOx and CO levels, they occur under south and southwestern wind regimes which are unusual wind regimes according to Figure 1. This points out the potential influence of industrial and port activities other than fossil fuel combustion. For instance, maximum concentrations of butanes occurred during the period of the marine-continental regime shift with well-established southwestern wind regime on 09/22, 09/23 and on 09/26 at the end of the day. Maximum concentrations of pentanes occurred during the night of 09/26 to 09/27 like for aromatics (e.g. benzene) (Figure 5).

Except during transition periods, the background levels of measured trace gases are not affected by the origin of air masses. This strongly suggests that the pollutants measured during TRANSEMED-Istanbul were from local and regional sources. Finally, time series would suggest the influence of multiple local and regional sources other than traffic on VOC concentrations, likely industrial and/or port activities, at the supersite.

Isoprene and its oxidation products (MACR+MVK) covariate most of the time. They usually show their typical diurnal profiles with higher concentrations during the warmest days and at midday due to biogenic emission processes. Their significant correlation with temperature (R = 0.7) implies the emission from biogenic sources. Around the Besiktas site, 49.5 % of the vegetation is occupied by hardwood and hardwood mix trees while only 6 % is occupied by softwood and hardwood mix trees. While Quercus (isoprene emitter) only occupies 7.7 % of the total vegetation coverage (personal communication from Ministry of Forestry), the presence if isoprene at the supersite is probably due to the surrounding trees.

Except during transition periods, the background levels of measured trace gases are not affected by the origin of air masses. The background levels stay constant under continental or marine influence and regardless of the atmospheric lifetime of the species. This strongly suggests that the pollutants measured during TRANSEMED-Istanbul were from local and regional sources. Finally, time series would suggest the influence of multiple local and regional sources other than traffic on VOC concentrations, likely industrial and/or port activities, at the supersite.

Taking into consideration time series variability, diurnal variations have been splitted into periods 1 and 3 and period 2 for selected VOC as well as two combustion derived trace gases (NOx and CO). Diurnal profiles of atmospheric concentrations are reported in Figure 6. Local traffic counts for road transport (personal communication from Istanbul Municipality for fall 2014) and ship (https://www.marinetraffic.com/en/ais/details/ports/724/Turkey_port:ISTANBUL) are also reported in Figure S6 in the supplement material. Maritime traffic is mostly for passenger shipping (58.02%) against 16% for cargo shipping. The diurnal profiles of ship and road traffic counts are similar.

Generally, concentrations during period 2 are higher than the ones during periods 1 and 3 and show different diurnal patterns for some compounds. The profile of NOx is consistent with the one of traffic counts (Figure S6 of the supplement material). NOx exhibits higher concentrations during the day and lower concentrations at night for both periods with a morning peak (7:30-8:30) and one early evening peak from 17:30 (Figure 6.a). This is typical of traffic emitted compounds with morning and evening rush-hour peaks as observed in many other urban areas like Paris, *France in Europe (Baudic et al., 2016) or Beirut, Lebanon in Eastern Mediterranean (Salameh et al., 2016). As already depicted in time series, CO diurnal profile is different from the one of NOx. CO concentrations show higher concentrations in the late evening and lower concentrations during the day. During the day, CO is also characterized by a double peak: one in the morning (8:30) and the other one in the middle of the day (Figure 6.b). Both NOx and CO show quite similar diurnal profile between the three periods even if morning concentrations tend to be higher.*

VOCs show different profiles from the one of NOx. Under marine influence (periods 1 and 3), primary anthropogenic VOC (ie. benzene, alkanes and other aromatics) almost exhibit a constant profile while they show higher concentration from midnight until 10:00 AM under continental influence (period 2), For instance, benzene (Figure 6.d) and isopentane (Figure 6.f) nighttime concentrations increase by four-fold compared to the levels under marine influence. In the middle of the day, the concentration levels are the same as during periods 1 and 3. The profiles of primary anthropogenic VOCs point out the complex interaction between local and regional emissions and dynamics. Period 2 points out the influence of VOC emissions other than traffic and combustion processes (no effect on NOx and CO) at night. While the influence of traffic emissions on CO and VOC cannot be excluded; it seems that their emission level is not high enough to counteract the dispersion effect during the day unlike NOx. This will be further investigated in the PMF analysis.

Isoprene concentrations increase immediately at sunrise and decrease at sunset during period 1 and 3 (marine influence) which indicates its well-known biogenic origin (Figure 6.g) which is light and temperature dependent. Isoprene and MACR+MVK's concentrations increase at night during period 2 like other alkanes and aromatics, suggesting their potential anthropogenic influence.

Provided some interferences like furans could contribute to isoprene signal by PTRMS measurements (Yuan et al., 2017), this would suggest an anthropogenic origin for isoprene. While the signals of m/z 71 are commonly attributed to the sum of MVK and MACR which are both oxidation products of isoprene under high-NO conditions, more recent GC-PTR-MS studies identified some potential interferences for MVK and MACR measurements, including crotonaldehyde in biomass-burning emissions, C5 alkenes, and C5 or higher alkanes in urban regions (Yuan et al., 2018). Such interferences cannot be ruled out here. During periods 1 and 3, MACR+MVK concentrations follow the same general pattern as of isoprene's.

With relatively long atmospheric lifetime, (≈ 68 days), acetone's concentration is quite constant throughout the day within period 1, a peak in the middle of the day and lower concentrations during the night for period 2 (Figure 6.c). The peak in the middle suggests the presence of a secondary origin. Acetone can have both primary and secondary source (Goldstein and Schade, 2000; Macdonald and Fall, 1993). Methanol and MEK have the same general pattern as for acetone during both periods without the peak in the middle of the day suggesting that they might have the same emission source[…].

8. There also some contradictions. In the lines 338-339 it is written that the NOx shows a clear diurnal profile with a maxima at midday. which is wrong according to Figure 5a where the NOx profile has 2 maxima coinciding with the morning and the evening traffic. Then at lines 371-375 it is stated that the NOx profile has 2 peaks and in the evening. which is actually what is shown in Figure 5a. Please delete the wrong description.

Thera et al.: The wrong description has been deleted and the part has been rephrase in lines 409-421: *[…]The profile of NOx is consistent with the one of traffic counts (Figure S6 of the supplement material). NOx exhibits higher concentrations during the day and lower concentrations at night for both periods with a morning peak 410 (7:30-8:30) and one early evening peak from 17:30 (Figure 6.a). This is typical of traffic emitted compounds with morning and evening rush-hour peaks […]*

9. Lines 334-335: NOx and CO are described as air quality trace gases? Why? So if NOx and CO are in low concentrations it means that the air quality is good enough?

Thera et al.: By air quality trace gases we meant inorganic trace gases. We replaced air quality by inorganic trace gas in lines 363: *[…]The time series of inorganic trace gases (NOx and CO) and some VOC […]*

10. Lines 391-398: Isoprene is reducing after 13:00-14:0 which implies possible consumption thus the corresponding isoprene products (MACR+MVK) should increase. But they don't. Please explain. Also explain why in period 2 MACR+MVK are increasing during the night. MACR+MVK have very similar profile to benzene and isopentane for both periods 1 and 2. Is it possible that m/z 71 (related to MACR+MVK) has interferences from other compounds related to anthropogenic activities? Please discuss.

Thera et al.: During period 2, when isoprene decreases, its oxidation products MACR+MVK do increase. During period 2 MACR+MVK concentration increases during the night like most of the anthropogenic VOCs in this study. As discussed in the main article, this is probably due to wind regimes during this period (low wind speed that favor the accumulation of pollutants). The increase in concentration of MACR+MVK also suggest an anthropogenic origin. While the signals of m/z 71 are commonly attributed to the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) which are both oxidation products of isoprene under high-NO conditions, more recent GC- PTR-MS studies identified some potential interferences for MVK and MACR measurements, including crotonaldehyde in biomass-burning emissions, C5 alkenes, and C5 or higher alkanes in urban regions (Yuan et al., 2018). Such interferences cannot be ruled out here. This discussion has been added into the main paper.

11. Lines 394-395: If furans contribute to isoprene signal (m/z 69) then this is an interference of another/different compound to this m/z. It is not an anthropogenic origin of isoprene. Please correct the corresponding sentence.

Thera et al.: the sentences has been changed in lines 431: *[…]Provided some interferences like furans do not contribute to isoprene signal by PTRMS measurements (Yuan et al.. 2017). this would suggest an anthropogenic origin for isoprene. During period 1 and 3. MACR+MVK also show high concentrations at night during period 2 like other alkanes and aromatics. suggesting their potential anthropogenic influence. During periods 1 and 3 (marine influence). MACR+MVK concentrations follow the same general pattern as of isoprene's[…]*

12. Lines 400-402: What does it mean a secondary source? Maybe you want to replace it with origin? Please rephrase.

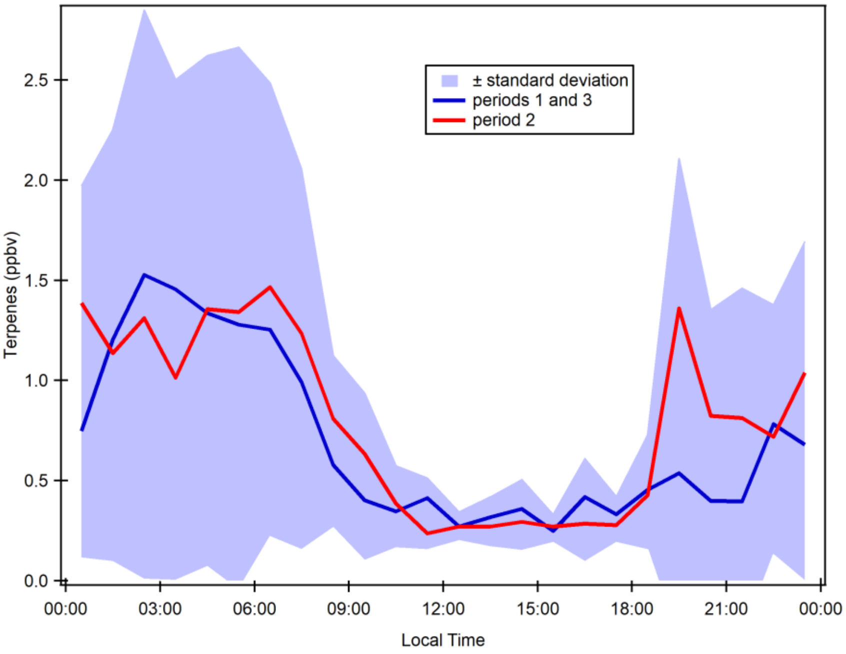
Thera et al.: By secondary source we wanted to express secondary origin. We rephrased by replacing source by origin in lines 438: "*The peak in the middle suggests the presence of a secondary origin*"

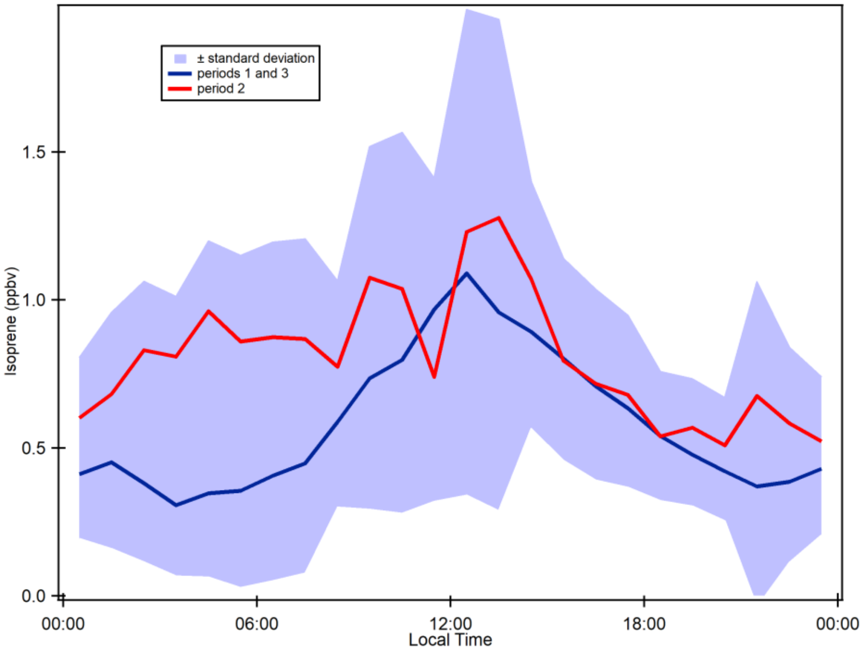
13. Lines 444-445: It is strange that isoprene has only 5% to the biogenic factor. This indicates that most of the signal in this m/z is probably attributed to other compounds rather than isoprene. Please discuss.

Thera et al.: isoprene and terpenes are known to be biogenic emitted compounds but their biogenic emissions are controlled by different environmental parameters: temperature for terpenes. light and temperature for isoprene (Fuentes et al.. 2000). This implies different diurnal variability of the resulted concentrations. Moreover both compounds show opposite diurnal trends which can also be explained by their different reactivity towards their major oxidants. This is developed in the text in lines 471-474: *[…] Moreover. the diurnal profile of these two compounds show opposite patterns as it can be seen in Figures 5 and 8 which indicates that their biogenic emissions are controlled by different environmental parameters: temperature for terpenes, light and temperature for isoprene (Fuentes et al.. 2000) […].*

The diurnal variability in terpenes in Istanbul with high concentrations at night and early morning and low concentrations during daytime is consistent with the ones already observed in forested or rural areas. This is further developed in the text in lines 480-482: *[…] This type of profile has already been observed at a background site in Cyprus (Debevec et al.. 2017). in a forest of Abies Boriqii-regis in the Agrafa Mountains of north western Greece (Harrison et al.. 2001) and at Castel Porziano near Rome. Italy (Kalabokas et al.. 1997).[…].*

Furthermore, diurnal variation of isoprene and terpenes (see figure below) show that isoprene behave like anthropogenic species which are characterized by a strong increase in concentration at night during period 2 compared to period 1 and 3. This suggests a potential anthropogenic origin for isoprene contrary to terpenes whose variability is poorly affected during period 2.





14. Lines 481. Again. Are you sure it is isoprene?

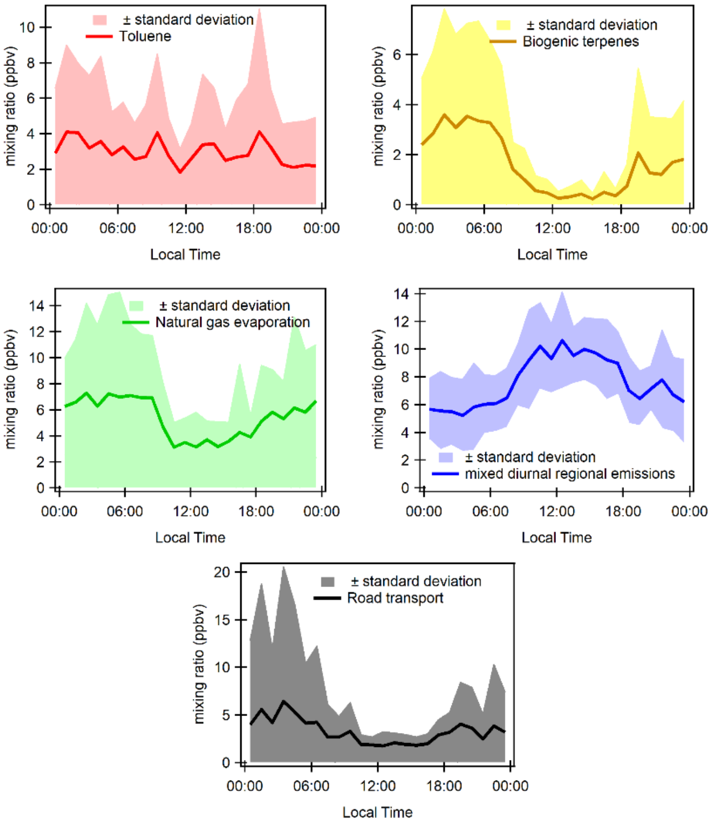
Thera et al.: Yes, it is isoprene. M/z 69 in PTRMS has some interferences like furans but the good correlations between m/z 69 and temperature suggests that the contribution of anthropogenic compounds to m/z 69 can be neglected.

15. Lines 486-487: Could you give some examples of “primary biogenic hydrocarbons”?

Thera et al.: Some examples of primary biogenic hydrocarbons are: monoterpenes and isoprene. This section was not clear and it has been modified for more clarity in lines 513-517: *[…]The factor 4 is also characterized by the presence of oxygenated compounds such as isoprene oxidation products like MACR+MVK (54 %) and acetaldehyde (66 %), acetone (57 %), methanol (59 %) and MEK (59 %,). These Oxygenated species can have primary sources (both anthropogenic and biogenic) and are also formed secondarily by the oxidation of primary hydrocarbons (Yáñez-Serrano et al., 2016; Millet et al., 2010; Goldstein and Schade, 2000; Singh, 2004; Schade et al., 2011) […]*

16. Line 497: No. the diurnal profile of the Factor 4 has the opposite behavior according to Fig 8. Please correct the text.

Thera et al. : The text is correct but the graph wasn't. The graph has been changed by taking individual contributions of the factors instead of the cumulated contributions of factors which alterated some of the prior results. The new graph has been reported below:



Technical comments:

Thera et al.: All the technical comments has been taken into account.

Reviewer 2

Main comment

The last two sections of the papers (3.3 and 3.4) are rather short but they are potentially important as they compare the results of this study with emission inventories data. Nevertheless, Currently the way the emission ratio is calculated and compared is not convincing at all. The authors say that they can not use the "linear fit regression" method in order to derive emission ratio because there is a poor correlation between targets VOC and CO. They use then the median value of each VOC to CO during all the observation period to estimate an emission ratio (before to compare it to other cities and then to emission inventories). In absence of any correlation between VOC and CO. I do not see how a ratio of median VOC/CO could be used to estimate an emission ratio: : :from what is representative this emission ratio? From all sources for the whole city? Indeed, as the whole dataset is used.,this means that all sources are mixed; and among them traffic contributes only 15%; so how can you compare your ratio to traffic emissions from inventories? As these 2 sections are based on this emission ratio calculation. so either this one is better justified and its representativity (and limitation) is discussed. or these sections have to be removed. We note also that there is no discussion about the fact that VOCs in the inventory stand for "all VOCs" whereas only a limited number of VOC were measured...

Thera et al.: Determining an emission ratio from the slope of a least square linear regression fit is meaningful when VOC and CO correlate which is not the case here as shown by the diurnal profiles and PMF results. The reason is that compounds do not come from the same sources. Indeed, it has been shown by the PMF that traffic was minor. Therefore we propose to calculate the individual ratios between VOCs and CO substracted from their background levels and to derive a statistic representive of this. Deriving a meaningful statistic is not trivial because of the great variability of the individual calculated ratios. At first sight we decided to use the median but the median is not representative of the extreme values that can be found in the ratio especially at night and during period 2. Therefore in this revised version we propose to work on an average emission ratio. From these values we will estimate VOC emissions and an associated standard deviation providing a range of VOC emissions rather than a single value. The contribution of the traffic does not have any impact on the emissions ratio calculation method. We used the following formula to estimate emissions:

$$\mathrm{VOC}_{\mathrm{estimated}} = \mathrm{ratio}\left(\frac{\mathrm{VOC}}{\mathrm{CO}}\right)_{\substack{\text{all observations}\\ \mathit{PMF\ Road\ transport\ factor}}} \mathrm{X}\ \mathrm{CO}_{\mathrm{inventory}}$$

For the traffic emission estimation, the VOC/CO was either individual VOC or a sum of VOC present in the family of VOC (like pentanes and xylenes) in PMF road traffic factor. CO inventory is the emission of CO for traffic in the inventories. According to the inventory either ACCMIP or EDGAR, a road transport emission was estimated and compared to the one obtained in the corresponding inventory either by species or by family. For more accurate results we could not use the sum of the traffic emissions of all VOCs but only individual or a family of species. The emission ratios and evaluation and global inventories section has been improved and the limitations has been discussed as suggested in lines 597-674:

3.4 Emission ratios of VOC/CO

The determination of emission ratios (ER) is a useful constraint to evaluate emission inventories (Warneke et al., 2007; Borbon et al., 2013). The emission ratio is the ratio of a selected VOC with a reference compound that does not undergo photochemical processing mostly CO or acetylene due to their low reactivity at urban scale and as tracers of incomplete combustion (Borbon et al., 2013; Salameh et al., 2017). The linear regression fit method (LRF) is a commonly used method to calculate emission ratios: the ER corresponds to the slope of the scatter plot between a given VOC vs CO or acetylene (Borbon et al., 2013; Salameh et al., 2017). Another method is the photochemical age method (de Gouw, 2005; de Gouw et al., 2018; Warneke et al., 2007; Borbon et al., 2013) which is based on the concentration ratios and the photochemical age. In this study, poor correlation between targets VOC and CO is found ($R^2 \leq 0.16$) as could be deduced from the time series analysis (see section 3.2.2) and the PMF analysis. Indeed, fossil fuel combustion derived activities are not dominating the VOC distribution. As a consequence the LRF method cannot be applied. Here the emission ratio was determined by the mean value of each Δ(VOC)-to-Δ(CO) concentration ratio over the whole period of measurements. The terms "Δ(VOC)" and "Δ(CO)" correspond to the measured concentrations of VOC and CO subtracted by VOC and CO background concentrations respectively. Given the diurnal and data day-to-day variability of dynamics (see section 3.3.2), one daytime and nighttime CO background values were estimated for each day by extracting the daytime and nighttime minimum concentration values. For CO, the daytime background values range between 213.5 and 367.2 ppb and the nighttime background values range between 211.5 and 406.7 ppb. For VOC, the background values depend on the compound. At night, the background values lie between 1.3 and 3.4 ppb for a long-lived compound like acetone and between 0.2 and 1.1 for a short-lived compound like (m+p)-xylenes. For the following discussion, we will refer to VOC-to-CO ratio instead of "Δ(VOC)-to-Δ(CO)" ratio.

Photochemistry can affect the value of emission ratios (Borbon et al., 2013). Comparing daytime to nighttime ratios is one way to evaluate the effect of daytime photochemistry by assuming that chemistry can be neglected at night except for alkenes (de Gouw et al., 2018) and the composition of emissions does not change between day and night. While the ratio between nighttime emission ratios and daytime emission ratios shows a decrease of 37% on average during the day, this decrease is not dependent on the OH kinetic constants of each VOC (Figure S9). This suggest that these differences are rather controlled by the changes in emission composition between day and night. As a consequence, the emission ratios have been determined on the whole dataset.

The emission ratios VOC-to-CO in Istanbul are displayed in Table 3 and compared to the ones in other urban areas worldwide. The emission ratios determined in Istanbul are usually higher than the ones of other cities but in the same range of magnitude. C4-C5 alkanes, toluene and oxygenated VOCs show the highest emission ratio values. Most of the values are consistent within a factor of 2 with, at least, one determined in other cities of post-industrialized or developing countries.

3.5 Evaluation of global emission inventories

In this section, the VOC emissions from anthropogenic sources and road transport source by three references global emission inventories downscaled to Istanbul are evaluated: MACCity (Granier et al.. 2011) for 2014, EDGAR (Crippa et al.. 2018) for 2012, and ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project) (Lamarque et al.. 2010) for 2000 (figure 11.a,b and c). Emission data for ACCMIP and MACCity inventories are available in the ECCAD database (http://eccad.aeris-data.fr/), and the one for EDGAR inventory is available in the EDGAR database (http://edgar.jrc.ec.europa.eu/). This evaluation is based on the VOC-to-CO emissions ratios calculated in the previous section (3.4) following Salameh et al. (2016):

$$VOC_{estimated} = ratio\left(\frac{VOC}{CO}\right)_{\substack{all\ observations \\ PMF\ Road\ transport\ factor}} X\ CO_{inventory} \qquad (4)$$

Where:

- VOC estimated is the estimated emission for an individual VOC or a group of VOC in tons/year for all anthropogenic emissions or road transport emissions.

- CO inventory is the extracted emission of CO from either ACCMIP (in Tg/year), MACCity (in Tg/year), or EDGAR (in tons/year).

- VOC/CO is either the VOC-to-CO ratio calculated in section 3.4 or the VOC-to-CO ratio determined from each VOC contribution in the PMF road transport factor (in µg.m^{-3} of VOC/µg.m^{-3} of CO).

Species in emission inventories are sometimes lumped (grouped) as a function of their reactivity for chemical modeling purpose and species label does not always correspond to a single species. For instance, methanol in Edgar not only corresponds to methanol itself but all alcohols. Moreover, summing some species from observations is sometimes needed to fit with the inventory lumping like alkanes higher than C4 in MACCITY but is limited to the number of the measured species. As a consequence, the comparison is not direct and requires special care (see the following discussion).

The annual VOC and CO emissions for EDGAR (0.1 x 0.1 resolution) was determined by summing the emissions of 12 grids over a domain encompassing the sampling site (longitude between 28.9 and 29.1°; latitude between 40.9 and 41.2°). For ACCMIP and MACCITY, the emissions values for the city of Istanbul was taken as available in the ECCAD database.

Further information about the emissions inventory will be found in Table S10 of the supplement material.

Figure 11 shows the comparison of the estimated emissions of some speciated VOCs derived from observations and PMF for the road transport and the ones from the three global emission inventories downscaled to Istanbul megacity.

The total annual VOC anthropogenic emissions by global inventories are usually either within the same range by a factor of two to three for alkanes and aromatics or underestimated by an order of magnitude, especially for oxygenated compounds up to a factor of 58 for acetone by Edgar. These results are consistent with previous evaluations carried out in the Middle East (Salameh et al., 2016) and for northern mid latitude urban areas (Borbon et al., 2013). One exception is methanol in Edgar which is 2.2 times higher than our estimations from observations. This might be due to the inclusion of other alcohols in the methanol label in Edgar as discussed above. One should note that the emissions of CO and VOCs from MACCITY are usually lower than the ones from ACCMIP and EDGAR which can be explained by the different year of reference. The global emissions by inventories were not within the same year: 2000 for ACCMIP, 2014 for MACCITY and 2012 for Edgar. The CO emissions by inventories were compared for the same year. It was found that ACCMIP and MACCITY had the same CO emissions while the emissions in Edgar were two times lower than those from MACCITY and ACCMIP. In 2012, emissions of CO by Edgar was similar to the ones of MACCITY.

The evaluation of the road transport emissions (Figure 11.d) is limited to the compounds from the unburned fuel fraction; while there is still an underestimation by the emission inventories except for benzene, the differences are lower than for all anthropogenic emissions. The differences never exceed a factor of 12.1 (pentanes). Again, the differences for pentanes should be seen as a lower limit because of the number of measured pentanes which are limited to n-pentane and isopentane.

While these results provide a first detailed evaluation of VOC annual emissions by global emission inventories, they are based on a limited period of observations in September 2014 (2 weeks). Additional VOC observations at different periods of the year including the heating and non-heating period will be very useful to strengthen this first evaluation by taking into account the seasonal variability of emissions. However, they confirm the urgent need in updating global emission inventories by taking into account regional specific emissions.

Specific comments:

-L64: Is the given standard deviation calculated between both calibrations or does it include the 5-ppb control points? How were the calibration coefficients applied to the data? An average value was used or an interpolated one? How was the blank value subtracted? An average value was used or an interpolated one? Please clarify all these points.

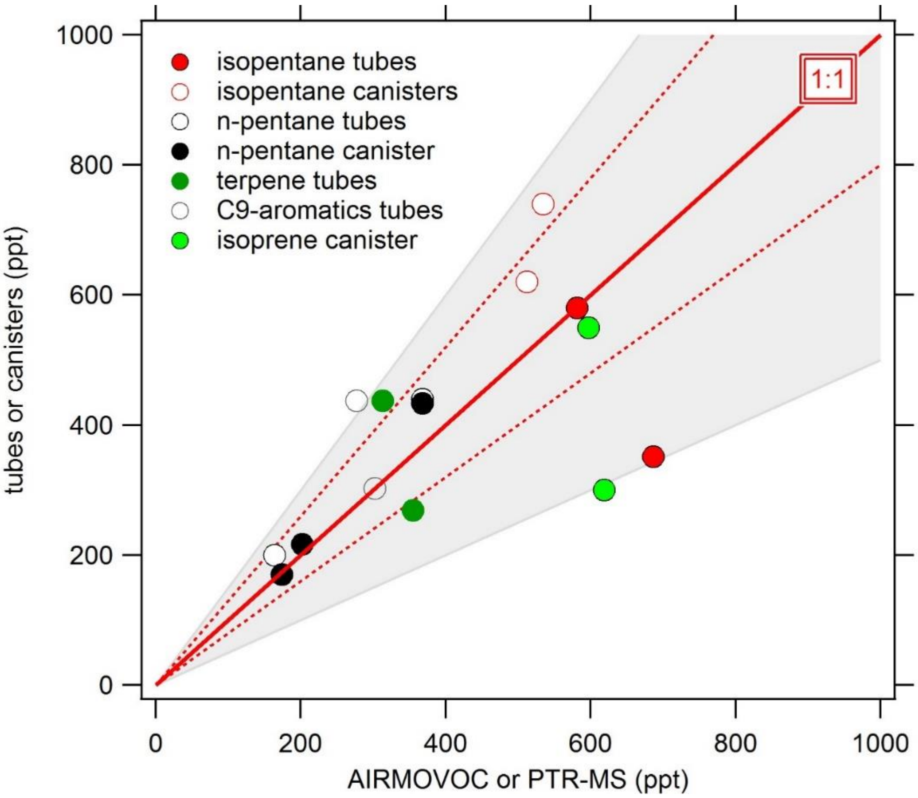
Thera et al.: the standard deviation includes the 5-ppb control points and the multi-point values. We clarify all the above mentioned issues in the text in lines 161-165: *[…]The mean calibration factor for all major VOC are derived from the slope of the mixing ratios of the diluted standards with respect to product ion signal normalized to H_3O+ and H_3O+H_2O. Calibration factors ranged from 2.54 (m/z 137) to 19.0 (m/z 59) normalized counts per seconds per ppbv (ncps.ppbv^{-1}). Linearly interpolated normalized background signals are substracted to the normalized signal before applying the calibration factor to determine ambient mixing ratios […]*

-L188: I agree with the author that the variability is highly consistent for aromatics between both techniques. Nevertheless. they claim that the difference in concentrations do not exceed 20%. although the slope for toluene is 22%. In addition, we note that for benzene. there is an underestimation of about 20% of the PTRMS compared to the GC; whereas for toluene. it is the contrary (overestimation by the PTRMS). How do you explain this feature? As ethyl benzene is known to fragment on the mass of benzene. I guess we would rather expect the contrary (i.e. an overestimation of benzene on the PTRMS). Moreover. there seems to exist an even higher difference between the sorbent tube and the GC. As the ratio toluene/benzene is later on used in the paper to comment on source origins. a more careful analysis on the uncertainty associated to this ratio. due to the differences which are pointed out by the intercomparison should be made (as the ratio could be over-estimated).

Thera et al.: The variability between PTRMS and AIRMOVOC is highly consistent ($r > 0.85$) and the differences in concentrations do not exceed ±22 %. It should be noted that both instruments are calibrated with the NPL and GCU standards respectively. The observed differences takes into account potential differences in calibration factors at least for 10%.

-L190: where is the graph showing the comparison for isoprene?

Thera et al.: the graph showing the comparison for isoprene has been added in the figure S3 of the supplement material and reported below.



-L228: How was calculated the 30-min data? Did it take into account the sampling time of the GC? If not. could it have an impact on the results as there was a high degree of variability of the compounds?

Thera et al.: The 30 minutes was calculated by taking into account the 20 minutes sampling times of the GCFID.

-L244 : With missing values higher than 40% and the use of median values instead of missing data. one can wonder about the meaningfulness of using such compounds? The authors could refer to their sensitivity tests to justify this point.

Thera et al.: As shown in the sensitivity test section, even by removing data with a percentage of missing values above 30%, the PMF results are not changed.

-L251: Even if all details are given in the SM. please give in the main text the values used as input for uncertainties (at least the range)

Thera et al.: The ranges of the input uncertainties has been added in the text in lines 248-249: *[…]The uncertainty of the PTRMS ranges between 5 % (toluene) and 59 % (acetaldehyde) of the concentrations while the uncertainty for the GC-FID ranges between 4 % (2-methyl-pentane) and 17 % (o-xylene) of the concentration[…]*

L265 to 269: I would suggest to move the part in the methodology section -Fig. S4 could be in the main text as it is discussed in details here

Thera et al.: The FLEXPART model description has been moved in the methodology section (section 2.5) in lines 287-293 and the Figure S4 (now Figure 2) has also been moved in the main text.

-L301: “terpens”: does it include isoprene?

Thera et al.: No. Terpenes does not include isoprene (C_5H_{10}) but $C_{10}C_{16}$ alkenes.

-L307: Give the references associate to the measurements in Paris. London and Beirut

Thera et al.: the references associate to the measurements in paris, London and Beirut have been added in the text in lines 332-333: *[…]Levels of alkanes, some alkenes and aromatics are compared to other European megacities: Paris and London (Borbon et al., 2018) at both urban and traffic site as well as at a suburban site in Beirut (Salameh et al., 2015) during summer[…]*

-L308: one general comment which could be made here is that despite different years and seasons. Istanbul is quite similar to other cities. except for toluene and xylens (and this could be later on reminded when analysing the sources to discuss which of the source(s) would explain these high values in Istanbul)

Thera et al.: this section has been rephrased by taking into account your suggestions in lines 335-339: *[…]Despite differences in absolute levels, the hydrocarbon 335 composition in Istanbul is quite similar to the other cities. Beirut has the highest concentrations of n-butane, isopentane and 2-methyl-pentane. Higher concentrations in toluene, (m+p)-xylenes were in Paris, Beirut and Istanbul. Such similarity would suggest that same sources control the hydrocarbon composition, especially traffic in all cities including Istanbul […]*

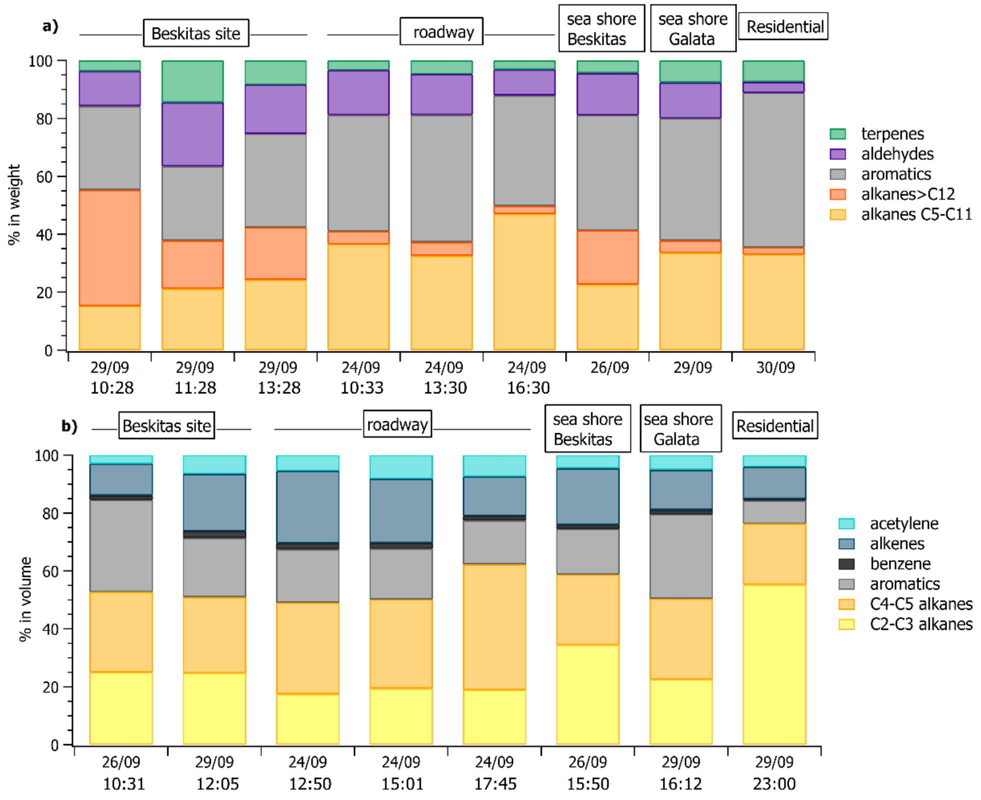
-L312: what element suggests the traffic influence? (“This would suggest: : :”)

Thera et al.: The similarity of the variability of hydrocarbon composition between different urban areas is the element that can suggest the traffic influence. This feature has been already observed in other cities worldwide. While the absolute levels are different the relative composition is almost the same. This implies that hydrocarbons are controlled by sources of same composition

-L314/Table S6: Why presenting a table of mean concentration which have been measured in different sites (and date/time). It would be more interesting to present a value (or a mean +/-std value) for a given time for each site for some compounds, this would allow a comparison with the main site.

Thera et al.: Table S6 is meant to give an overall view of the concentrations of species measured by tubes and canisters that were not measured by the GCFID nor the PTRMS. Furthermore, lines 346-358 discussed already the relative composition divided into major VOC chemical groups at each sites by sorbent tubes and canisters at different location and date : *[…]The relative composition divided into major VOC chemical groups at each sites by sorbent tubes and canisters is reported on Figure 4a and 4b, respectively. The composition is variable across the megacity for the aliphatic fraction of high and intermediate volatility hydrocarbons (C2-C16). As expected, the composition of the 29/09 12:05 sample at the Besiktas site is like the ones derived from the roadway side measurements highlighting the influence of road transport emissions at the supersite. Interestingly, the VOC composition of the three samples from sorbent tubes at the Besiktas site are different from the ones at the roadway side with a higher proportion of IVOC. The VOC composition of the 26/09 10:31 sample by canister is rather similar to the one from the seashore sample in Galata (29/09 16:12 sample). In the same way the VOC composition of the samples at the supersite derived from tubes are rather like the Besiktas seashore one. For both of them, the proportion of IVOC is significant (from 15 % to 40 % in weight). While light VOC are expected to be of minor importance when considering ship emissions, the higher presence of heavier organics is however expected as observed for alkanes by Xiao et al. (2018) in ship exhaust at berth. The VOC composition comparison would thus suggest not only the impact of road traffic emissions on their composition but also the potential impact of local ship traffic emissions. Finally the composition at Besiktas is not affected by Residential emissions which are enriched in light C2-C3 alkanes (canisters) or aromatics (canisters[…]*

The figure below is the corresponding graph of the text.



-L331: The section 3.2.2. could be re-arranged. in order to directly introduce the discussion on diurnal variations. In the current version. the overall variability is discussed and then the diurnal variation is discussed but this leads to some confusions (for example, L338 diurnal cycles of NOx and CO are discussed, although the figures of the diurnal cycles of are not yet properly introduced) and several repetitions (for example, the vegetation type in Istanbul: : :).

Thera et al.: this section has been rearranged in lines 360-441: *[…]The variability of VOC concentrations is driven by several factors: emissions (anthropogenic or biogenic), photochemical reactions (especially with the OH radical during the day and ozone and nitrates at night for alkenes) and the dynamic of the atmosphere (including dilution due to the height of the boundary layer) (Filella and Peñuelas, 2006). The time series of inorganic trace gases (NOx and CO) and some VOC representing the diversity of sources and reactivity are reported in Figure 5. The meteorological periods 1, 2 and 3 described in the previous section 3.1 are also indicated. Because NOx at the super site were only measured from 09/25 to 09/30, data from the air quality station in Besiktas were used (see Figure 1). One should note that the time series of NOx at the supersite and at the Besiktas station are consistent.*

Time series of NOx and CO show high concentrations but a different pattern regardless of the origin of air masses. While a daily cycle of NOx is depicted, CO does not show any clear pattern. The NO2/NOx ratio fluctuates between 0.34 to 0.93 with an average and median value of 0.53 and 0.55, respectively. These values are very high compared to what is usually found in the literature (Grice et al., 2009; Kousoulidou et al., 2008; Keuken et al., 2012) which are mostly low and below 0.50. However higher values of NO2/NOx ratio can be found in diesel passenger cars (Grice et al., 2009. Vestreng et al., 2009) and vans (Kousoulidou et al., 2008). This ratio would reflect the impact of the combustion of heavy fuels in the megacity. After road transport, cargo shipping is a second highest contributor to NOx levels according to the local/regional inventory (Markakis et al., 2012).

Anthropogenic VOC time series (benzene, isopentane and isobutane) exhibit a high frequency variability but usually show higher concentrations during the night especially during period 2. One cause are the very low wind speeds at night especially during period 2 (Figure 3), which would reinforce the accumulation of pollutants. Under marine influence (periods 1 and 3), VOC concentrations are the lowest, especially during period 3, which is characterized by rainy days (September 27th and 28th), high wind speed and colder temperatures (Figure 5). These conditions favor atmospheric dispersion. During transition periods and under continental influence (period 2), VOC concentrations exhibit a strong day-by-day variability with episodic nocturnal peaks especially on September 25th and 26th. While these peaks are not always concomitant between VOC and are not associated with any increase in NOx and CO levels, they occur under south and southwestern wind regimes which are unusual wind regimes according to Figure 1. This points out the potential influence of industrial and port activities other than fossil fuel combustion. For instance, maximum concentrations of butanes occurred during the period of the marine-continental regime shift with well-established southwestern wind regime on 09/22, 09/23 and on 09/26 at the end of the day. Maximum concentrations of pentanes occurred during the night of 09/26 to 09/27 like for aromatics (e.g. benzene) (Figure 5).

Except during transition periods, the background levels of measured trace gases are not affected by the origin of air masses. This strongly suggests that the pollutants measured during TRANSEMED-Istanbul were from local and regional sources. Finally, time series would suggest the influence of multiple local and regional sources other than traffic on VOC concentrations, likely industrial and/or port activities, at the supersite.

Isoprene and its oxidation products (MACR+MVK) covariate most of the time. They usually show their typical diurnal profiles with higher concentrations during the warmest days and at midday due to biogenic emission processes. Their significant correlation with temperature (R = 0.7) implies the emission from biogenic sources. Around the Besiktas site, 49.5 % of the vegetation is occupied by hardwood and hardwood mix trees while only 6 % is occupied by softwood and hardwood mix trees. While Quercus (isoprene emitter) only occupies 7.7 % of the total vegetation coverage (personal communication from Ministry of Forestry), the presence if isoprene at the supersite is probably due to the surrounding trees.

Except during transition periods, the background levels of measured trace gases are not affected by the origin of air masses. The background levels stay constant under continental or marine influence and regardless of the atmospheric lifetime of the species. This strongly suggests that the pollutants measured during TRANSEMED-Istanbul were from local and regional sources. Finally, time series would suggest the influence of multiple local and regional sources other than traffic on VOC concentrations, likely industrial and/or port activities, at the supersite.

Taking into consideration time series variability, diurnal variations have been splitted into periods 1 and 3 and period 2 for selected VOC as well as two combustion derived trace gases (NOx and CO). Diurnal profiles of atmospheric concentrations are reported in Figure 6. Local traffic counts for road transport (personal communication from Istanbul Municipality for fall 2014) and ship (https://www.marinetraffic.com/en/ais/details/ports/724/Turkey_port:ISTANBUL) are also reported in Figure S6 in the supplement material. Maritime traffic is mostly for passenger shipping (58.02%) against 16% for cargo shipping. The diurnal profiles of ship and road traffic counts are similar.

Generally, concentrations during period 2 are higher than the ones during periods 1 and 3 and show different diurnal patterns for some compounds. The profile of NOx is consistent with the one of traffic counts (Figure S6 of the supplement material). NOx exhibits higher concentrations during the day and lower concentrations at night for both periods with a morning peak (7:30-8:30) and one early evening peak from 17:30 (Figure 6.a). This is typical of traffic emitted compounds with morning and evening rush-hour peaks as observed in many other urban areas like Paris, France in Europe (Baudic et al., 2016) or Beirut, Lebanon in Eastern Mediterranean (Salameh et al., 2016). As already depicted in time series, CO diurnal profile is different from the one of NOx. CO concentrations show higher concentrations in the late evening and lower concentrations during the day. During the day, CO is also characterized by a double peak: one in the morning (8:30) and the other one in the middle of the day (Figure 6.b). Both NOx and CO show quite similar diurnal profile between the three periods even if morning concentrations tend to be higher.

VOCs show different profiles from the one of NOx. Under marine influence (periods 1 and 3), primary anthropogenic VOC (ie. benzene, alkanes and other aromatics) almost exhibit a constant profile while they show higher concentration from midnight until 10:00 AM under continental influence (period 2), For instance, benzene (Figure 6.d) and isopentane (Figure 6.f) nighttime concentrations increase by four-fold compared to the levels under marine influence. In the middle of the day, the concentration levels are the same as during periods 1 and 3. The profiles of primary anthropogenic VOCs point out the complex interaction between local and regional emissions and dynamics. Period 2 points out the influence of VOC emissions other than traffic and combustion processes (no effect on NOx and CO) at night. While the influence of traffic emissions on CO and VOC cannot be excluded; it seems that their emission level is not high enough to counteract the dispersion effect during the day unlike NOx. This will be further investigated in the PMF analysis.

Isoprene concentrations increase immediately at sunrise and decrease at sunset during period 1 and 3 (marine influence) which indicates its well-known biogenic origin (Figure 6.g) which is light and temperature dependent. Isoprene and MACR+MVK's concentrations increase at night during period 2 like other alkanes and aromatics, suggesting their potential anthropogenic influence.

Provided some interferences like furans could contribute to isoprene signal by PTRMS measurements (Yuan et al., 2017), this would suggest an anthropogenic origin for isoprene. While the signals of m/z 71 are commonly attributed to the sum of MVK and MACR which are both oxidation products of isoprene under high-NO conditions, more recent GC-PTR-MS studies identified some potential interferences for MVK and MACR measurements, including crotonaldehyde in biomass-burning emissions, C5 alkenes, and C5 or higher alkanes in urban regions (Yuan et al., 2018). Such interferences cannot be ruled out here. During periods 1 and 3, MACR+MVK concentrations follow the same general pattern as of isoprene's.

With relatively long atmospheric lifetime, (≈ 68 days), acetone's concentration is quite constant throughout the day within period 1, a peak in the middle of the day and lower concentrations during the night for period 2 (Figure 6.c). The peak in the middle suggests the presence of a secondary origin. Acetone can have both primary and secondary source (Goldstein and Schade, 2000; Macdonald and Fall, 1993). Methanol and MEK have the same general pattern as for acetone during both periods without the peak in the middle of the day suggesting that they might have the same emission source[…].

-L338 and the corresponding paragraph: The discussion of this section is not clear and might be improved, once the discussion includes as well the diurnal cycles (see previous comment). In addition the discussion focusses mainly on local meteorological conditions (wind. dispersion..) but no discussion is made on the possible influence of long-range transport. If not discussed at all, why studying Flexpart back-trajectories over such long periods?

Thera et al.: The discussion of this section has been improved more clarity in lines 360-441. The objective of studying Flexpart was to see air mass trajectory. The Time series of our species did not enabled us to the see long range transport since we couldn't distinguish long or local range transport.

-L338: At midday it is not a maximum. In addition, why a midday concentrations max is expected from traffic-related compounds, Usually a morning and an evening peak are observed

Thera et al.: this section has been corrected and rearranged in lines 409-413: *The profile of NOx is consistent with the one of traffic counts (Figure S6 of the supplement material). NOx exhibits higher concentrations during the day and lower concentrations at night for both periods with a morning peak 410 (7:30-8:30) and one early evening peak from 17:30 (Figure 6.a). This is typical of traffic emitted compounds with morning and evening rush-hour peaks as observed in many other urban areas like Paris, France in Europe (Baudic et al., 2016) or Beirut, Lebanon in Eastern Mediterranean (Salameh et al., 2016).*

-L341: Isoprene and its oxidation products co-variate most of the time. This is not true for period 2. Be more precise in your analysis and description.

Thera et al.: Precision has been made in this section in lines 391-392: *[…]Isoprene and its oxidation products (MACR+MVK) covariate most of the time. They usually show their typical diurnal profiles with higher concentrations during the warmest days and at midday due to biogenic emission processes[…].*

-L384 and Figure 5: there is a large peak of benzene. isopentane. isobutene. m71 during the night of event 2. How do you interpret it? Is it due to a single event or it was observed several times? It could be useful to show toluene on this figure (directly near to benzene)

Thera et al.: during period 2 large peaks are observed during several nights for many VOCs. It is probably due the wind regimes (low wind speed that will favor the accumulation of pollutants). Moreover they occur under south and southwestern wind regimes which correspond to unusual wind regimes according to Figure 1This points out the potential influence of industrial and portactivities other than fossil fuel combustion as detailed in the Time Series section in lines 375-377: *[…]Anthropogenic VOC time series show highest concentrations during the night especially during period 2. One cause are the very low wind speeds at night especially during period 2 (Figure 3), which would reinforce the accumulation of pollutants […]*

We did not show toluene directly near benzene because it will be difficult to show all the compounds and we also have a specific PMF factor for toluene in section 3.3 where its diurnal profile and time series are discussed.

-L406 to L418: I would suggest to move this part in the methodology section

Thera et al.: This section has been moved in the methodology section in lines 260-271: *[…]PMF reference run has been performed by removing the period during which there were no GC-FID data (night from 09/24 to 09/25). In addition, these data set have been chosen as PMF reference run because of the higher correlation between observed and reconstructed data by the PMF model (see also section 3.2). A good correlation (R2 = 0.97) between total reconstructed VOC and measured VOC was obtained. For most compounds the variability is well reproduced with an R2 usually higher than 0.70. Poorer correlation was found for alkenes (1-pentene (R2 = 0.55), 1,3-butadiene (R2 = 0.22) and isoprene (R2 = 0.57) as well as for n-hexane (R2 = 0.09), MEK (R2 = 0.41) and acetaldehyde (R2 = 0.32). Moreover, the R2 between the five factors does not exceed 0.28 and is usually less than 0.05 indicating the statistical independence of the five factors. The R2 of the contribution of the five factors between each other has been calculated, it was found that the value of R2 does not exceed 0.28. There is therefore no significant correlation between the factors which means that the factors are independent.*

The PMF output uncertainties were estimated by three models: the DISP model (base model displacement error estimation), the BS model (base model bootstrap error estimation) and the DISP+ BS model. Further information for the estimation of model prediction uncertainties can be found in Norris et al. (2014) and Paatero et al. (2014). The DISP results of the PMF run show that the 5-factor solution is stable and sufficiently robust to be used because no swaps occurred. All the factors were well reproduced through the BS technique at 100 % for factor 1, 96 % for factor 2, 100 % for factor 3, 99 % for the factor 4 and 100 % for factor 5; there were not any unmapped run. The DISP+BS model shows that the solution is well constrained and stable[…].

-L422: why naming a source after a compound and not only “solvent use”?

Thera et al.: We named the source after a compound and not only solvent use because even though toluene is the main compound in this factor (57 %), it also contribute up to 29 % to the road transport factor.

-L422: The recent study about VOCs from petrochemical sources in urban areas (Mac Donald et al;. Science. 2018) must be referenced somewhere when discussing about solvent use

Thera et al.: Mac Donald et al., (2018) has been referenced in the last section while discussing about the PMF results as a whole in lines 587-592: *[…]these differences in contributions with this study could be due to the differences in input data. Thus, PMF results depends strongly on input data. Furthermore, it was shown in McDonald et al. (2018) that source apportionment studies largely underestimated the influence of Volatile Chemical Species (including organic solvents, personal care products, adhesives …) as source of urban VOC. This underestimation could be explained by the fact that VOC are not measured in all their diversity in source apportionment studies in contrast with what was done in McDonald et al., (2018) […].*

-L432: The sentence “low T/B ratio indicates the influence of traffic emissions on measured VOCs: : :..” could be mis-leading and should be checked /re-formulated (see for example Gaeggeler et al.. 2008 which says the opposite: “Another indicator for traffic emissions is a low benzene/toluene ratio (Stemmler et al.. 2002)”. In addition, the uncertainty of the T/B ratio should be reminded here (see comment L188). Therefore, this section should be either removed or discussed more thoroughly.

Thera et al.: Low B/T (0.38) in Stemmler et al. (2002) correspond to our low T/B ([2-3]). Indeed as you said the sentence could be misleading. The section has been rephrased with more clarification and uncertainties of T/B prior to the GCFID and PTRMS have been added in lines 458-469: *Toluene/benzene ratio (T/B) is used as an indicator of non-traffic source influence (Elbir et al., 2007; Lee et al., 2002; Yurdakul et al.,2013). T/B ratio ≤ 2-3 indicates the influence of traffic emissions on measured VOC concentrations (Gelencsér et al.,1997; Heeb et al., 2000; Muezzinoglu et al., 2001; Brocco et al., 1997) whereas T/B ratios ≥ 2-3 suggests the influence of other sources than traffic (such as solvent evaporation or industrial sources). The T/B ratio for this study is between 0.4 (with only 4 points below 2) and 48.6 (Only 1 point above 29). Only 5.8 % of the ratios were between 2 and 3, 48 % were between 3 and 6 while 45 % were above 6 with 34 % between 6 and 10. This strongly suggests the influence of sources of toluene other than traffic. High value of T/B ratio is mostly found at industrial sites (Pekey and Hande, 2011). The median and mean value of T/B in this experiment are respectively 5.6 and 6.7 which can also indicate gasoline related emissions (Batterman et al., 2006). However the absence of other unburned fuel compounds like pentanes excludes this source. These ratios were calculated with toluene and benzene measured by the PTRMS since the PMF run was done by those data. By looking at the T/B ratio measured by the GCFID, we found approximatively the same conclusion: Only 1 % of the ratios were between 2 and 3, 47 % were between 3 and 6 while 51 % were above 6 with 38 % between 6 and 10. This factor represents 14.2 % of the total contribution.*

-L477: could this factor represents the "regional background"? If so. the discussion could be shortened. as there is no specific source associated and therefore no need to detail all biogenic/anthropogenic. primary/secondary source. That would avoid some vague statement. For example. L486 "these species are formed by the oxidation of primary biogenic hydrocarbons. However these oxygenated can have also primary both anthropogenic and biogenic sources". And the mention of 1.3-butadiene and 1-pentene being emitted by plants is not so convincing in such a highly populated city.

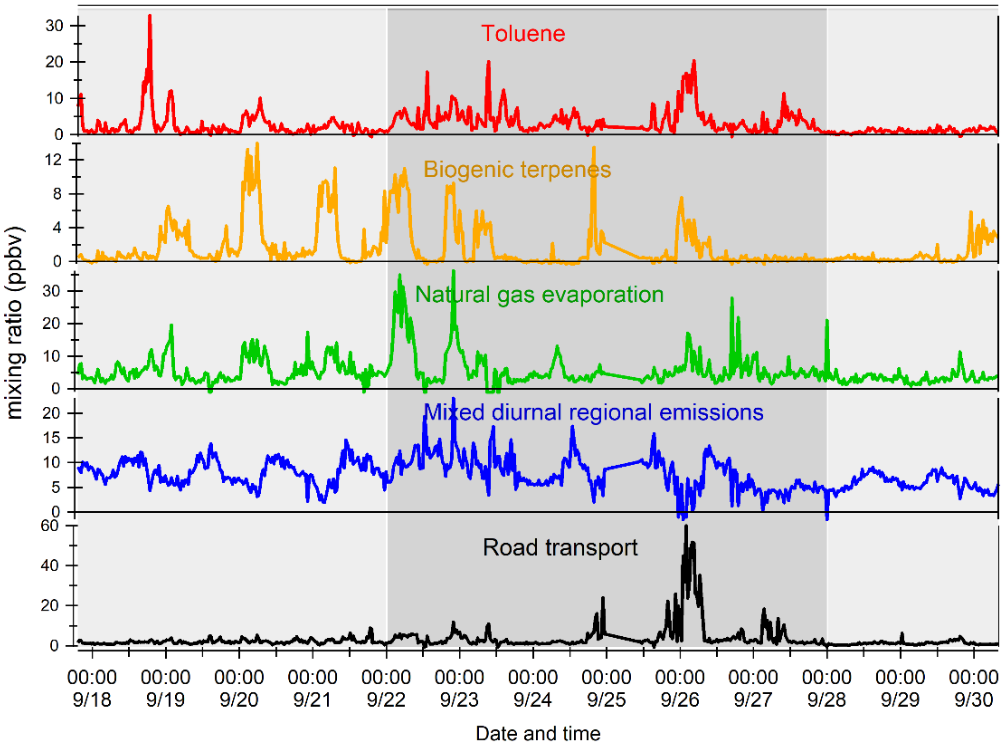
Thera et al.: Since this factor has a large contribution of isoprene which is reactive (lifetime less than 2 hours), it cannot be assigned to a "regional background" factor. To name a factor after regional background there must only be species with long lifetime so, which low reactivity; which is not the case in our study : we have a mixed of species of low and high reactivity see Baudic et al. (2016) and of different primary and secondary. Moreover one would expect this background to increase during period 2 (continental influence) which is not the case except during the first transition period.

-L480: the sensitivity study should be mentioned here (otherwise the 70% missing value would lead to the comment that this compound should not be taken into account).

Thera et al.: The sentitivity study has been moved to the methodology section in section 2.4.5.

L517: it is difficult to see on the figure that a strong increase in minimum concentrations is observed during period 2

Thera et al.: Strong has been removed and replaced by "an increase in minimum concentration" and the graph has been changed from cumulative contribution of factors time series by simple contributions of factors. The graph is reported below and has also been changed in the article.



-L549: This sentence is too vague; how has it been analyzed? Either remove or give a bit more information on this point.

Thera et al.: More information has been added in this section in lines581-583: *[…]As it was discussed in Yuan et al., (2012), the effect of photochemistry on factors composition had been analyzed by looking at the scatterplots of the contribution of the PMF factors to each VOC as a function of its OH rate constant (k_OH). Nevertheless, no clear evidence from photochemistry was founded on the Istanbul PMF factor's contributions. […]*

-L551: This section on sensitivity tests is important and is convincing to show that the most appropriate run has been selected. As these results are needed before. I'm wondering if it would not be more appropriate to move it at the beginning of the PMF results section (or even in the methodology part). The second part of the section (starting from L560) does not really belong to a section called "sensitivity tests" and it is not clear what it brings to the discussion. Therefore. It is suggested either to remove it or to discuss it in more details (probably in another section then).

Thera et al.: The sensitivity tests section have been moved in the methodology section. The second part of the second has been deleted as you suggested.

-L551: Before to start a new section, it would be useful to have a section which comments the PMF results as a whole (for example. the contribution of the different sources compared to the other cities where levels and variability were compared: : :)

Thera et al.: A comparison of PMF factors between our study and some cities where levels and variabilities were compared has been made in lines 584-596*: […] This study show that PMF was able to extract easily some factors (like biogenic terpenes) than others (like diurnal regional factors). These results are consistent with other Turkish cities where other source than traffic (mostly industrial source) drive the VOC emissions (Yurdakul et al., 2013; Pekey and Hande, 2011; Civan et al., 2015; Dumanoglu et al., 2014). However, in the EMB, traffic related emissions are the most dominant source and accounted for 51 and 74 % in winter and summer respectively in Beirut, Lebanon (Salameh et al., 2016). Kaltsonoudis et al. (2016) also found that traffic and biogenic emissions were the dominant source of VOC during summer in Patras and Athens. In Paris, Baudic et al. (2016) found that 25 % of the total VOC contributions were related to traffic, 15 % to biogenic factor, 20 % to solvent use against 14.2 % and 23% to natural gas and background factor that the PMF has not able to dissociate. These differences in contributions with this study could be due to the differences in input data. Thus, PMF results depends strongly on input data. Furthermore, it was shown in McDonald et al. (2018) that source apportionment studies largely underestimated the influence of Volatile Chemical Species (including organic solvents, personal care products, adhesives …) as source of urban VOC. This underestimation could be explained by the fact that VOC are not measured in all their diversity in source apportionment studies in contrast with what was done in McDonald et al. (2018). […]*

Technical comments:

Thera et al. : All the technical comments has been taken into account.

Composition and variability of gaseous organic pollution in the port megacity of Istanbul: source attribution, emission ratios and inventory evaluation

Baye T.P. Thera[1], Pamela Dominutti[2], Fatma Öztürk[3], Thérèse Salameh[4], Stéphane Sauvage[4], Charbel Afif [5,6], Banu Çetin[6], Cécile Gaimoz[7], Melek Keleş[2], Stéphanie Evan[8], Agnès Borbon[1]

[1] Université Clermont Auvergne, CNRS, Laboratoire de Météorologie Physique (LaMP), F-63000 Clermont-Ferrand, France

[2]Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

[3]Environmental Engineering Department, Bolu Abant Izzet Baysal University (BAIBU), 14030, Bolu, Turkey.

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

[5]Emissions, Measurements, and Modeling of the Atmosphere (EMMA) Laboratory, GEP Unit, Centre for Analysis and Research, Faculty of Sciences, Saint Joseph University, Beirut, Lebanon.

[6]Environmental Engineering Department, Gebze Technical University (GTU), 41400, Gebze, Kocaeli, Turkey.

[7]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) Créteil, France.

[8]LACY, Ile de La Réunion.

Correspondence to: Baye T.P. Thera (baye_toulaye_pehan.thera@uca.fr) and Agnès Borbon (agnes.borbon@uca.fr).

Abstract

In the framework of the TRANSport Emissions and Mitigation in the East Mediterranean (TRANSEMED/ChArMEx) program; Volatile Organic Compound (VOC) measurements were performed for the first time in Istanbul (Turkey) at an urban site in September 2014. One commercial gas-chromatograph coupled to a flame ionization detector (GC-FID) and one proton transfer mass spectrometer (PTR-MS) were deployed. In addition, sorbent tubes and canisters were implemented within the megacity close to major emission sources. More than 70 species including non-methane hydrocarbons (NMHC), oxygenated VOCs (OVOC) and organic compounds of intermediate volatility (IVOC) have been quantified. Among these compounds, 23 anthropogenic and biogenic species were continuously collected at the urban site.

VOC concentrations show a great variability with maxima exceeding 10 ppb (i.e. n-butane, toluene, methanol, and acetaldehyde) and mean values between 0.1 (methacrolein+methylvinylketone) to 4.9 ppb (methanol). OVOC represent

43.9 % of the total VOC concentrations followed by alkanes (26.3 %), aromatic compounds (20.7 %), alkenes (4.8 %), terpenes 30 (3.4 %) and acetonitrile (0.8 %).

Five factors have been extracted from the Positive Matrix Factorization model (EPA/PMF 5.0) and have been compared to source profiles established by near-field measurements and other external variables (meteorological parameters, NOx, CO, SO_2…). Surprisingly, road transport is not the dominant source by only explaining 15.8 % of measured VOC concentrations contrary to the local emission inventory. Other factors are toluene from solvent use (14.2 %), biogenic terpenes (7.8 %), natural gas evaporation (25.9 %), composed of butanes, and a last factor characterized by mixed regional emissions and composed of most of the species (36.3 %). The PMF results point out the influence of industrial emissions while there is no clear evidence of the impact of ship emissions on the measured VOC distribution. For the latter additional measurements of organic compounds of lower volatility like IVOC would be helpful. The sensitivity of PMF results on input data (time resolution, meteorological period, peak episode, interpolation method) was tested. While some PMF run are statistically less performant than the reference run, sensitivity tests show that same factors (number and type) are found with slightly different factor contributions (up to 16 % of change).

Finally, the emission ratios (ER) of VOC relative to carbon monoxide (CO) were established. These ratios are usually higher than the ones of other cities worldwide but in the same range of magnitude. These ER and the road transport factor from PMF were used to estimate VOC emissions and to evaluate three downscaled global emissions inventories (EDGAR, ACCMIP and MACCity). It was found that the total annual VOC anthropogenic emissions by global inventories were either within the same range by a factor of two to three for alkanes and aromatics or underestimated by an order of magnitude, especially for oxygenated VOC.

1 Introduction

Clean air is a vital need for all living beings. However, air pollution continues to pose a significant threat to health worldwide (WHO, 2005; Nel, 2005; Batterman et al., 2014) air quality, climate change, ecosystems (crop yield loss, acidity of ecosystem) (Matson et al., 2002), and buildings corrosion (Primerano et al., 2000; Ferm et al., 2005; Varotsos et al., 2009). The World Health Organization (WHO) estimates that 4.2 million people die every year as a result of exposure to ambient (outdoor) air pollution and 3.8 million people from exposure to smoke from dirty cook stoves and fuels, and 91 % of the world's population lives in places where air quality exceeds WHO guidelines limits (WHO,2018).

Among the various types of air pollutants in the atmosphere, Volatile Organic Compounds (VOC) include hundreds of species grouped in different families (alkanes, alkenes, aromatics, alcohol, ketone, aldehydes …) and with lifetimes ranging from minutes to months. They can be released directly into the atmosphere by anthropogenic (vehicular exhausts, evaporation of gasoline, solvents use, natural gas emissions, industrial process) and natural sources (vegetation, ocean). Even though biogenic emissions of VOC are more important than anthropogenic emissions at a global scale (Finlayson-Pitts and Pitts 2000; Goldstein and Galbally 2007; Müller 1992), the latter are the most dominant in urban areas.

Once released into the atmosphere primary VOC undergo chemical transformations (oxidations) due mainly to the presence of OH radical during the day. This yields to the formation of secondary oxygenated VOC (Atkinson 2000; Goldstein and Galbally 2007), tropospheric ozone (Seinfeld and Pandis, 2016) and secondary organic aerosols (SOA) (Koppmann 2007; Hester and Harrison 1995; Fuzzi et al., 2006).

Some areas on the earth are more impacted by air pollution than others, which is the case in the Eastern Mediterranean Basin (EMB). This region is affected by both particulate and gaseous pollutants. The EMB undergoes environmental and anthropogenic pressures. Future decadal projections point to the EMB as a possible “hotspot” of poor air quality with a gradual and continual increase in temperature (Pozzer et al., 2012; Lelieveld et al., 2012). In this region, fast urbanization, high population density, industrial activities and on-road transport emissions, enhance the accumulation of anthropogenic emissions. Natural emissions and climatic conditions (i.e. intense solar radiations, rare precipitations, and poor ventilation) also favor the photochemical processes. Therefore, the characterization and quantification of present and future emissions in the EMB are crucial for the understanding and management of atmospheric pollution and climate change at local and regional scales.

In this context, the project TRANSEMED (TRANSport, Emissions and Mitigation in the East Mediterranean, (http://charmex.lsce.ipsl.fr/index.php/sister-projects/transemed.html) associated to the international project ChArMEx (Chemistry-Aerosol Mediterranean Experiment, http://charmex.lsce.ipsl.fr/) aims to assess the state of atmospheric pollution due to anthropogenic activities in the East Mediterranean basin urban areas. Up to now VOCs and their sources have been extensively characterized by implementing receptor oriented approaches in Beirut, Lebanon (Salameh et al., 2016) , in Athens and Patras, Greece (Kaltsonoudis et al., 2016) and in a background site in Cyprus (Debevec et al., 2017) . Field work and source-receptor analyses in Beirut (Salameh et al., 2014; Salameh et al., 2016) have provided the first observational constraints to evaluate local and regional emission inventories in the EMB. A large underestimation up to a factor of 10 by the emission inventories was found suggesting that anthropogenic VOC emissions could be much higher than expected in the EMB (Salameh et al., 2016).

The megacities of Istanbul (15 million inhabitants, this work) and Cairo are the next target urban areas. Istanbul has experienced rapid growth in urbanization and industrialization (Markakis et al., 2012). The region undergoes very dense industrial activities with approximatively 37 % of industrial activities from the textile, 30 % from metal, 21 % from chemical industry, 5 % from food and 7 % from the other industries (Markakis et al., 2012). Most of the experimental studies have focused on particulate matter (PM) and ozone in Istanbul in order to evaluate factors controlling their distribution. According to these studies, the major source of PM is of anthropogenic origin: refuse incineration, fossil fuel burning, traffic, mineral industries and marine salt (Koçak et al., 2011; Yatkin and Bayram, 2008). Markakis et al. (2012) determined that PM_{10} originates mainly from industrial sources while fine particles ($PM_{2.5}$) are as much emitted by industry and transport. The geographical location of Istanbul, (Black Sea in the North and the Marmara Sea in the South) produces surface heating differences leading to different meteorological conditions that play an important role in the transport of pollutants, especially of ozone (İm et al., 2008). Over the last two decades the only VOC measurements have been reported for other cities in Turkey by the use of off-line sampling and GC-FID or GC-MS (gas chromatography-mass spectrometry) analysis (Bozkurt et al., 2018; Yurdakul et al., 2013; 2018; Civan et al., 2015; Kuntasal, et al., 2013; Demir et al., 2011; Pekey and Hande, 2011; Elbir et al., 2007; Muezzinoglu et al., 2001).

More recently VOCs source apportionment have been performed in an urban sites in Izmir (Elbir et al., 2007), and Ankara (Yurdakul et al., 2013) and in industrialized areas in Kocaeli (Pekey and Hande, 2011) in Aliaga (Civan et al., 2015; Dumanoglu et al., 2014) on a VOC dataset usually including alkanes, alkenes and aromatic compounds. Except for Izmir, traffic was not the dominant source for urban VOC in any of these source apportionment studies and industrial emissions drive the VOC distribution. This is in contrast with what is usually found in mid latitudes cities as well as in Beirut where traffic exhaust and gasoline evaporation seem to dominate (Salameh et al., 2016).

The objective of this work is to analyze the VOC concentration levels at one season (September 2014), their variability and to apportion their emission sources in the megacity of Istanbul in order to evaluate emission inventories downscaled to the megacity. According to the local emission inventory by Markakis et al. (2012), the main emission sources of VOC in Istanbul would come from traffic (45%), solvent use (30%), waste treatment (20%) while less than 1% originates from industrial processes. Our methodology is based on the Positive Matrix Factorization model (PMF) which can be applied without prior knowledge of the source compositions. Moreover the model is constrained to non-negative species concentrations and source contribution. VOC source apportionment by PMF have been already successfully conducted in many urban areas: Los Angeles (Brown et al., 2007), Paris (Gaimoz et al., 2011; Baudic et al. 2016), Beirut in Lebanon (Salameh et al., 2016), Athens and Patras in Greece (Kaltsonoudis et al.,2016), Zurich, Switzerland (Lanz et al., 2008) in Taipei (Liao et al., 2017) and Taichung (Huang and Hsieh, 2019) in Taiwan. A large set of speciated VOC were continuously collected during a 2-week intensive field campaign in September 2014 at an urban site in Istanbul, along with ambient measurements at various locations in the megacity.

2 Methods

2.1 Domain and measuring sites

The megacity of Istanbul has a unique geographical location spanning on two continents, Europe and Asia (Anatolia) (Figure 1). Due to its location in a transitional zone, the city experiences Mediterranean, humid subtropical and oceanic climates with warm/dry summers and cold/wet winters. The Black Sea in the North and the Marmara Sea (Figure 1) in the South produce a heat gradient at the surface leading to meteorological conditions likely to play a major role in atmospheric pollution (İm et al., 2008). The wind roses observed during the campaign period are reported in Figure 1 and are typical of summertime conditions. They show that the wind direction is mainly North-East (NE).

The urban site (labelled as supersite in Figure 1) is located along the Barbaros Boulevard (Blvd) in the district of Besiktas in Istanbul, Turkey (41°02′33″N, 29°00′26″E) on the European shore of the Bosphorus strait. Barbaros Blvd is a high traffic density street, which is a major route between the city center (a.k.a. “Historical Peninsula”) and the Bosphorus Bridge that connects Asia and Europe. The Besiktas district is also expected to be impacted by the mixture of major anthropogenic emissions (Markakis et al., 2012). Note that the sampling site was 500 m away from the Besiktas Pier (Bsks-shore on Figure 1) and the Bosphorus Strait 4-km away from the Haydarpasa Port. Dense industrial areas like Ikitelli area are located in the southwestern part of the city 20-km away from Besiktas. Trace gases measurements including VOC were conducted at the supersite from September 14th to September 30th of 2014 (during the non-heating season). In parallel, punctual VOC sampling at four other locations have been performed to assess the spatial variability of VOC composition and to support the interpretation of PMF factors. Punctual sampling included one residential area in the district of Kagithane (Kag –09/29/2014 and 09/30/2014), one roadside site on the Barbaros Blvd (Bskts – 09/24/2014), two sea-shore sites at the Besiktas Pier (Bskts-shore 09/26/2014), and on the Galata Bridge (Gal-shore 09/29/2014). Local ferries that connect the European and Asian sides continuously travel to the Besiktas pier with few minutes parking time at berth. The Galata Bridge spans the Golden Horn in Istanbul with a roadway on its upper part. For data analysis the Greater Municipality of Istanbul provided air quality data (CO, NO_x and SO_2) from its operated Bskts site (Figure 1), and meteorological data were obtained from Turkish State Meteorological Office (wind speed, wind direction, temperature, relative humidity and ambient pressure) from its network (Sariyer and Florya stations on Figure 1).

2.2 VOC instrumentation

The on-line instrumentation for VOC at the supersite included an AIRMOVOC GC-FID (Gas Chromatograph Flame Ionisation Detector, Chromatotec®) and a high sensitivity PTR-MS (Proton Transfer Reaction Mass Spectrometer, Ionicon®) at 30-min and 5-min time resolution, respectively. Principle, performances and operation conditions of both instruments have been described elsewhere (Gaimoz et al., 2011; Borbon et al., 2013 ; Ait-Helal et al., 2014).

Ambient air sampling was performed at the height of 2 m a.g.l. Air was pulled through two independent 3-m Teflon lines (PFA, ¼" outside diameter) towards the instruments. During the TRANSEMED campaign, the GC-FID measured 15 VOC from C4 to C8 (alkanes, alkenes, aromatics). VOC-free zero air and a certified ppb level gaseous standard from NPL (National Physical Laboratory, UK) at 4 ppb ± 0.8 ppb were injected every three-days. Eleven protonated masses were monitored with the PTR-MS. The background signal was determined every 2 days for 30 min by passing air through a catalytic converter containing platinum-coated pellets heated to 320°C. The drift pressure was maintained at 2.20 mbars and the drift voltage at 600 V. The primary H_3O^+ ion counts at m/z 21 ranged between 0.9×10^7–1.4×10^7 cps with a contribution from the monitored first water cluster at m/z 37 < 5 %. Two multi-point calibrations were performed using a Gas Calibration Unit (GCU), and a standard mixture of 17 species (Ionimed Analytik GmbH, Innsbruck, Austria), (Singer et al., 2007) before and after the campaign over a 0.1-20 ppb range ; the linearity was higher than 0.99 (R^2). The species used for the calibration were methanol (contributing to m/z 33), acetaldehyde (m/z 45), acetone (m/z 59), isoprene (m/z 69), crotonaldehyde (m/z 71), 2-butanone (m/z 73), benzene (m/z 79), toluene (m/z 93) and α-pinene (m/z 137). In addition, five regular 5-ppb control points were carried out during the campaign. Except m/z 33 (17 %), the standard deviation of the calibration coefficients lay between 3 % (m/z 93) and 9 % (m/z 42). The NPL standard was used to cross-check the quality of the calibration and to perform regular one-point calibration control for isoprene and C6-C9 aromatics (4.0 ± 0.8 ppb). A relative difference of less than 10 % was found between both standards. The mean calibration factor for all major VOC are derived from the slope of the mixing ratios of the diluted standards with respect to product ion signal normalized to H_3O+ and H_3O+H_2O. Calibration factors ranged from 2.54 (m/z 137) to 19.0 (m/z 59) normalized counts per seconds per ppbv (ncps.ppbv^{-1}). Linearly interpolated normalized background signals are subtracted to the normalized signal before applying the calibration factor to determine ambient mixing ratios. Detection limits were taken as 2σ of the normalized background signal divided by the normalized calibration factor. Detection limits lay between 50 ppt (e.g. monoterpenes) and 790 ppt (methanol). Finally eleven protonated target masses have been monitored here: methanol (m/z 33.0), acetonitrile (m/z 42.0), acetaldehyde (m/z 45.0), acetone (m/z 59.0), methyl vinyl ketone (MVK) and methacrolein (MACR) (m/z 71.0), benzene (m/z 79.0), toluene (m/z 93.0) and C8-aromatics (m/z 107.0), C9-aromatics (m/z 121.0) and terpenes (m/z 137.0). While Yuan et al. (2017) reports interferences in its review paper (Yuan et al., 2017) for some of these protonated masses they can be excluded in high-NOx environment like Istanbul megacity.

Off line instrumentation, which included sorbent tubes and canisters, provides a lighter set-up to describe emission source composition and the spatial variability of VOC composition to support the PMF analysis. The instrumentation was deployed at the supersite and at the four locations reported on Figure 1 (VOC label). Off-line measurements of C5 to C16 NMHCs (alkanes, aromatics, alkenes, aldehydes) were performed onto multibed sorbent tubes of Carbopack B & C (Sigma–Aldrich Chimie S.a.r.l., St Quentin Fallavier, France), at a 200 mL min^{-1} flow rate for 2 h using a flow-controlled pump from GilAir. Samples were first thermodesorbed and then analyzed by TD-GC-FID/MS within one month after the campaign. The sampling and analysis method are detailed elsewhere (Detournay et al., 2011). Air samples were also collected by withdrawing air, for 2–3 min, into preevacuated 6-L stainless steel canisters (14 samples) through a stainless steel line equipped with a filter (pore diameter = 2 μm) installed at the head of the inlet. Prior to sampling, all canisters were cleaned at least five times by repeatedly filling and evacuating zero air. Tubes and canisters were sent back to the laboratory (Salameh et al., 2014). The frequency of off-line samplings is reported on Figure S1 at the various site reported in Figure 1.

The compounds commonly measured by on-line and off-line techniques, namely aromatics, isoprene, pentanes and terpenes were used to cross-check the quality of the results at the supersite on September 26th and 29th. The comparison is provided in Figure S2 in the Supplement Material. The variability between PTRMS and AIRMOVOC is highly consistent ($R^2 > 0.85$) and the differences in concentrations do not exceed ±22 %. While the number of off-line samples is limited (5 samples), the values are consistent. The pentanes, terpenes and C9-aromatics collected by tubes or canisters are also compared to AIRMOVOC (Figure S3). Most of the data compare well at ±20 % with few exceptions which do not exceed ±50 %. Finally, the correlation between PTRMS and AIRMOVOC is surprisingly weak for isoprene. Despite some interferences like furans cannot be excluded for m/z 69 with PTR-MS (Yuan et al., 2017), the good correlation between m/z 69 from PTRMS with ambient temperature led to use the PTRMS data for isoprene.

2.3 Other instrumentation

At the supersite, other trace gases like carbon monoxide (CO) and NO_x ($NO+NO_2$) have been performed on a 1-minute basis. NO_x was monitored by the Thermo Scientific model TEI 42I instrument model, which is based on chemiluminescence and NO_2-to-NO conversion by a heated molybdenum converter. The NO_x analyzer was installed after September 25th at the supersite. CO was monitored by the Horiba APMA-370 instrument model which is based on Non-Dispersive Infra-Red (NDIR) technique. Basic meteorological parameters (wind speed and direction, temperature, relative humidity, and atmospheric pressure) were measured on a 1 min basis. Air quality data with additional sulfur dioxide (SO_2) and meteorological data from other stations operated by the Greater Istanbul Municipality have been also used to test the consistency of our data and to support PMF interpretation (see Figure 1 and section 1.1).

In addition to gaseous and meteorological parameters, particulate matter samples were also collected at the site. Partisol $PM_{2.5}$ sequential sampler (Thermo Scientific, USA) was deployed (24 hours between 28th of August and 13th of November 2014 and every 6 hours until 28th of January 2015) and collected samples were analyzed in terms of metals by ICPMS. Moreover, Tecora PM_{10} sampler (Italy) was used to collect daily PM_{10} samples (30th of August 2014-3rd of February 2015) and collected samples were analyzed in terms of EC and OC by means of Sunset Lab (Oregon, USA) thermal optical analyzer, molecular organic markers by using GCMS (Varian CP 3800 GC equipped with a TR-5MS fused silica capillary column) and WSOC by means of an organic carbon analyzer (TOC-VCSH, Shimadzu). The sampling time and availability of the data are reported in Figure S1 of the Supplement Material.

2.4 Positive Matrix Factorization (PMF)

2.4.1 PMF description

The US EPA PMF 5.0 was used for VOC source apportionment. The method is described in detail in Paatero and Tapper, 1994; Paatero, 1997 and Paatero and Hopke, 2003.

The general principle of the model is as follow: any matrix X (input chemical data set matrix), can be decomposed in a factorial product of two matrixes G (source contribution) and F (source profile), and a residual part not explained by the model E. Equation 1 summarizes this principle in its matrix form:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (1)$$

Where i is the number of observations, j the amount of the measured VOC species and k the number of factors.

The goal of the PMF is to find the corresponding non-negative matrixes that lead to the minimum value of Q.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{{e_{ij}}^2}{{s_{ij}}^2} = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{s_{ij}} \right)^2 \qquad (2)$$

Where $f_{kj} \geq 0$ and $g_{kj} \geq 0$ and where n is the number of samples, m the number of considered species, and s_{ij} an uncertainty estimates for the j^{th} species measured in the i^{th} sample.

2.4.2 Preparation of input data

Two input dataset (or matrixes) are required by the PMF: the first one contains the concentrations of the individual VOC and the second one contains the uncertainty associated with each concentration.

The VOC input dataset combines data from both the PTRMS and the GC-FID. The PTR-MS data have been synchronized with the ones from the GC-FID on its 20-min sampling time every 30 minutes. The final chemical database used for this study comprises a selection of 23 hydrocarbons and masses divided into 7 compound families: alkanes (isobutane, n-butane, n-hexane, n-heptane, isopentane, n-pentane and 2-methyl-pentane), alkenes (1-pentene, isoprene, and 1,3-butadiene), aromatics (ethylbenzene, benzene, toluene, (m+p)-xylenes, o-xylene, and C9-aromatics), carbonyls (methylethylketone (MEK), methacroleine+methylvinylketone (MACR+MVK), acetaldehyde, and acetone), alcohol (methanol), nitrile (acetonitrile), and terpenes. Alkanes and alkenes were measured by the GCFID while benzene, toluene, isoprene, C8- aromatic, carbonyls, alcohol, nitrile, and terpenes were the ones measured by the PTRMS. For benzene, toluene and C8 aromatics the PTR-MS data were selected because of the smallest number of missing data.

Since the PMF does not accept missing values, missing data must be replaced. The percentage of missing values ranges from 8 to 79 % for species measured by the GC-FID. Butanes (iso/n), pentanes (iso/n), and (m+p)-xylenes have the lowest missing values percentage (ranging from 8 to 12 %) while o-xylene (30 %), 2-methyl-pentane (32 %), ethylbenzene (42 %), 1-pentene (62 %), n-hexane (66 %), n-heptane (72 %), and 1,3-butadiene (79 %) have the highest percentage of missing values. There were only 2 missing values (0.33 %) for species measured by the PTRMS.

For those species with a proportion of missing values below 40 %, missing data were replaced by a linear interpolation. For species with a proportion of missing data exceeding 40 %, each missing data point was substituted with the median concentration over all the measurement period. All the concentrations were above the detection limit.

The uncertainty σ_{ij} associated to each concentration (Equation 3) is determined using the method developed within the ACTRIS (Aerosol, Cloud and Trace Gases Research Infrastructure) network (Hoerger et al., 2015) and used in (Salameh et al., 2016):

$$\sigma_{ij} = \sqrt{\text{precision}^2 + \text{accuracy}^2} \qquad (3)$$

This uncertainty considers the different sources of uncertainty affecting the precision and the accuracy terms. The precision is associated with the detection limit of the instrument, the repeatability of the measurement, while the accuracy includes the uncertainty of the calibration standards and the dilution when needed.

The uncertainty of the PTRMS ranges between 5 % (toluene) and 59 % (acetaldehyde) of the concentrations while the uncertainty for the GC-FID ranges between 4 % (2-methyl-pentane) and 17 % (o-xylene) of the concentration. Further information about the uncertainties calculation are found in the section 1 of the supplement material.

2.4.3 Determination of the optimal solution

The objective of the PMF is to determine the optimal number of factors (p) based on several statistical criteria. Several base runs were performed with a different number of factors from 2 to 12. Statistical criteria were then used to determine the appropriate p value such as Q (residual sum of squares), IM (maximum individual Column mean), IS (maximum individual column standard deviation) as defined by Lee and al. (1999) and R^2 (indicator of the degree of correlation between predicted and observed concentrations). Q, IM , IS and R^2 are then plotted against the number of factor (from 2 to 12) (Salameh et al., 2016). The number of chosen factors corresponds to a significant decrease of Q, IM, and IS. In our study, an optimal solution of 5 factors was retained. In order to ensure the robustness of the solution, a Fpeak value of -1 was set by considering the highest mean ratio of the total contribution vs the model as well as the numbers of independent factors (Salameh et al., 2016).

2.4.4 PMF reference run

PMF reference run has been performed by removing the period during which there were no GC-FID data (night from 09/24 to 09/25). In addition, these data set have been chosen as PMF reference run because of the higher correlation between observed and reconstructed data by the PMF model (see also section 3.2). A good correlation ($R^2 = 0.97$) between total reconstructed VOC and measured VOC was obtained. For most compounds the variability is well reproduced with an R^2 usually higher than 0.70. Poorer correlation was found for alkenes (1-pentene ($R^2 = 0.55$), 1,3-butadiene ($R^2 = 0.22$) and isoprene ($R^2 = 0.57$) as well as for n-hexane ($R^2 = 0.09$), MEK ($R^2 = 0.41$) and acetaldehyde ($R^2 = 0.32$). The R^2 of the contribution of the five factors between each other has been calculated, it was found that the value of R^2 does not exceed 0.28 and is usually less than 0.05 indicating the statistical independence of the five factors. There is therefore no significant correlation between the factors which means that the factors are independent.

The PMF output uncertainties were estimated by three models: the DISP model (base model displacement error estimation), the BS model (base model bootstrap error estimation) and the DISP+ BS model. Further information for the estimation of model prediction uncertainties can be found in Norris et al. (2014) and Paatero et al. (2014). The DISP results of the PMF run show that the 5-factor solution is stable and sufficiently robust to be used because no swaps occurred. All the factors were well reproduced through the BS technique at 100 % for factor 1, 96 % for factor 2, 100 % for factor 3, 99 % for the factor 4 and 100 % for factor 5; there were not any unmapped run. The DISP+BS model shows that the solution is well constrained and stable.

2.4.5 Sensitivity tests to evaluate PMF results

The sensitivity of PMF results on input data have been tested in order to evaluate the representativeness of the PMF reference run results. These tests evaluates the effect of some time period selection described in section 3 (periods 1, 2 and 3, night-time peaks) and the incorporation of species with a high number of missing data as well as a test where all missing data were directly replaced by the median of species over all the measurement period instead of interpolation.

Table 2 summarizes the contribution of each factor for every sensitivity scenario as well as the values of the correlations between observed vs modelled concentrations. The reference run has the best fit with $R^2_{\text{total}} = 0.97$ and more than 82 % of species were well reconstructed by the PMF ($r^2 \geq 0.5$). While the sensitivity tests are statistically less performant than the reference run, they all show that the same factors are extracted even though the relative contributions could be slightly modified by ±16%. Factors will be discussed in section 3.3.

2.5 FLEXPART model

FLEXPART is a Lagrangian particle dispersion model and is widely used to stimulate atmospheric transport. It gives information about long range and mesoscale dispersion of air pollutants such as air mass origin (back trajectories) (Brioude et al., 2013). FLEXPART was driven by ECMWF analysis (at 00, 12 UTC) and their 3 hourly forecast fields from the operational European Centre for Medium Range Weather Forecasts - Integrated Forecast System (ECMWF-IFS). To compute the FLEXPART trajectories, the ECMWF meteorological fields were retrieved at 0.25° resolution and 91 vertical levels. The FLEXPART output are reported in Figure 2.

3 Results and discussion

3.1 Meteorological conditions and air mass origin

The time series of meteorological parameters are reported in Figure 3. Based on in situ observations and FLEXPART simulations (Figure 2), the meteorological situation has been divided into three types of periods:

- Periods 1 and 3 from 09/15 to 09/21 and from 09/28 to 09/30 with marine air masses coming from Black Sea and Russia and/or Ukraine and Northern Europe, respectively (Figure 2). During period 1, in-situ temperature and relative humidity were characterized by a clear and opposite diurnal cycle while no cycle is depicted during period 3. During both periods relative humidity is high with two rain events (09/18 and 09/28). Relative humidity is high during the night (80 %) while temperature is high during the day (from 14.7 to 27.6°C with an average of 21.2 °C). Wind speed are the highest (>3 $m.s^{-1}$ in Besiktas and up to 12 $m.s^{-1}$ at Sariyer) with a northern wind direction.
- Period 2 from 09/23 to 09/26 with continental air masses coming from Eastern and Northern Europe (Figure 2). Locally wind direction is variable. Temperature and relative humidity were characterized by the same diurnal cycles as in Period 1. Temperature decreased, ranging between 11.8 and 25.4 °C with an average of 17.9 °C. Lower wind speeds were recorded (3.1 $m.s^{-1}$ in Besiktas and up to 6 $m.s^{-1}$ in Sariyer). Wind direction varied between WSW (West-South-West) and SSE (South-South-East), and between North and ENE (East-North-East).
- A first transition period between period 1 and 2 (09/21 to 09/23) showed a wind direction shift towards the southern sector (Marmara Sea) (Figure 2). Wind speed recorded the lowest values (<1.3 $m.s^{-1}$ in Besiktas and <5 $m.s^{-1}$ in Sariyer). It rained on 09/23. A second transition period between period 2 and 3 (from 09/26 to 09/28) showed a wind direction shift toward the NNE (North-North-East) (Figure 2). On 09/06, the temperature went up to 26 °C. It rained

from the night of 09/26 until the end of the period during which temperature went down to 14.7 °C. This period was also characterized by higher wind speed (up to 9 m.s^{-1} in Sariyer and 2.7 m.s^{-1} in Besiktas) coming from ESE (East-South-East) and North.

3.2 VOC distribution

3.2.1 Ambient concentration level and composition

Observed VOC at the supersite of Besiktas are representative of the ones usually encountered at urban background sites. Biogenic compounds are isoprene and terpenes while anthropogenic compounds include both primary (alkanes, alkenes, aromatic compounds) and secondary compounds (oxygenated VOC).

Statistics on the VOC concentrations measured by GC-FID and PTR-MS at the supersite of Besiktas are reported in Table 1. VOC show a high temporal variability with maxima reaching several tens of ppb (isopentane, ethylbenzene, methanol, and acetone). Most of VOC median concentrations are below 1 ppb except for n-butane (1.48 ppb), toluene (1.25 ppb) and some oxygenated compounds like acetaldehyde (1.39 ppb) and acetone (2.33 ppb). The average composition of VOC is mainly composed of OVOC (0.12-4.92 ppb) which represent 43.9 % of the total VOC (TVOC) observed mixing ratio, followed by alkanes (0.21-2.00 ppb; 26.33 %), aromatic compounds (0.26-2.27 ppb; 20.66 %), alkenes (0.19-0.68 ppb; 4.81 %), terpenes (3.44 %) and acetonitrile (0.84 %). Both OVOC and alkanes contribute up to 70.2 % of the TVOC concentrations. Methanol (22.40 %, 4.92 ppb on average) is the main oxygenated compound measured in this study, followed by acetone (11 %, 2.63 ppb). N-butane (9.11 %, 2.00 ppb) and isopentane (6.43 %, 1.41 ppb) are the two major alkanes. Toluene is the most abundant aromatic compound (50 %, 2.27 ppb). This was the case of most of the previous VOC studies made in Istanbul (Demir et al., 2011; Kuntasal et al., 2013; Muezzinoglu et al., 2001; Bozkurt et al., 2018; Elbir et al., 2007).

Levels of alkanes, some alkenes and aromatics are compared to other European megacities: Paris and London (Borbon et al., 2018) at both urban and traffic site as well as at an urban site in Beirut (Salameh et al., 2015) during summer (Figure S4 in the supplement material). Consistency in urban hydrocarbon composition worldwide has been already observed (Borbon et al., 2002; von Schneidemesser et al., 2010; Dominutti et al., 2016). Despite differences in absolute levels, the hydrocarbon composition in Istanbul is quite similar to the other cities. Beirut has the highest concentrations of n-butane, isopentane and 2-methyl-pentane. Higher concentrations in toluene, (m+p)-xylenes were in Paris, Beirut and Istanbul. Such similarity would suggest that same sources control the hydrocarbon composition, especially traffic in all cities including Istanbul (see also section 3.3 on PMF).

Off-line VOC concentrations collected with tubes are reported in Table S5 in the Supplement material at various locations including the Besiktas supersite. While the number of samples is limited in time, off-line measurements provide a general picture of a wider spectrum of VOC that are not measured at the supersite like light hydrocarbons (C2-C3 alkanes and alkenes), C6-C11 carbonyls, speciated terpenes (camphene, limonene, β-pinene) and C12-C16 IVOC. Therefore, these dataset allow to address the spatial variability of VOC concentrations and composition within the megacity. The comparison of concentrations between different areas is limited because of the different sampling times. Therefore, the analysis only focuses on VOC relative composition. The relative composition divided into major VOC chemical groups at each sites by sorbent tubes and canisters is reported on Figure 4a and 4b, respectively. The composition is variable across the megacity for the aliphatic fraction of high and intermediate volatility hydrocarbons (C2-C16). As expected, the composition of the *29/09 12:05* sample at the Besiktas site is like the ones derived from the roadway side measurements highlighting the influence of road transport emissions at the supersite. Interestingly, the VOC composition of the three samples from sorbent tubes at the Besiktas site are different from the ones at the roadway side with a higher proportion of IVOC. The VOC composition of the *26/09 10:31* sample by canister is rather similar to the one from the seashore sample in Galata (*29/09 16:12* sample). In the same way the VOC composition of the samples at the supersite derived from tubes are rather like the Besiktas seashore one. For both of them, the proportion of IVOC is significant (from 15 % to 40 % in weight). While light VOC are expected to be of minor importance when considering ship emissions, the higher presence of heavier organics is however expected as observed for alkanes by Xiao et al. (2018) in ship exhaust at berth. The VOC composition comparison would thus suggest not only the impact of road traffic emissions on their composition but also the potential impact of local ship traffic emissions. Finally the composition at Besiktas is not affected by Residential emissions which are enriched in light C2-C3 alkanes (canisters) or aromatics (canisters).

3.2.2 Time series and diurnal variations

The variability of VOC concentrations is driven by several factors: emissions (anthropogenic or biogenic), photochemical reactions (especially with the OH radical during the day and ozone and nitrates at night for alkenes) and the dynamic of the atmosphere (including dilution due to the height of the boundary layer) (Filella and Peñuelas, 2006). The time series of inorganic trace gases (NO_x and CO) and some VOC representing the diversity of sources and reactivity are reported in Figure 5. The meteorological periods 1, 2 and 3 described in the previous section 3.1 are also indicated. Because NO_x at the super site were only measured from 09/25 to 09/30, data from the air quality station in Besiktas were used (see Figure 1). One should note that the time series of NOx at the supersite and at the Besiktas station are consistent.

Time series of NO_x and CO show high concentrations but a different pattern regardless of the origin of air masses. While a daily cycle of NOx is depicted, CO does not show any clear pattern. The NO_2/NO_x ratio fluctuates between 0.34 to 0.93 with an average and median value of 0.53 and 0.55, respectively. These values are very high compared to what is usually found in the literature (Grice et al., 2009; Kousoulidou et al., 2008; Keuken et al., 2012) which are mostly low and below 0.50. However higher values of NO_2/NO_x ratio can be found in diesel passenger cars (Grice et al., 2009. Vestreng et al., 2009) and vans (Kousoulidou et al., 2008). This ratio would reflect the impact of the combustion of heavy fuels in the megacity. After road transport, cargo shipping is a second highest contributor to NO_x levels according to the local/regional inventory (Markakis et al., 2012).

Anthropogenic VOC time series (benzene, isopentane and isobutane) exhibit a high frequency variability but usually show higher concentrations during the night especially during period 2. One cause are the very low wind speeds at night especially during period 2 (Figure 3), which would reinforce the accumulation of pollutants. Under marine influence (periods 1 and 3), VOC concentrations are the lowest, especially during period 3, which is characterized by rainy days (September 27th and 28th), high wind speed and colder temperatures (Figure 5). These conditions favor atmospheric dispersion. During transition periods and under continental influence (period 2), VOC concentrations exhibit a strong day-by-day variability with episodic nocturnal peaks especially on September 25th and 26th. While these peaks are not always concomitant between VOC and are not associated with any increase in NOx and CO levels, they occur under south and southwestern wind regimes which are unusual wind regimes according to Figure 1. This points out the potential influence of industrial and port activities other than fossil fuel combustion. For instance, maximum concentrations of butanes occurred during the period of the marine-continental regime shift with well-established southwestern wind regime on 09/22, 09/23 and on 09/26 at the end of the day. Maximum concentrations of pentanes occurred during the night of 09/26 to 09/27 like for aromatics (e.g. benzene) (Figure 5).

Except during transition periods, the background levels of measured trace gases are not affected by the origin of air masses. This strongly suggests that the pollutants measured during TRANSEMED-Istanbul were from local and regional sources. Finally, time series would suggest the influence of multiple local and regional sources other than traffic on VOC concentrations, likely industrial and/or port activities, at the supersite.

Isoprene and its oxidation products (MACR+MVK) covariate most of the time in period 1 and 3. They usually show their typical diurnal profiles with higher concentrations during the warmest days and at midday due to biogenic emission processes. Their significant correlation with temperature (R = 0.7) implies the emission from biogenic sources. Around the Besiktas site, 49.5 % of the vegetation is occupied by hardwood and hardwood mix trees while only 6 % is occupied by softwood and hardwood mix trees. While Quercus (isoprene emitter) only occupies 7.7 % of the total vegetation coverage (personal communication from Ministry of Forestry), the presence if isoprene at the supersite is probably due to the surrounding trees.

Except during transition periods, the background levels of measured trace gases are not affected by the origin of air masses. The background levels stay constant under continental or marine influence and regardless of the atmospheric lifetime of the species. This strongly suggests that the pollutants measured during TRANSEMED-Istanbul were from local and regional sources. Finally, time series would suggest the influence of multiple local and regional sources other than traffic on VOC concentrations, likely industrial and/or port activities, at the supersite.

Taking into consideration time series variability, diurnal variations have been splitted into periods 1 and 3 and period 2 for selected VOC as well as two combustion derived trace gases (NO_x and CO). Diurnal profiles of atmospheric concentrations are reported in Figure 6. Local traffic counts for road transport (personal communication from Istanbul Municipality for fall 2014) and ship (https://www.marinetraffic.com/en/ais/details/ports/724/Turkey_port:ISTANBUL) are also reported in Figure S6 in the supplement material. Maritime traffic is mostly for passenger shipping (58.02%) against 16% for cargo shipping. The diurnal profiles of ship and road traffic counts are similar.

Generally, concentrations during period 2 are higher than the ones during periods 1 and 3 and show different diurnal patterns for some compounds. The profile of NO_x is consistent with the one of traffic counts (Figure S6 of the supplement material). NO_x exhibits higher concentrations during the day and lower concentrations at night for both periods with a morning peak (7:30-8:30) and one early evening peak from 17:30 (Figure 6.a). This is typical of traffic emitted compounds with morning and evening rush-hour peaks as observed in many other urban areas like Paris, France in Europe (Baudic et al., 2016) or Beirut, Lebanon in Eastern Mediterranean (Salameh et al., 2016). As already depicted in time series, CO diurnal profile is different from the one of NO_x. CO concentrations show higher concentrations in the late evening and lower concentrations during the day. During the day, CO is also characterized by a double peak: one in the morning (8:30) and the other one in the middle of the day (Figure 6.b). Both NOx and CO show quite similar diurnal profile between the three periods even if morning concentrations tend to be higher.

VOCs show different profiles from the one of NOx. Under marine influence (periods 1 and 3), primary anthropogenic VOC (ie. benzene, alkanes and other aromatics) almost exhibit a constant profile while they show higher concentration from midnight until 10:00 AM under continental influence (period 2), For instance, benzene (Figure 6.d) and isopentane (Figure 6.f) nighttime concentrations increase by four-fold compared to the levels under marine influence. In the middle of the day, the concentration levels are the same as during periods 1 and 3. The profiles of primary anthropogenic VOCs point out the complex interaction between local and regional emissions and dynamics. Period 2 points out the influence of VOC emissions other than traffic and combustion processes (no effect on NO_x and CO) at night. While the influence of traffic emissions on CO and VOC cannot be excluded; it seems that their emission level is not high enough to counteract the dispersion effect during the day unlike NO_x. This will be further investigated in the PMF analysis.

Isoprene concentrations increase immediately at sunrise and decrease at sunset during period 1 and 3 (marine influence) which indicates its well-known biogenic origin (Figure 6.g) which is light and temperature dependent. Isoprene and MACR+MVK's concentrations increase at night during period 2 like other alkanes and aromatics, suggesting their potential anthropogenic influence.

Provided some interferences like furans could contribute to isoprene signal by PTRMS measurements (Yuan et al., 2017), this would suggest an anthropogenic origin for isoprene. While the signals of m/z 71 are commonly attributed to the sum of MVK and MACR which are both oxidation products of isoprene under high-NO conditions, more recent GC-PTR-MS studies identified some potential interferences for MVK and MACR measurements, including crotonaldehyde in biomass-burning emissions, C5 alkenes, and C5 or higher alkanes in urban regions (Yuan et al., 2018). Such interferences cannot be ruled out here. During periods 1 and 3, MACR+MVK concentrations follow the same general pattern as of isoprene's.

With relatively long atmospheric lifetime, (≈ 68 days), acetone's concentration is quite constant throughout the day within period 1, a peak in the middle of the day and lower concentrations during the night for period 2 (Figure 6.c). The peak in the middle suggests the presence of a secondary origin. Acetone can have both primary and secondary source (Goldstein and Schade, 2000; Macdonald and Fall, 1993). Methanol and MEK have the same general pattern as for acetone during both periods without the peak in the middle of the day suggesting that they might have the same emission source.

3.3 PMF results

3.3.1 Factor identification

The factor profiles have been analyzed using the variability of their contribution together with several external variables (NO_x, SO_2, CO, meteorological parameters, emission profiles). PMF factors are displayed in Figure 7. The time series and diurnal profiles of their contributions are displayed in Figures 8 and 9, respectively.

Factor 1: Toluene from solvent use

The speciation profile of factor 1 exhibits high concentrations of toluene with 57 % of its variability explained by this factor (Figure 7). There is also a small contribution of acetone (18 %), MEK (18 %) and xylenes (17 %). While toluene and xylenes are related to traffic emissions, this factor does not correlate well with any traffic tracer gases (R = 0.33 for NO_x,) and combustion trace gases in general (R = -0.03 for CO and 0.13 for SO_2). Moreover toluene also contributes to the Road transport factor (factor 5) but to a lesser extent. The time series are highly variable with erratic peaks regardless of the time of the day especially during period 2 and to a lesser extent during period 1 (Figure 8). The average diurnal profile looks like constant but the relative standard deviation is ±100% (Figure 9). Sources related to solvent use are among the expected non-combustive sources for toluene (Baudic et al., 2016; Gaimoz et al., 2011; Brocco et al., 1997; Na and Kim, 2001). In Turkey, toluene was already found in gasoline vehicle, solvent and industrial emissions (Bozkurt et al., 2018; Yurdakul et al.,2013; Demir et al., 2011).

Toluene/benzene ratio (T/B) is used as an indicator of non-traffic source influence (Elbir et al., 2007; Lee et al., 2002; Yurdakul et al.,2013). T/B ratio ≤ 2-3 indicates the influence of traffic emissions on measured VOC concentrations (Gelencsér et al.,1997; Heeb et al., 2000; Muezzinoglu et al., 2001; Brocco et al., 1997) whereas T/B ratios ≥ 2-3 suggests the influence of other sources than traffic (such as solvent evaporation or industrial sources). The T/B ratio for this study is between 0.4 (with only 4 points below 2) and 48.6 (Only 1 point above 29). Only 5.8 % of the ratios were between 2 and 3, 48 % were between 3 and 6 while 45 % were above 6 with 34 % between 6 and 10. This strongly suggests the influence of sources of toluene other than traffic. High value of T/B ratio is mostly found at industrial sites (Pekey and Hande, 2011). The median and mean value of T/B in this experiment are respectively 5.6 and 6.7 which can also indicate gasoline related emissions (Batterman et al., 2006). However the absence of other unburned fuel compounds like pentanes excludes this source. These ratios were calculated with toluene and benzene measured by the PTRMS since the PMF run was done by those data. By looking at the T/B ratio measured by the GCFID, we found approximatively the same conclusion: Only 1 % of the ratios were between 2 and 3, 47 % were between 3 and 6 while 51 % were above 6 with 38 % between 6 and 10. This factor represents 14.2 % of the total contribution.

Factor 2: Biogenic terpenes

Factor 2 exhibits high contribution of terpenes with more than 73 % of their variability explained by this factor (Figure 7). Terpenes are known as tracers of biogenic emissions (Kesselmeier and Staudt, 1999). Isoprene which is also a biogenic tracer has only 5 % of its variability explained by this factor. Moreover, the diurnal profile of these two compounds show opposite patterns as it can be seen in Figures 6 and 9 which indicates that their biogenic emissions are controlled by different environmental parameters: temperature for terpenes, light and temperature for isoprene (Fuentes et al., 2000). Furthermore, Besiktas site is also surrounded by Pinus which are terpenes emitter and represent the maximum overall vegetation in Istanbul (up to 33%) (Personal communication from Ministry of Forestry). This factor shows high concentrations and contribution during period 1 and the transition periods (Figures 2 and 7) probably due to higher temperature while they are almost not significant during period 3. As expected, terpenes do not correlate with any combustion related gases (R<0.14 for NO_x, CO and SO_2).

The diurnal profile of this factor is characterized by high concentrations at night and early morning (until 8:30) and low concentrations during daytime (Figure 9). This type of profile has already been observed at a background site in Cyprus (Debevec et al., 2017); in a forest of Abies Boriqii-regis in the Agrafa Mountains of north western Greece (Harrison et al., 2001) and at Castel Porziano near Rome, Italy (Kalabokas et al., 1997). In a shallower nocturnal boundary layer, low chemical reactions together with persistent emissions lead to the enhancement of their nocturnal mixing ratios. Terpene's lifetime toward OH and ozone are 1.2 to 2.6 h and 5 min (for α-pinene) to 50 min (for camphene) respectively (Fuentes et al., 2000). Dilution processes of the boundary layer in addition to the higher reactivity of terpenes towards the OH radical and ozone could explain the decrease of their concentrations during the day.

This factor is called "biogenic terpenes" and represents 7.8 % of the total contribution.

Factor 3: Natural gas evaporation

Factor 3 is essentially composed of butanes (iso/n) with more than 97 % of their variability explained by this factor (Figure 7). Isobutane is a typical marker of fossil fuel evaporative source (Debevec et al., 2017; Na et al., 1998). This factor significantly explains the contributions of 1,3-butadiene (32 %), acetonitrile (23 %), acetaldehyde (24 %), MACR + MVK (21 %), C9-aromatics (22 %) and benzene (20 %). Iso/n butanes correlate poorly with CO (R = 0.09) and NO (R = 0.33). The alkanes/alkenes ratio of this factor is high (55), which points out the evaporative source of this factor (Salameh et al., 2014). At the same time, the pentanes (n/iso) and the other aromatic compounds are not well represented in factor 3. This suggests that butanes evaporation is not related to evaporation from storage, extraction and distribution of gasoline but rather to natural gas evaporation.

The diurnal profile of factor 3 is characterized by an increase in concentration at night and constant concentration from 10:00 to 18:00 with a slight peak in the middle of the day and in the evening (Figure 9). This points out a source linked to the use of natural gas as energy source, especially for cooking at lunch time with the proximity of many restaurants near the measurement site. This type of profile has already been observed in Paris (Baudic et al., 2016). The time series are characterized by several peaks during period 2, which corresponds to the marine transition by the south-southwest of Istanbul and the Marmara Sea (Figure 8). It is noteworthy the presence of a power plant with a capacity of 1350 MW located in the southwest of Ambarli that uses natural gas as fuel and which can also contributes to the butane loads . This factor does not depend on temperature or on other trace gas (NO_x, CO and SO_2). The average relative contribution of natural gas factor is 25.9 %.

Factor 4: Mixed diurnal regional emissions

Factor 4 has a significant contribution of several primary and secondary as well as biogenic and anthropogenic species (Figure 7). N-hexane is the most dominant species (81.6 % of its variability is explained by this factor). However, knowing that this compound has more than 70 % of missing values, the analysis related to this compound should be done carefully. The great contribution of isoprene (66 %) in factor 4 points out its biogenic emissions. Biogenic emissions of isoprene are directly related to temperature as well as solar radiation (Steiner and Goldstein, 2007; Owen et al., 1997; Geron et al., 2000). Note that this factor correlates well with the ambient temperature (R = 0.70). Despite the percentage of missing values, the biogenic contribution on this factor can also be explained by the presence of 1,3-butadiene and 1-pentene likewise emitted by plants (Goldstein et al., 1996). The factor 4 is also characterized by the presence of oxygenated compounds such as isoprene oxidation products like MACR+MVK (54 %) and acetaldehyde (66 %), acetone (57 %), methanol (59 %) and MEK (59 %). These Oxygenated species can have primary sources (both anthropogenic and biogenic) and are also formed secondarily by the oxidation of primary hydrocarbons (Yáñez-Serrano et al., 2016; Millet et al., 2010; Goldstein and Schade, 2000; Singh, 2004; Schade et al., 2011).

Aromatic compounds (benzene 40 %, ethylbenzene 29 %, C9-aromatics 24 % and xylenes 20 % on average) are also well represented in this factor. While they enter in the composition of fossil fuel combustion by constituting the unburned fraction of vehicle exhaust emissions as for C5-alkanes (Buzcu and Fraser, 2006), their proportion in factor 4 does not compare with the one of traffic emissions derived from canister measurements along the Barbaros (Bd) (Figure 10). Solvent use activities from domestic or industrial sector can also emit aromatics higher than C6. Therefore, the presence of aromatics in factor 4 would be rather related to solvent use activities. Acetonitrile, highly present in factor 4, is usually used as a biomass burning tracer (Holzinger et al., 1999).

The diurnal profile is characterized by an increase in concentration during the day and a decrease in concentrations at night (Figure 9). When looking at external variables, this factor correlates well with SO_2 (R = 0.5), which is a tracer of industrial emissions and ship emissions (Lee et al., 2011) but neither with NO_x (R = 0.25) nor CO (R = -0.06). Indeed the city of Istanbul experiences the highest industrial activities in the country (Markakis et al., 2012) while the Bosphorus strait is 500 m away. The diurnal shape is also similar to the one of ship traffic counts (Figure S6 of the supplement material) which follows the one of road traffic.

The potential influence of ship emissions has been investigated by looking at the ratio of V/Ni derived from the elemental composition of $PM_{2.5}$. This ratio have been commonly used as a tracer of ship emissions influence (Viana et al., 2014; Pey et al., 2013; Becagli et al., 2012). While some papers assume that a ratio of 3 usually signs the impact of ship emissions (Mazzei et al., 2008; Pandolfi et al., 2011) , a deeper analysis of the literature suggests that this ratio is highly variable from 0.7 up to 4.5 (Isakson et al., 2001; Agrawal et al.,2008). When plotting particulate V versus Ni concentrations integrated over a 24h-period in September 2014, a ratio of 2.72 ± 0.89 is found (see Figure S7 of the supplement material). However, the scatterplot of 6h-integrated data reveals a more scattered distribution of points on both sides of the fitting line. First, the derived V-to-Ni value seems to be controlled by the sampling time resolution and a fixed value cannot be used as an evidence of ship emission influence. Second, while the Istanbul points lie between the upper and lower limits some of them are higher than 4.5. Other sources like coal combustion can affect the V and Ni distribution (Oztürk et al., in preparation). Finally, by comparing this factor (C5-C7 alkanes, aromatic compounds, 1- pentene and acetone) to the one of ship emissions at berth in Jingtang port (Xiao et al. 2018), no similarity was found. While an influence of ship emissions is not excluded, there is no direct evidence from VOC measurements.

The analysis of the time series shows that the background level of this factor varies as a function of the meteorological period (Figure 8). During the period 2, an increase in minimum concentrations is observed, which may be related to the lower wind speed that favors the stagnation of pollutants. We assume that secondary production affects this factor since the presence of many secondary compounds (MACR+MVK, MEK, acetaldehyde etc.) is observed. To conclude, this factor can be related to a combination of primary and secondary anthropogenic (combustion, industrial and ship emissions) as well as biogenic emissions. By considering the different origins of species and its diurnal emission, this factor was labelled as "mixed regional emissions factor". It represents 36.3 % of the total VOC contribution.

By increasing the number of factors, isoprene was isolated into a 7^{-}factor solution. By increasing the number of factors to 8, isoprene was not isolated anymore (Figure S8). By using only the PTRMS data (10 min time resolution) for PMF run, isoprene and its oxidation products have been isolated as well. Synchronizing the PTRMS data with the GC-FID time step (30 minutes resolution) degrades the time resolution and smooths the variability of the data and, consequently, the ability of the PMF model to isolate biogenic emissions from other sources.

Factor 5: Road Transport

The profile of factor 5 exhibits high contributions of pentanes (iso, n and 2-methyl) with on average 84 % of their variability explained by this factor (Figure 7), followed by n-heptane (58 %). The 32 % of the variability of 1-pentene is also explained by this factor. Aromatic compounds, such as ethylbenzene (45 %), o-xylenes, (m+p)-xylenes (47 %), C9-aromatics (37 %), benzene (28 %) and toluene (28 %), which are considered as typical fossil fuel combustion products (Sigsby et al., 1987) are also predominant species in this factor. Isopentane is one of the most abundant VOC in the traffic related sources (Buzcu and Fraser, 2006).

To help in identifying the main sources related to this factor, a comparison between its profile and the one obtained from near-source traffic measurements was performed (see Figure 10). Contrary to factor 4 (mixed regional emissions), both profiles are similar. Factor 5 is much more enriched in aromatics compared to C5-alkanes by almost a factor of 2.

The diurnal profile of factor 5 showed an increase in concentrations from midnight until sunrise and an almost constant concentration during the rest of the day with several small peaks (Figure 9). Morning peaks (6:30 and 9:30) and a night peak (19:30) are observed. This increase in concentrations corresponds to the morning and evening traffic rush hour periods. After 18:30 the absolute concentration of this factor stayed high and increased for several reasons: ongoing emissions until 3h30, lower photochemical reactions and atmospheric dynamics (the swallower boundary layer leads to more accumulation of pollutants at night. Lower concentrations are observed during late morning until 18:30. The reduction of concentration of this factor during the day could be explained by dilution process and OH oxidation process.

The time series shows a period of peak and a relatively high contribution of this factor in the night of 09/26 to 09/27 (Figure 8). The factor 5 is the closest to traffic related source which covers exhaust emissions and gasoline evaporation emissions. However, the contribution of this factor does not correlate with the traffic tracer NO_x. This factor represents 15.8 % of the total VOC contribution.

As it was discussed in Yuan et al., (2012), the effect of photochemistry on factors composition had been analyzed by looking at the scatterplots of the contribution of the PMF factors to each VOC as a function of its OH rate constant (k_{OH}). Nevertheless, no clear evidence from photochemistry was founded on the Istanbul PMF factor's contributions.

This study show that PMF was able to extract easily some factors (like biogenic terpenes) than others (like diurnal regional factors). These results are consistent with other Turkish cities where other source than traffic (mostly industrial source) drive the VOC emissions (Yurdakul et al., 2013; Pekey and Hande, 2011; Civan et al., 2015; Dumanoglu et al., 2014). However, in the EMB, traffic related emissions are the most dominant source and accounted for 51 and 74 % in winter and summer respectively in Beirut, Lebanon (Salameh et al., 2016). Kaltsonoudis et al. (2016) also found that traffic and biogenic emissions were the dominant source of VOC during summer in Patras and Athens. In Paris, Baudic et al. (2016) found that 25 % of the total VOC contributions were related to traffic, 15 % to biogenic factor, 20 % to solvent use against 14.2 % and 23% to natural gas and background factor that the PMF has not able to dissociate. These differences in contributions with this study could be due to the differences in input data. Thus, PMF results depends strongly on input data. Furthermore, it was shown in McDonald et al. (2018) that source apportionment studies largely underestimated the influence of Volatile Chemical Species (including organic solvents, personal care products, adhesives …) as source of urban VOC. This underestimation could be explained by the fact that VOC are not measured in all their diversity in source apportionment studies in contrast with what was done in McDonald et al. (2018).

3.4 Emission ratios of VOC/CO

The determination of emission ratios (ER) is a useful constraint to evaluate emission inventories (Warneke et al., 2007; Borbon et al., 2013). The emission ratio is the ratio of a selected VOC with a reference compound that does not undergo photochemical processing mostly CO or acetylene due to their low reactivity at urban scale and as tracers of incomplete combustion (Borbon et al., 2013; Salameh et al., 2017). The linear regression fit method (LRF) is a commonly used method to calculate emission ratios: the ER corresponds to the slope of the scatter plot between a given VOC vs CO or acetylene (Borbon et al., 2013; Salameh et al., 2017). Another method is the photochemical age method (de Gouw, 2005; de Gouw et al., 2018; Warneke et al., 2007; Borbon et al., 2013) which is based on the concentration ratios and the photochemical age. In this study, poor correlation between targets VOC and CO is found ($R^2 \leq 0.16$) as could be deduced from the time series analysis (see section 3.2.2) and the PMF analysis. Indeed, fossil fuel combustion derived activities are not dominating the VOC distribution. As a consequence the LRF method cannot be applied. Here the emission ratio was determined by the mean value of each Δ(VOC)-to-Δ(CO) concentration ratio over the whole period of measurements. The terms "Δ(VOC)" and "Δ(CO)" correspond to the measured concentrations of VOC and CO subtracted by VOC and CO background concentrations respectively. Given the diurnal and data day-to-day variability of dynamics (see section 3.3.2), one daytime and nighttime CO background values were estimated for each day by extracting the daytime and nighttime minimum concentration values. For CO, the daytime background values range between 213.5 and 367.2 ppb and the nighttime background values range between 211.5 and 406.7 ppb. For VOC, the background values depend on the compound. At night, the background values lie between 1.3 and 3.4 ppb for a long-lived compound like acetone and between 0.2 and 1.1 for a short-lived compound like (m+p)-xylenes. For the following discussion, we will refer to VOC-to-CO ratio instead of "Δ(VOC)-to-Δ(CO)" ratio.

Photochemistry can affect the value of emission ratios (Borbon et al., 2013). Comparing daytime to nighttime ratios is one way to evaluate the effect of daytime photochemistry by assuming that chemistry can be neglected at night except for alkenes (de Gouw et al., 2018) and the composition of emissions does not change between day and night. While the ratio between nighttime emission ratios and daytime emission ratios shows a decrease of 37% on average during the day, this decrease is not dependent on the OH kinetic constants of each VOC (Figure S9). This suggest that these differences are rather controlled by the changes in emission composition between day and night. As a consequence, the emission ratios have been determined on the whole dataset.

The emission ratios VOC-to-CO in Istanbul are displayed in Table 3 and compared to the ones in other urban areas worldwide. The emission ratios determined in Istanbul are usually higher than the ones of other cities but in the same range of magnitude. C4-C5 alkanes, toluene and oxygenated VOCs show the highest emission ratio values. Most of the values are consistent within a factor of 2 with, at least, one determined in other cities of post- industrialized or developing countries.

3.5 Evaluation of global emission inventories

In this section, the VOC emissions from anthropogenic sources and road transport source by three references global emission inventories downscaled to Istanbul are evaluated: MACCity (Granier et al.. 2011) for 2014, EDGAR (Crippa et al.. 2018) for 2012, and ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project) (Lamarque et al.. 2010) for 2000 (figure 11.a,b and c). Emission data for ACCMIP and MACCity inventories are available in the ECCAD database (http://eccad.aeris-data.fr/), and the one for EDGAR inventory is available in the EDGAR database (http://edgar.jrc.ec.europa.eu/). This evaluation is based on the VOC-to-CO emissions ratios calculated in the previous section (3.4) following Salameh et al. (2016):

$$\mathrm{VOC_{estimated}} = \mathrm{ratio}\left(\frac{\mathrm{VOC}}{\mathrm{CO}}\right)_{\substack{\mathrm{all\ observations} \\ PMF\ Road\ transport\ factor}} \mathrm{X\ CO_{inventory}} \qquad (4)$$

Where:

- VOC estimated is the estimated emission for an individual VOC or a group of VOC in tons/year for all anthropogenic emissions or road transport emissions.

- CO inventory is the extracted emission of CO from either ACCMIP (in Tg/year), MACCity (in Tg/year), or EDGAR (in tons/year).

- VOC/CO is either the VOC-to-CO ratio calculated in section 3.4 or the VOC-to-CO ratio determined from each VOC contribution in the PMF road transport factor (in µg.m^{-3} of VOC/µg.m^{-3} of CO).

Species in emission inventories are sometimes lumped (grouped) as a function of their reactivity for chemical modeling purpose and species label does not always correspond to a single species. For instance, methanol in Edgar not only corresponds to methanol itself but all alcohols. Moreover, summing some species from observations is sometimes needed to fit with the inventory lumping like alkanes higher than C4 in MACCITY but is limited to the number of the measured species. As a consequence, the comparison is not direct and requires special care (see the following discussion).

The annual VOC and CO emissions for EDGAR (0.1 x 0.1 resolution) was determined by summing the emissions of 12 grids over a domain encompassing the sampling site (longitude between 28.9 and 29.1°; latitude between 40.9 and 41.2°). For ACCMIP and MACCITY, the emissions values for the city of Istanbul was taken as available in the ECCAD database. Further information about the emissions inventory will be found in Table S10 of the supplement material.

Figure 11 shows the comparison of the estimated emissions of some speciated VOCs derived from observations and PMF for the road transport and the ones from the three global emission inventories downscaled to Istanbul megacity.

The total annual VOC anthropogenic emissions by global inventories are usually either within the same range by a factor of two to three for alkanes and aromatics or underestimated by an order of magnitude, especially for oxygenated compounds up to a factor of 58 for acetone by Edgar. These results are consistent with previous evaluations carried out in the Middle East (Salameh et al., 2016) and for northern mid latitude urban areas (Borbon et al., 2013). One exception is methanol in Edgar which is 2.2 times higher than our estimations from observations. This might be due to the inclusion of other alcohols in the methanol label in Edgar as discussed above. One should note that the emissions of CO and VOCs from MACCITY are usually lower than the ones from ACCMIP and EDGAR which can be explained by the different year of reference. The global emissions by inventories were not within the same year: 2000 for ACCMIP, 2014 for MACCITY and 2012 for Edgar. The CO emissions by inventories were compared for the same year. It was found that ACCMIP and MACCITY had the same CO emissions while the emissions in Edgar were two times lower than those from MACCITY and ACCMIP. In 2012, emissions of CO by Edgar was similar to the ones of MACCITY.

The evaluation of the road transport emissions (Figure 11.d) is limited to the compounds from the unburned fuel fraction; while there is still an underestimation by the emission inventories except for benzene, the differences are lower than for all anthropogenic emissions. The differences never exceed a factor of 12.1 (pentanes). Again, the differences for pentanes should be seen as a lower limit because of the number of measured pentanes which are limited to n-pentane and isopentane.

While these results provide a first detailed evaluation of VOC annual emissions by global emission inventories, they are based on a limited period of observations in September 2014 (2 weeks). Additional VOC observations at different periods of the year including the heating and non-heating period will be very useful to strengthen this first evaluation by taking into account the seasonal variability of emissions. However, they confirm the urgent need in updating global emission inventories by taking into account regional specific emissions.

4 Conclusion

VOC measurements were performed in Istanbul (Turkey) at an urban site in Besiktas in September 2014. The VOC measurements instruments include an AIRMOVOC GC-FID and a PTRMS at the super site completed with sorbent tubes and canisters within the megacity close to major emission sources. 23 of the 70 NMHCs quantified were continuously collected at the urban site.

During the intense field campaign, three periods had been selected from the meteorological parameters analysis and limited by two transitional periods. VOC variabilities were driven by the meteorological conditions observed, with higher concentrations during period 2 (under continental influence) and lower concentrations during period 1 and 3 (under marine influence). Also, most of the VOC were characterized by an increased in concentrations at night and early morning and lower concentrations during the day.

The average composition of VOC is mainly composed of OVOC which represent 43.9 % of the total VOC mixing ratio observed), followed by alkanes (26.33 %), aromatic compounds (20.66 %), alkenes (4.81 %), terpenes (3.44 %) and acetonitrile (0.84 %). The average atmospheric composition of anthropogenic VOC is similar to those observed in European megacities like Paris and London, suggesting the impact of traffic emissions for those compounds. However, multiple evidences of the impact of sources other than traffic like industrial activities under continental and south-southwesterly wind regimes or ship emissions on IVOC loads have been found. This evidence was also observed in the time series analysis where the influence of multiple sources other than traffic was also suggested.

Time series + diurnal profiles analyses suggest the influence of multiple sources other than traffic on VOC concentrations at the supersite and likely industrial and/or port activities.

Five factors have been extracted by the model and then compared to source profiles established by off-line near-source measurements. These results also confirmed that road transport is not the dominant source by only explaining 15.8 % (factor 5) of measured VOC concentrations, differing to the local emission inventory. Other factors as sources resolved by the model were Toluene (14.2 %), a Biogenic terpenes (7.8 %), a Natural gas evaporation (25.9 %, mainly composed of butanes) and a last factor characterized by Mixed regional emissions (36.3 % and composed of most of the species). Evaluating the PMF results, there is no evidence of the impact of ship emissions on VOC distribution. It is also shown that the commonly used ship emission tracer derived from $PM_{2.5}$ composition should be used with cautious.

Several sensitivity tests on PMF results based on input data have been carried out to evaluate the effect of the time resolution when combining different instrumentation measurements. Sensitivity tests also analyzed the impacts due to the number of missing values and the number of species integrated in each model run as well as the impact of interpolation on input data. While some sensitivity tests are less performant than the reference run, they all showed that the same factors are identified even though their relative contributions could be slightly modified.

Considering our results and knowing that the measurement period was quite short, long-term measurements at different time of the year will be valuable to assess the seasonality effect on source contributions in Istanbul.

Emission ratios (ER) of VOC relative to carbon monoxide (CO) were calculated and compared to that of many megacities. The emission ratios determined in Istanbul was found to be usually higher than the ones of other cities. These ER have then been used to evaluate three global emission inventories: MACCity, ACCMIP and EDGAR. The results showed that the total annual VOC anthropogenic emissions by global inventories are usually either within the same range by a factor of two to three for alkanes and aromatics or underestimated by an order of magnitude, especially for oxygenated compounds. For the road transport emissions, there is still an underestimation by global inventories except for benzene.

Even though these results provide a first detailed evaluation of VOC annual emissions by global emission inventories in Istanbul, measurements are carried out on a limited period of time (2 weeks). Thus, longer measurement period at different seasons of the year will be very useful to strengthen and complete these results.

Author contribution

Baye Thera is a PhD student; she is responsible for the data analysis presented work, Pamela Dominutti supported the data analysis, Fatma Öztürk was the Turkish PI of the TRANSEMED-Istanbul campaign. She dealt with the implementation of the super site and the aerosol measurements, Thérèse Salameh supported the PMF output analysis, Stéphane Sauvage was one of the French partner of the project ; he took part to the field campaign and supervised the analysis of VOC samples at the laboratory, Charbel Afif was the Lebanese partner of the project ; he took part of the field campaign for trace gas analysis and to the scientific discussions, Banu Çetin is one of the Turkish partner ; together with Fatma Ozturk she was in charge of the supersite implementation and took part to the field campaign, Cécile Gaimoz was in charge of the trace gas measurements 675 (GCFID, PTRMS) on the field and chromatogram's treatment, Melek Keleş is a PhD student ; she took in charge the PM measurements on the field and their analysis at the laboratory, Stéphanie Evan implemented the FLEXPART model and Agnès Borbon is the PI of the TRANSEMED project. She coordinates the project and supervises Baye Thera's PhD.

Acknowledgement: The field campaign in Istanbul was supported by the ENVIMED/MISTRALS 2013 call. This work is also part of the ChArMEx program. ChArMEx is the atmospheric component of the French multidisciplinary program MISTRALS (Mediterranean Integrated Studies at Regional and Local Scales). ChArMEx-France was principally funded by INSU, ADEME, ANR, CNES, CTC (Corsica region), EU/FEDER, Météo-France, and CEA. This study is also partly supported by the Scientific and Technological Research Council of Turkey (TUBITAK) with the project number of 113Y025. Moreover, the grant provided by Bolu Abant Izzet Baysal University (BAIBU) Scientific Research Projects Coordination Office (BAP) are also acknowledged for grant number of 2015.09.02.825.

References

Agrawal, H., Malloy, Q. G. J., Welch, W. A., Wayne Miller, J., and Cocker, D. R.: In-use gaseous and particulate matter emissions from a modern ocean going container vessel, Atmos. Environ., 42, 5504–5510, https://doi.org/10.1016/j.atmosenv.2008.02.053, 2008.

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., Fronval, I., 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., 14, 10439-10464, https://doi.org/10.5194/acp-14-10439-2014, 2014.

Atkinson, R.: Atmospheric chemistry of VOCs and NOx, Atmos. Environ, 34, 2063–2101, https://doi.org/10.1016/S1352-2310(99)00460-4, 2000.

Batterman, S., Hatzivasilis, G., and Jia, C.: Concentrations and emissions of gasoline and other vapors from residential vehicle garages, Atmos. Environ, 40, 1828-1844, https://www.sciencedirect.com/science/article/pii/S1352231005010812, 2006.

Batterman, S., Su, F.C., Li, S., Mukherjee, B., and Jia, C.,: Personal exposure to mixtures of volatile organic compounds: modeling and further analysis of the RIOPA Data, Res. Rep. Health Eff. Inst., 181, 3–63, Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/25145040, 2014.

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., 16, 11961-11989, https://doi.org/10.5194/acp-16-11961-2016, 2016.

Bon, D. M., Ulbrich, I. M., de Gouw, J. A., Warneke, C., Kuster, W. C., Alexander, M. L., Baker, A., Beyersdorf, A. J., Blake, D., Fall, R., Jimenez, J. L., Herndon, S. C., Huey, L. G., Knighton, W. B., Ortega, J., Springston, S., and Vargas, O.: Measurements of volatile organic compounds at a suburban ground site (T1) in Mexico City during the MILAGRO 2006 campaign: measurement comparison, emission ratios, and source attribution, Atmos. Chem. Phys., 11, 2399-2421, https://doi.org/10.5194/acp-11-2399-2011, 2011.

Borbon, A., Gilman, J. B., Kuster, W. C., Grand, N., Chevaillier, S., Colomb, A., Dolgorouky, C., Gros, V., Lopez, M., Sarda-Esteve, R., Holloway, J., Stutz, J., Petetin, H., McKeen, S., Beekmann, M., Warneke, C., Parrish, D. D., and de Gouw, J. A.: Emission ratios of anthropogenic volatile organic compounds in northern mid-latitude megacities: Observations versus emission inventories in Los Angeles and Paris, J. Geophys. Res. Atmos., 118, 2041–2057, https://doi.org/10.1002/jgrd.50059, 2013.

Borbon, A., Boynard, A., Salameh, T., Baudic, A., Gros, V., Gauduin, J., Perrussel, O., and Pallares, C.: Is Traffic Still an Important Emitter of Monoaromatic Organic Compounds in European Urban Areas?, Environ. Sci. Technol., 52, 513–521. https://doi.org/10.1021/acs.est.7b01408, 2018.

Bozkurt, Z., Özden, Ö., Dö, T., Artun, G., and Gaga, E. O.: Atmospheric concentrations of SO2, NO2 , ozone and VOCs in Düzce, Turkey using passive air samplers : Sources, spatial and seasonal variations and health risk estimation, APR, 1146–1156, https://doi.org/10.1016/j.apr.2018.05.001, 2018.

Brioude, J., Arnold, D., Stohl, A., Cassiani, M., Morton, D., Seibert, P., Angevine, W., Evan, S., Dingwell, A., Fast, J. D., Easter, R. C., Pisso, I., Burkhart, J., and Wotawa, G.: The Lagrangian particle dispersion model FLEXPART-WRF version 3.1, Geosci. Model Dev., 6, 1889-1904, https://doi.org/10.5194/gmd-6-1889-2013, 2013.

Brocco, D., Fratarcangeli, R., Lepore, L., Petricca, M., and Ventrone, I.: Determination of aromatic hydrocarbons in urban air of Rome, Atmos. Environ, 31, 557–566, https://doi.org/10.1016/S1352-2310(96)00226-9, 1997.

Brown, S. G., Frankel, A., and Hafner, H. R.: Source apportionment of VOCs in the Los Angeles area using positive matrix factorization, Atmos. Environ, 41, 227–237, https://doi.org/10.1016/J.ATMOSENV.2006.08.021, 2007.

Buzcu, B., and Fraser, M. P.: Source identification and apportionment of volatile organic compounds in Houston, TX, Atmos. Environ., 40, 2385–2400, https://doi.org/10.1016/j.atmosenv.2005.12.020, 2006.

Civan, M. Y., Elbir, T., Seyfioglu, R., Kuntasal, Ö. O., Bayram, A., Dogan, G., Yurdakul, S., Andiç, O.,Müezzinoglu, A.,Sofuoglu, S. C., Pekey, H.,Pekey, B., Bozlaker, A., Odabasi, M., and Tuncel, G.: Spatial and temporal variations in atmospheric VOCs , NO 2 , SO 2 , and O3 concentrations at a heavily industrialized region in Western Turkey , and assessment of the carcinogenic risk levels of benzene, Atmos. Environ., 103, 102–113, http://dx.doi.org/10.1016/j.atmosenv.2014.12.031, 2015.

Crippa, M., Guizzardi, D., Muntean, M., Schaaf, E., Dentener, F., van Aardenne, J. A., Monni, S., Doering, U., Olivier, J. G. J., Pagliari, V., and Janssens-Maenhout, G.: Gridded emissions of air pollutants for the period 1970–2012 within EDGAR v4.3.2, Earth Syst. Sci. Data, 10, 1987-2013, https://doi.org/10.5194/essd-10-1987-2018, 2018.

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, J. Geophys. Res., 110, D16305, https://doi.org/10.1029/2004JD005623, 2005.

de Gouw, J. A., Gilman, J. B., Kim, S. W., Lerner, B. M., Isaacman-VanWertz, G., McDonald, B. C., Alvarez, S. L., Dusanter, S., Stutz, J., Graus, M., Griffith, S. M., Kuster, W. C., Lefer, B. L., Rappenglück, B., Roberts, J. M., Stevens, P. S., Thalman, R., Veres, P. R., Volkamer, R., Warneke, C., Washenfelder, R. A., and Young, C. J.: Chemistry of Volatile Organic Compounds in the Los Angeles basin: Nighttime Removal of Alkenes and Determination of Emission Ratios, J. Geophys. Res. Atmos., 122, 11,843-11,861, https://doi.org/10.1002/2017JD027459, 2017.

de Gouw, J. A., Gilman, J. B., Kim, S. W., Lerner, B. M., Isaacman-VanWertz, G., McDonald, B. C., Alvarez, S. L., Dusanter, S., Stutz, J., Graus, M., Griffith, S. M., Kuster, W. C., Lefer, B. L., Rappenglück, B., Roberts, J. M., Stevens, P. S., Thalman, R., Veres, P. R., Volkamer, R., Warneke, C., Washenfelder, R. A. and Young, C. J.:Chemistry of Volatile Organic Compounds in the Los Angeles Basin: Formation of Oxygenated Compounds and Determination of Emission Ratios, J. Geophys. Res. Atmos., 123, 2298–2319, https://doi.org/10.1002/2017JD027976, 2018.

Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., and Locoge, N.: Origin and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus), Atmos. Chem. Phys., 17, 11355-11388, https://doi.org/10.5194/acp-17-11355-2017, 2017.

Demir, S., Saral, A., Išik, D., Akyildiz, A., Levent Kuzu, S., Mert, S., Demir, G., and Goncaloğlu, B. I.: Characterization of ambient volatile organic compounds and their diurnal variations in Istanbul, Turkey, FRESEN. ENVIRON. BULL., 20, 2951–2958, 2011.

Detournay, A., Sauvage, S., Locoge, N., Gaudion, V., Leonardis, T., Fronval, I., Kaluzny, P., and Galloo, J.-C.: Development of a sampling method for the simultaneous monitoring of straight-chain alkanes, straight-chain saturated carbonyl compounds and monoterpenes in remote areas, J. Environ. Monit., 13, 983–990, https://doi.org/10.1039/c0em00354a, 2011.

Dominutti, P. A., Nogueira, T., Borbon, A., Andrade, M. de F., and 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, 142, 371–382, https://doi.org/10.1016/j.atmosenv.2016.08.008, 2016.

Dumanoglu, Y., Kara, M., Altiok, H., Odabasi, M., Elbir, T., and Bayram, A.: Spatial and seasonal variation and source apportionment of volatile organic compounds (VOCs) in a heavily industrialized region, Atmos. Environ., 98, 168–178, https://doi.org/10.1016/J.ATMOSENV.2014.08.048, 2014.

Elbir, T., Cetin, B., Cetin, E., Bayram, A., and Odabasi, M.: Characterization of Volatile Organic Compounds (VOCs) and Their Sources in the Air of Izmir, Turkey, Environ. Monit. Assess., 133, 149–160, https://doi.org/10.1007/s10661-006-9568-z, 2007.

Ferm, M., De Santis, F., and Varotsos, C.: Nitric acid measurements in connection with corrosion studies, Atmos. Environ., 39, 6664–6672, https://doi.org/10.1016/J.ATMOSENV.2005.07.044, 2005.

Filella, I., and Peñuelas, J.: Daily, weekly, and seasonal time courses of VOC concentrations in a semi-urban area near Barcelona, Atmos. Environ., 40, 7752–7769, https://doi.org/10.1016/j.atmosenv.2006.08.002, 2006.

Finlayson-Pitts, B. J., and Pitts, J. N.: Chemistry of the Upper and Lower Atmosphere Theory, Experiments, and Applications, Academic Press, available at: http://www.sciencedirect.com/science/book/9780122570605, 2000.

Fuentes, J. D., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J. W., Ciccioli, P., Lamb, B., Geron, C., Gu, L., Guenther, A., Sharkey, T.D., and Stockwell, W.: Biogenic Hydrocarbons in the Atmospheric Boundary Layer: A Review. Bulletin of the American Meteorological Society, 81, 1537–1575, https://doi.org/10.1175/1520-0477(2000)081<1537:BHITAB>2.3.CO;2, 2000.

Fuzzi, S., Andreae, M. O., Huebert, B. J., Kulmala, M., Bond, T. C., Boy, M., Doherty, S. J., Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.M., Lohmann, U., Russell, L. M., and Pöschl, U.: Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, Atmos. Chem. Phys., 6, 2017-2038, https://doi.org/10.5194/acp-6-2017-2006, 2006.

Gaimoz, C., Sauvage, S., Gros, V., Herrmann, F., Williams, J., Locoge, N., Perrusel, O., Bonsang, B., d'Argouges, O., Sarda-Estève, R., and Sciare, J.: Volatile organic compounds sources in Paris in spring 2007. Part II: source apportionment using positive matrix factorization, Environ. Chem., 8, 91, https://doi.org/10.1071/EN10067, 2011.

Gelencsér, A., Siszler, K., and Hlavay, J.: Toluene-benzene concentration ratio as a tool for characterizing the distance from vehicular emission sources, Environ. Sci. Technol., 31, 2869–2872. https://doi.org/10.1021/es970004c, 1997.

Geron, C., Guenther, A., Sharkey, T., and Arnts, R. R.: Temporal variability in basal isoprene emission factor, Tree Physiology, 20, 799–805, https://doi.org/10.1093/treephys/20.12.799, 2000.

Goldstein, A., and Galbally, I.: Known and unexplored organic constituents in the earth's atmosphere, 1514–1527, Retrieved from http://pubs.acs.org/doi/pdf/10.1021/es072476p, 2007.

Goldstein, A. H., Fan, S. M., Goulden, M. L., Munger, J. W., and Wofsy, S. C: Emissions of ethene, propene, and 1 -butene by a midlatitude forest, J. Geophys. Res. Atmos., 101, 9149–9157, https://doi.org/10.1029/96JD00334, 1996.

Goldstein, A. H., and Schade, G. W.: Quantifying biogenic and anthropogenic contributions to acetone mixing ratios in a rural environment, Atmos. Environ, 34, 4997–5006, https://doi.org/10.1016/S1352-2310(00)00321-6, 2000.

Granier, C., Bessagnet, B., Bond, T., D'Angiola, A., Denier van der Gon, H., Frost, G. J., Heil, A., Kaiser, J. W., Kinne, S., Klimont, Z., Kloster, S., Lamarque, J-F., Liousse, C., Masui, T., Meleux, F., Mieville, A., Ohara, T., Raut, J-C., Riahi, K., Schultz, M. G., Smith, S. J., Thompson, A., Aardenne, J. V., van der Werf, G. R., and van Vuuren, D. P.: Evolution of anthropogenic and biomass burning emissions of air pollutants at global and regional scales during the 1980–2010 period, Climatic Change, 109, 163–190, https://doi.org/10.1007/s10584-011-0154-1, 2011.

Grice, S., Stedman, J., Kent, A., Hobson, M., Norris, J., Abbott, J., and Cooke, S.: Recent trends and projections of primary NO2 emissions in Europe, Atmos. Environ, 43, 2154–2167, https://doi.org/10.1016/j.atmosenv.2009.01.019, 2009.

Harrison, D., Hunter, M., Lewis, A., Seakins, P., Nunes, T., and Pio, C.: Isoprene and monoterpene emission from the coniferous species Abies Borisii-regis—implications for regional air chemistry in Greece, Atmos. Environ, 35, 4687–4698, https://doi.org/10.1016/S1352-2310(01)00092-9, 2001.

Heeb, N., Forss, A., Bach, C., Reimann, S., Herzog, A., and Jäckle, H.: A comparison of benzene, toluene and C2-benzenes mixing ratios in automotive exhaust and in the suburban atmosphere during the introduction of catalytic, Atmos. Environ., 34, 3103–3116, https://doi.org/10.1016/S1352-2310(99)00446-X, 2000.

Hester, Ronald E. and Harrison, Roy M. (ed.): Volatile organic compounds in the atmosphere, Royal Society of Chemistry, 1995.

,Holzinger, R., Wameke, C., Hansel, A., Jordan, A., Lindinger, W., Scharffe, D. H., Schade, G., and Crutzen, P. J.: Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide, Geophys. Res. Lett., 26, 1161–1164. https://doi.org/10.1029/1999GL900156, 1999.

Huang, Y. S., and Hsieh, C. C.: Ambient volatile organic compound presence in the highly urbanized city: source apportionment and emission position, Atmos. Environ., 206, 45–59, https://doi.org/10.1016/J.ATMOSENV.2019.02.046, 2019.

İm, U., Tayanç, M., and Yenigün, O.: Interaction patterns of major photochemical pollutants in Istanbul, Turkey, Atmos. Res., 89, 382–390, https://doi.org/10.1016/J.ATMOSRES.2008.03.015, 2008.

Isakson, J., Persson, T. A., and Selin Lindgren, E.: Identification and assessment of ship emissions and their effects in the harbour of Göteborg, Sweden, Atmos. Environ, 35, 3659–3666, https://doi.org/10.1016/S1352-2310(00)00528-8, 2001.

Kalabokas, P., Bartzis, J. G., Bomboi, T., Ciccioli, P., Cieslik, S., Dlugi, R., Foster, P., Kotzias, D., and Steinbrecher, R.: Ambient atmospheric trace gas concentrations and meteorological parameters during the first BEMA measuring campaign on May 1994 at Castelporziano, Italy, Atmos. Environ, 31, 67–77, https://doi.org/10.1016/S1352-2310(97)00075-7, 1997.

Kaltsonoudis, C., Kostenidou, E., Florou, K., Psichoudaki, M., and Pandis, S. N.: Temporal variability and sources of VOCs in urban areas of the eastern Mediterranean, Atmos. Chem. Phys., 16, 14825-14842, https://doi.org/10.5194/acp-16-14825-2016, 2016.

Kesselmeier, J., and Staudt, M.: Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology and Ecology, J. Atmos. Chem., 33, 23–88, https://doi.org/10.1023/A:1006127516791, 1999.

Keuken, M. P., Roemer, M. G. M., Zandveld, P., Verbeek, R. P., and Velders, G. J. M.: Trends in primary NO2 and exhaust PM emissions from road traffic for the period 2000–2020 and implications for air quality and health in the Netherlands, Atmos. Environ, 54, 313–319, https://doi.org/10.1016/J.ATMOSENV.2012.02.009, 2012.

Koçak, M., Theodosi, C., Zarmpas, P., Im, U., Bougiatioti, A., Yenigun, O., and Mihalopoulos, N.: Particulate matter (PM10) in Istanbul: Origin, source areas and potential impact on surrounding regions, Atmos. Environ, 45, 6891–6900, https://doi.org/10.1016/j.atmosenv.2010.10.007, 2011.

Koppmann, R. (ed.).: Volatile organic compounds in the atmosphere, Blackwell Pub., 2007.

Kousoulidou, M., Ntziachristos, L., Mellios, G., and Samaras, Z.: Road-transport emission projections to 2020 in European urban environments, Atmos. Environ, 42, 7465–7475, https://doi.org/10.1016/j.atmosenv.2008.06.002, 2008.

Kuntasal, Ö. O., Kılavuz, S. A., Karman, D., Wang, D., and Tuncel, G.: C5–C12 volatile organic compounds at roadside, residential, and background locations in Ankara, Turkey: Temporal and spatial variations and sources, J. Air. Waste. Manage. Assoc., 63, 1148–1162, https://doi.org/10.1080/10962247.2013.804012, 2013.

Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Van Aardenne, J., Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, V., Riahi, K., and van Vuuren, D. P.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, Atmos. Chem. Phys., 10, 7017-7039, https://doi.org/10.5194/acp-10-7017-2010, 2010.

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., 8, 2313-2332, https://doi.org/10.5194/acp-8-2313-2008, 2008.

Lee, C., Martin, R. V., van Donkelaar, A., Lee, H., Dickerson, R. R., Hains, J. C., Krotkov, N., Richter, A., Vinnikov, A., and Schwab, J. J.: SO2 emissions and lifetimes: Estimates from inverse modeling using in situ and global, space-based (SCIAMACHY and OMI) observations, J. Geophys. Res., 116, D06304, https://doi.org/10.1029/2010JD014758, 2011.

Lee, E., Chan, C. K., and Paatero, P.: Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong, Atmos. Environ, 33, 3201–3212, https://doi.org/10.1016/S1352-2310(99)00113-2, 1999.

Lee, S. C., Chiu, M. Y., Ho, K. F., Zou, S. C., and Wang, X.: Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong. Chemosphere, 48, 375–382, https://doi.org/10.1016/S0045-6535(02)00040-1, 2002.

Lelieveld, J., Hadjinicolaou, P., Kostopoulou, E., Chenoweth, J., El Maayar, M., Giannakopoulos, C., Hannides, C., Lange, M. A., Tanarhte, M., Tyrlis, E., and Xoplaki, E.: Climate change and impacts in the Eastern Mediterranean and the Middle East. Climatic Change, 114, 667–687, https://doi.org/10.1007/s10584-012-0418-4, 2012.

Liao, H.T., Yau, Y.C., Huang, C.S., Chen, N., Chow, J.C., Watson, J.G., Tsai, S.W., Chou, C.C.K., and Wu, C.F.: Source apportionment of urban air pollutants using constrained receptor models with a priori profile information, Environ. Pollut., 227,323–333, https://doi.org/10.1016/J.ENVPOL.2017.04.071, 2017.

Macdonald, R. C., and Fall, R.: Acetone emission from conifer buds, Phytochemistry, 34, 991–994, https://doi.org/10.1016/S0031-9422(00)90700-3, 1993.

McDonald, Brian C.,de Gouw, Joost A., Gilman, J. B., Jathar, Shantanu H., Akherati, Ali, Cappa, Christopher D., Jimenez, Jose L., Julia, Lee-Taylor, Hayes, Patrick L., McKeen, Stuart A., Cui, Yu Yan, Kim, Si-Wan, Gentner, Drew R., Isaacman-VanWertz, Gabriel, Goldstein, Allen H., Harley, Robert A., Frost, Gregory J., Roberts, James M., Ryerson, Thomas B., and Trainer, M.: Volatile chemical products emerging as largest petrochemical source of urban organic emissions, Science, 764(February), 760–764, 10.1126/science.aaq0524, 2018.

Markakis, K., Im, U., Unal, A., Melas, D., Yenigun, O., and Incecik, S.: Compilation of a GIS based high spatially and temporally resolved emission inventory for the greater Istanbul area, Atmos. Pollut. Res., 3, 112–125. https://doi.org/10.5094/APR.2012.011, 2012.

Matson, P., Lohse, K. A., and Hall, S. J.: The Globalization of Nitrogen Deposition: Consequences for Terrestrial Ecosystems, AMBIO: J. Hum. Environ. Syst., 31, 113–119, https://doi.org/10.1579/0044-7447-31.2.113, 2002.

Mazzei, F., D'Alessandro, A., Lucarelli, F., Nava, S., Prati, P., Valli, G., and Vecchi, R.: Characterization of particulate matter sources in an urban environment, Sci. Total. Environ., 401, 81–89, https://doi.org/10.1016/j.scitotenv.2008.03.008, 2008.

Millet, D. B., Guenther, A., Siegel, D. A., Nelson, N. B., Singh, H. B., de Gouw, J. A., Warneke, C., Williams, J., Eerdekens, G., Sinha, V., Karl, T., Flocke, F., Apel, E., Riemer, D. D., Palmer, P. I., and Barkley, M.: Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations, Atmos. Chem. Phys., 10, 3405-3425, https://doi.org/10.5194/acp-10-3405-2010, 2010.

Muezzinoglu, A., Odabasi, M., and Onat, L.: Volatile organic compounds in the air of Izmir, Turkey, Atmos. Environ., 35, 753–760, https://doi.org/10.1016/S1352-2310(00)00420-9, 2001.

Müller, J.-F.: Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases, J. Geophys. Res., 97, 3787, https://doi.org/10.1029/91JD02757, 1992.

Na, G., Kim, Y., and Kim, Y.: Concentrations of C2~C9 Volatile Organic Compounds in Ambient Air in Seoul, Journal of Korean Society for Atmospheric Environment, 14, 95-106, Retrieved from http://www.koreascience.or.kr/article/ArticleFullRecord.jsp?cn=DGHGBJ_1998_v14n2_95, 1998.

Nel, A.: Atmosphere. Air pollution-related illness: effects of particles, Science (New York, N.Y.), 308, 804–806. https://doi.org/10.1126/science.1108752, 2005.

Norris, G.: EPA Positive Matrix Factorization (PMF) 3.0 Fundamentals & User Guide, US, Environmental Protection Agency. http://www.epa.gov/heasd/products/pmf/pmf.html, 2008.

Owen, S., Boissard, C., Street, R. A., Duckham, S. C., Csiky, O., and Hewitt, C. N.: Screening of 18 Mediterranean plant species for volatile organic compound emissions. Atmos. Environ, 31, 101–117, https://doi.org/10.1016/S1352-2310(97)00078-2, 1997.

Paatero, P., Eberly, S., Brown, S. G., and Norris, G. A.: Methods for estimating uncertainty in factor analytic solutions, Atmos. Meas. Tech., 7, 781–797, https://doi.org/10.5194/amt-7-781-2014, 2014.

Paatero, P., and Hopke, P. K.: Discarding or downweighting high-noise variables in factor analytic models, Analytica Chimica Acta, 490, 277–289, https://doi.org/10.1016/S0003-2670(02)01643-4, 2003.

Pandolfi, M., Gonzalez-Castanedo, Y., Alastuey, A., de la Rosa, J. D., Mantilla, E., de la Campa, A. S., Querol, X., Pey, J., Amato, F., Moreno, T.: Source apportionment of PM10 and PM2.5 at multiple sites in the strait of Gibraltar by PMF: impact of shipping emissions. Environ. Sci. Pollut. Res., 18, 260–269, https://doi.org/10.1007/s11356-010-0373-4, 2011.

Pekey, B., and Hande, Y.: The use of passive sampling to monitor spatial trends of volatile organic compounds (VOCs) at an industrial city of Turkey, 97, 213–219, https://doi.org/10.1016/j.microc.2010.09.006, 2011.

Pey, J., Pérez, N., Cortés, J., Alastuey, A., and Querol, X.: Chemical fingerprint and impact of shipping emissions over a western Mediterranean metropolis: Primary and aged contributions, Sci. Total. Environ., 463–464, 497–507, https://doi.org/10.1016/J.SCITOTENV.2013.06.061, 2013.

Pozzer, A., Zimmermann, P., Doering, U. M., van Aardenne, J., Tost, H., Dentener, F., Janssens-Maenhout, G., and Lelieveld, J.: Effects of business-as-usual anthropogenic emissions on air quality, Atmos. Chem. Phys., 12, 6915–6937. https://doi.org/10.5194/acp-12-6915-2012, 2012.

Primerano, P., Marino, G., Di Pasquale, S., Mavilia, L., and Corigliano, F.: Possible alteration of monuments caused by particles emitted into the atmosphere carrying strong primary acidity, Atmos. Environ., 34, 3889–3896, https://doi.org/10.1016/S1352-2310(00)00183-7, 2000.

Salameh, T., Afif, C., Sauvage, S., Borbon, A., and Locoge, N.: Speciation of non-methane hydrocarbons (NMHCs) from anthropogenic sources in Beirut, Lebanon. Environ. Sci. Pollut. Res., 21, 10867–10877, https://doi.org/10.1007/s11356-014-2978-5, 2014.

Salameh T., Sauvage, S., Afif, C., Borbon, A., Léonardis, T., Brioude, J., Waked, A., and 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., http://dx.doi.org/10.1071/EN14154, 2015.

Salameh, T., Sauvage, S., Afif, C., Borbon, A., and Locoge, N.: Source apportionment vs. emission inventories of non-methane hydrocarbons (NMHC) in an urban area of the Middle East: Local and global perspectives, Atmos. Chem. Phys., 16, 3595–3607, https://doi.org/10.5194/acp-16-3595-2016, 2016.

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., 17, 193–209, https://doi.org/10.5194/acp-17-193-2017, 2017.

Schade, G. W., Solomon, S. J., Dellwik, E., Pilegaard, K., and Ladstätter-Weissenmayer, A.: Methanol and other VOC fluxes from a Danish beech forest during late springtime, Biogeochemistry, 106, 337–355, https://doi.org/10.1007/s10533-010-9515-5, 2011.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: from air pollution to climate change, John Wiley & Sons, 2016.

Sigsby, J. E., Tejada, S., Ray, W., Lang, J. M., and Duncan, J. W.: Volatile organic compound emissions from 46 in-use passenger cars, Environ. Sci. Technol., 21, 466–475, https://doi.org/10.1021/es00159a007, 1987.

Steiner, A. H., and Goldstein, A. L.: Biogenic VOCs. Volatile organic compounds in the atmosphere, 82-128, 2007.

Varotsos, C., Tzanis, C. and Cracknell, A.: The enhanced deterioration of the cultural heritage monuments due to air pollution, Environ. Sci. Pollut. Res., 16, 590-592, https://doi.org/10.1007/s11356-009-0114-8, 2009.

Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I. S. A., and Tarrasón, L.: Evolution of NOx emissions in Europe with focus on road transport control measures, Atmos. Chem. Phys., 9, 1503–1520, https://doi.org/10.5194/acp-9-1503-2009, 2009.

Viana, M., Hammingh, P., Colette, A., Querol, X., Degraeuwe, B., Vlieger, I. de, and van Aardenne, J. : Impact of maritime transport emissions on coastal air quality in Europe, Atmos. Environ., 90, 96–105, https://doi.org/10.1016/J.ATMOSENV.2014.03.046, 2014.

von Schneidemesser, E., Monks, P. S., and Plass-Duelmer, C.: Global comparison of VOC and CO observations in urban areas, Atmos. Environ., 44, 5053–5064, https://doi.org/10.1016/j.atmosenv.2010.09.010, 2010.

Warneke, C., McKeen, S. 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. Atmos., 112, https://doi.org/10.1029/2006JD007930, 2007.

WHO. (2005). Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide. World Health Organization, Geneva, Switzerland.

WHO | Air pollution. (2018). WHO. Retrieved from http://www.who.int/airpollution/en/

Xiao, Q., Li, M., Liu, H., Fu, M., Deng, F., Lv, Z., Man, H., Jin, X., Liu, S., and He, K.: Characteristics of marine shipping emissions at berth: profiles for particulate matter and volatile organic compounds, Atmos. Chem. Phys., 18, 9527-9545, https://doi.org/10.5194/acp-18-9527-2018, 2018.

Yáñez-Serrano, A. M., Nölscher, A. C., Bourtsoukidis, E., Derstroff, B., Zannoni, N., Gros, V., Lanza, M., Brito, J., Noe, S. M., House, E., Hewitt, C. N., Langford, B., Nemitz, E., Behrendt, T., Williams, J., Artaxo, P., Andreae, M. O., and Kesselmeier, J.: Atmospheric mixing ratios of methyl ethyl ketone (2-butanone) in tropical, boreal, temperate and marine environments, Atmos. Chem. Phys., 16, 10965-10984, https://doi.org/10.5194/acp-16-10965-2016, 2016.

Yatkin, S., and Bayram, A.: Source apportionment of PM10 and PM2.5 using positive matrix factorization and chemical mass balance in Izmir, Turkey, Sci. Total. Environ., 390, 109–123, https://doi.org/10.1016/j.scitotenv.2007.08.059, 2008.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K., and Gouw, J. A. De.: Proton-Transfer-Reaction Mass Spectrometry : Applications in Atmospheric Sciences, 13187–13229, https://doi.org/10.1021/acs.chemrev.7b00325, 2017.

Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, J. Geophys. Res. Atmos., 117, D24302, https://doi.org/10.1029/2012JD018236, 2012.

Yurdakul, S., Civan, M., Kuntasal, Ö., Doğan, G., Pekey, H., and Tuncel, G.: Temporal variations of VOC concentrations in Bursa atmosphere, Atmos. Pollut. Res., 9, 189–206, https://doi.org/10.1016/j.apr.2017.09.004, 2018.

Yurdakul, S., Civan, M., Kuntasal, Ö. O., and Tuncel, G.: Temporal variations of BTX compounds in Bursa/Turkey atmosphere, International Journal Of Global Warming, 5, 326–344, 2013.

Yurdakul, S., Civan, M., and Tuncel, G.: Volatile organic compounds in suburban Ankara atmosphere, Turkey: Sources and variability, Atmos. Res., 120–121, 298–311, https://doi.org/10.1016/J.ATMOSRES.2012.09.015, 2013.

Table 1: Statistical summary of VOC concentrations (in ppbv) measured at the urban site of Besiktas from September 17th to September 30th. The initials N, GC, P, T and C stands for the number of samples and instruments measured by the GCFID, PTRMS, tubes and canisters respectively.

	Species	Min	25th percentile	Median	Mean	75th percentile	Max	σ	N/instrument
Alkanes	isobutane	0.11	0.47	0.69	0.96	1.04	7.68	0.88	549/GC
	n-butane	0.34	1.05	1.48	2.00	2.23	12.2	1.67	551/ GC
	isopentane	0.14	0.55	0.82	1.41	1.36	19.3	2.14	546/ GC
	n-pentane	0.07	0.20	0.30	0.55	0.56	7.50	0.82	544/ GC
	n-hexane	0.17	0.24	0.34	0.44	0.53	2.53	0.33	205/ GC
	n-heptane	0.08	0.09	0.13	0.21	0.22	1.23	0.20	166/ GC
	2-methyl-pentane	0.06	0.08	0.11	0.21	0.17	6.06	0.58	410/ GC
Alkenes	1,3-butadiene	0.11	0.13	0.15	0.19	0.21	0.71	0.11	126/ GC
	1-pentene	0.11	0.13	0.15	0.19	0.19	1.19	0.13	226/ GC
	isoprene	0.13	0.34	0.55	0.68	0.81	3.24	0.52	580/P
Aromatics	benzene	0.07	0.18	0.23	0.31	0.32	2.54	0.30	580/P
	toluene	0.16	0.83	1.25	2.27	2.38	23.5	2.92	580/P
	ethylbenzene	0.11	0.14	0.18	0.26	0.27	1.68	0.23	350/GC
	(m+p)-xylenes	0.20	0.46	0.63	0.85	0.93	6.74	0.77	530/GC
	o-xylene	0.13	0.20	0.27	0.38	0.41	3.17	0.38	424/GC
	C9 aromatics (m/z121)	0.07	0.24	0.33	0.45	0.48	3.31	0.44	580/P
Oxygenated compounds	methanol (m/z 33)	1.20	3.49	4.31	4.92	6.00	19.3	2.28	580/P
	acetaldehyde (m/z 45)	0.24	0.98	1.39	1.59	1.81	14.6	1.12	580/P
	acetone (m/z 59)	1.26	1.88	2.33	2.63	2.98	19.7	1.30	580/P
	MACR+MVK (m/z 73)	0.01	0.07	0.09	0.12	0.14	0.67	0.09	580/P
	MEK (m/z 71)	0.11	0.22	0.30	0.38	0.43	2.27	0.28	580/P
Nitrile	Acetonitrile (m/z 42)	0.09	0.14	0.17	0.18	0.20	0.68	0.06	580/P
Terpenes	Terpenes (m/z 137)	0.06	0.22	0.33	0.76	0.91	5.19	0.91	580/P

Table 2: Contributions of each factor on each sensitivity test (in percentage)

Scenario	**Reference run**	**All data (incl. night of 09/24**	**Only periods 1 & 3**	**Only period 2**	**missing values > 60% excluded**	**missing values > 30% excluded**	**No interpolation**
$\mathbf{r^2_{total}}$ **obs. vs mod.**	0.97	0.86	0.97	0.86	0.90	0.92	0.90
% of species with $\mathbf{r^2 \geq 0.5}$	82.6	56.5	65.2	60.9	65.0	70.6	65.2
F1. Toluene	14.2	14.8	13.4	8.9	15.4	16.4	14.0
F2. Terpenes	7.8	11.5	12.7	12.1	5.5	6.9	12.3
F3. NG evaporation	25.9	11.4	26.7	13.6	25.8	22.3	10.0
F4. Mixed emissions	36.3	47.7	38.2	45.5	40.2	42.7	43.6
F5. Road transport	15.8	14.5	9.1	19.8	13.1	11.8	20.2
Contributions							

Table 3: Urban VOC-to-CO emission ratios determined during Istanbul field campaign and compared to the ones determined in Los Angeles (North America), Paris (Europe), Mexico (Central America) and Beirut (Middle East) during previous field campaigns. Bolded values are the ones within a range of factor of +/- 2 between Istanbul and at least one other urban area.

VOC	Istanbul September 2014 mean ratio (pptv VOC [ppbv CO]$^{-1}$ This study	Los Angeles May-June 2010 (de Gouw et al., 2018; Borbon et al., 2013) (pptv[ppbvCO]$^{-1}$	Paris July 2009 (Borbon et al.,2013) (pptv[ppbvCO]$^{-1}$	Mexico March 2009 (Bon et al., 2011b) (pptv[ppbvCO]$^{-1}$	Beirut January 2012 (Salameh et al., 2017) (pptv[ppbvCO]$^{-1}$
isobutane	**9.74**	3.08	4.53	**7.2**	3.30
n-butane	**20.2**	4.42	**10.1**	**21.7**	6.70
Isopentane	**19.3**	8.69	**10.8**	3.3	5.30
n-pentane	8.87	3.26	3.08	2.5	1.10
n-hexane	8.06	1.13	1.15	1.49	0.90
n-heptane	**2.61**		**2.03**	0.36	0.40
2-methyl-pentane	3.55		1.29	1.33	1.20
1.3-butadiene	**0.64**	**0.35**	**0.39**	0.27	**0.50**
1-pentene	**1.51**			0.15	**1.40**
Benzene	**3.27**	1.30	1.07	1.21	**2.00**
Toluene	30.9	3.18	12.3	4.2	11.10
Ethylbenzene	**2.66**	0.57	0.95		**1.40**
(m+p)- xylenes	**8.98**	1.79	4.59		**4.80**
o-xylene	4.16	0.67	1.09		1.70
C9-aromatics	**5.10**			**2.8**	
Methanol	**35.9**	**21.2**		2.1	
Acetaldehyde	14.0	5.42		1.0	
Acetone	**15.2**	**11.6**		0.51	
MEK	4.69	0.88		0.29	

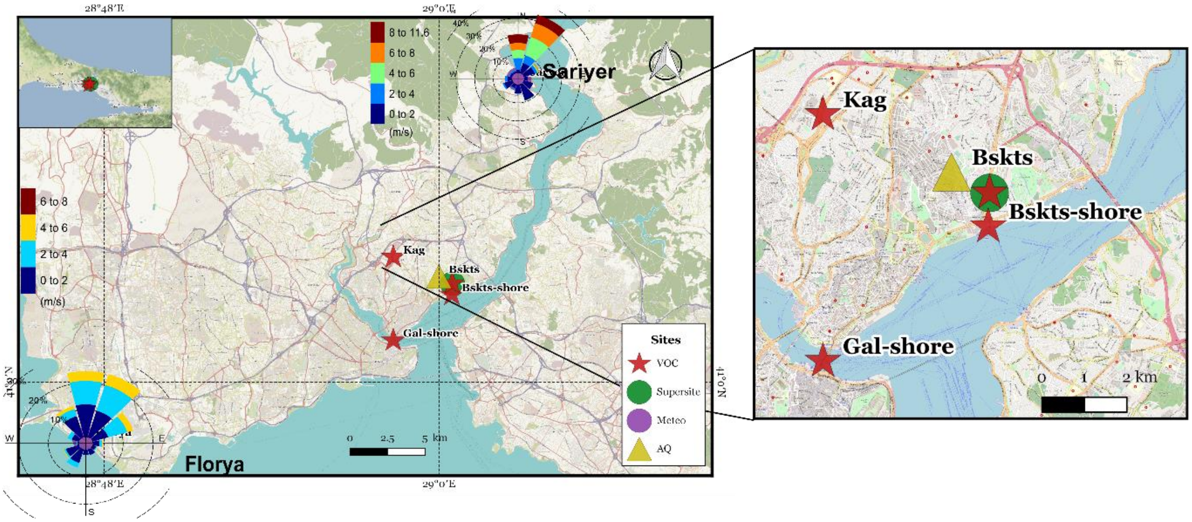
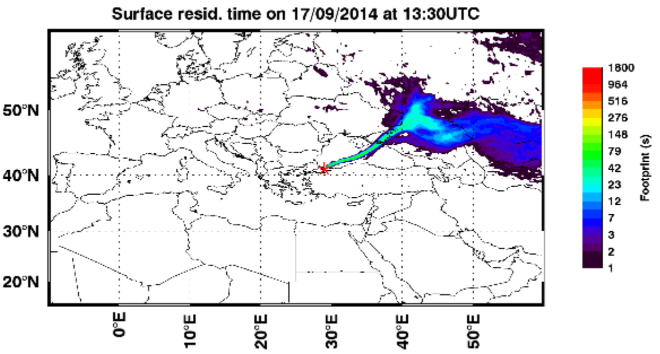
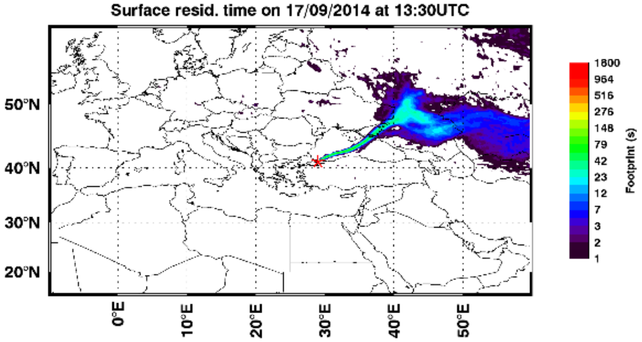


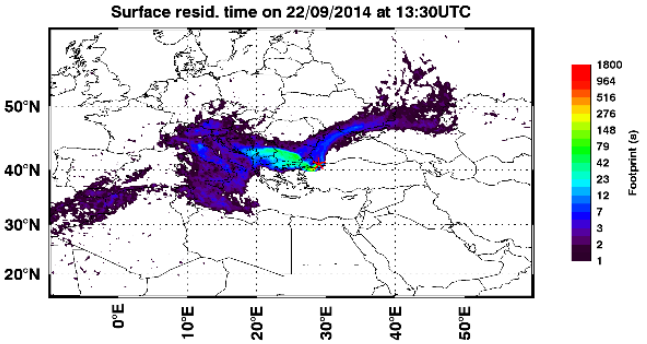
Figure 1: Different measuring sites during the TRANSEMED campaign: Besiktas (Bskts), Kagithane (Kag), Galata (Gal), Florya (Flo) and Sariyer (Sar) and wind roses at Florya and Sariyer stations

15/09-21/09: Period 1 **Marine influence from NNE (Black Sea and Russia)**	

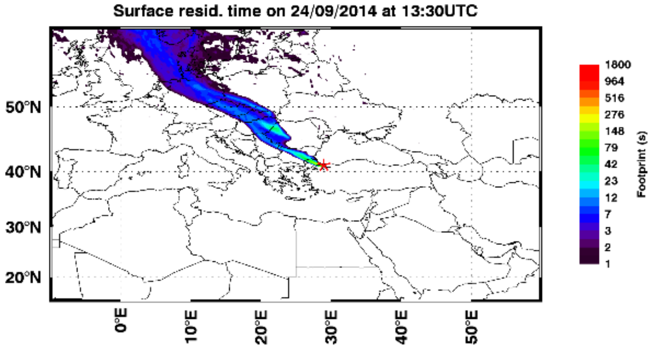
15/09-21/09: Period 1 - Marine From NNE (Black Sea and Russia)



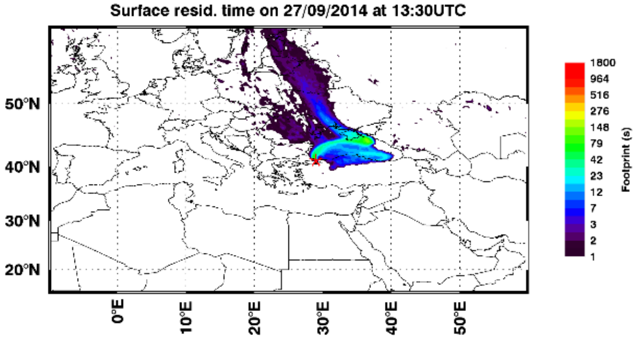
21/09-23/09: Transition period - Shift to SW (Marmara Sea - Southern Europe and Mediterranean)



23/09-26/09 : Period 2 Continental (Eastern and Northern Europe)



26/09-28/09: Transition period - Shift to NNE



28/09-30/09 : Period 3 - Marine - Black Sea, Ukraine, and Northern Europe

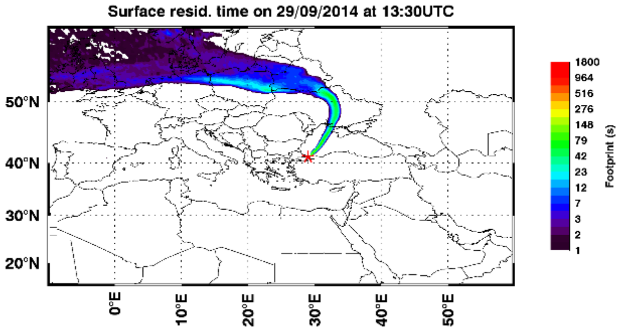


Figure 2: Surface residence time of representative air mass trajectories from FLEXPART model during the TRANSEMED-Istanbul campaign

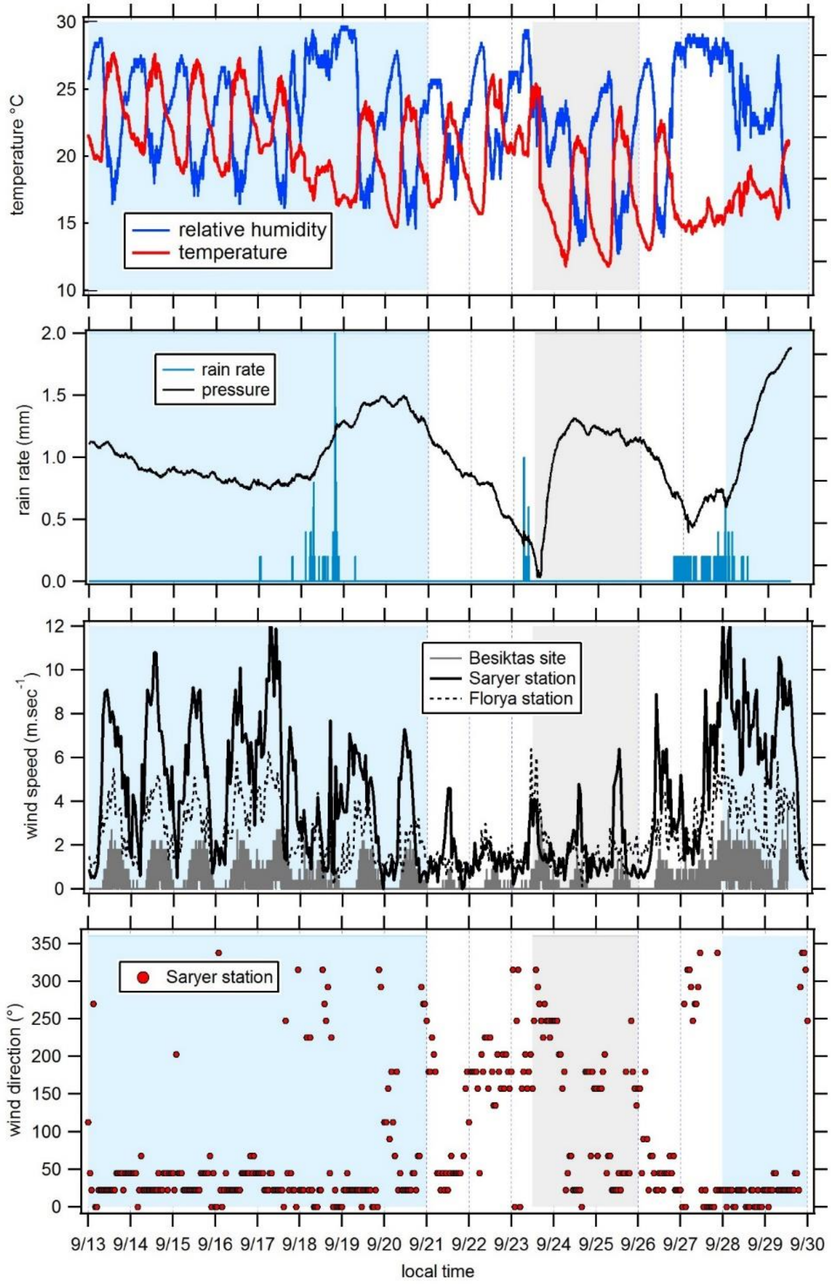


Figure 3: Variations of meteorological parameters at the super site of Besiktas. Wind speed were recorded in the stations of Florya and Sariyer. Wind direction displayed in this Figure were recorded in the station of Sariyer. Period 1 and 3 are in blue, transition periods are in white and period 2 is in grey.

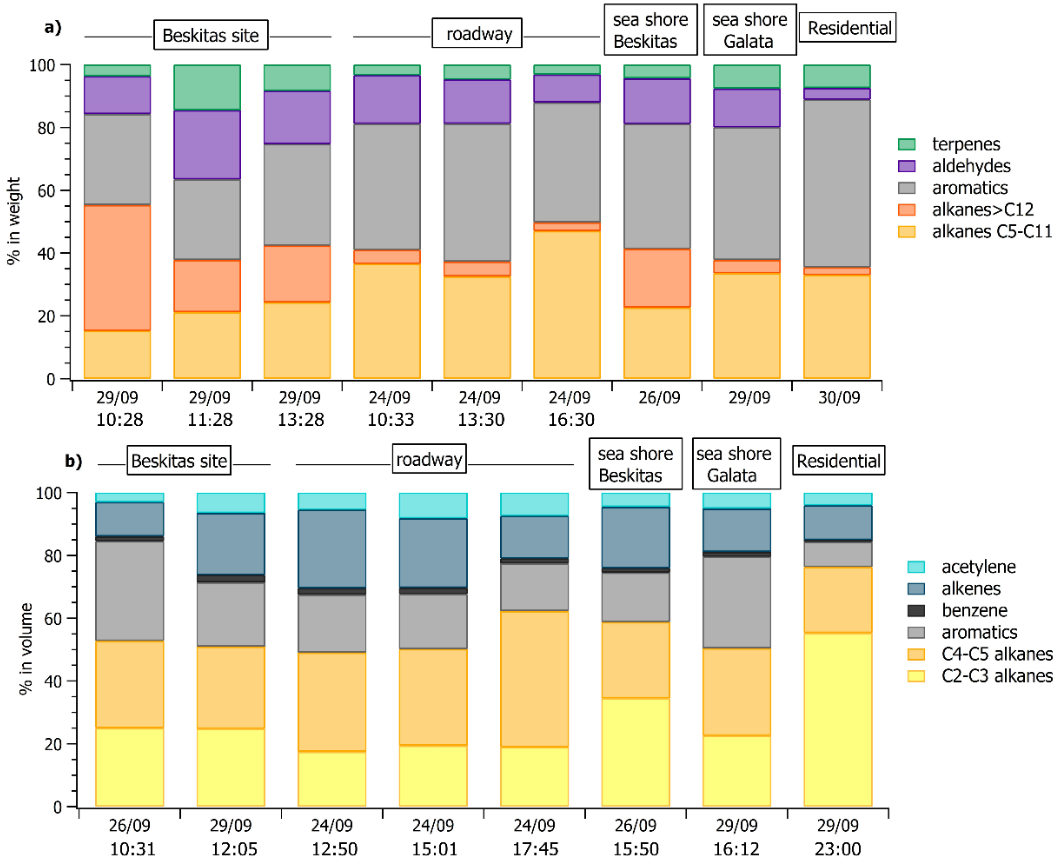
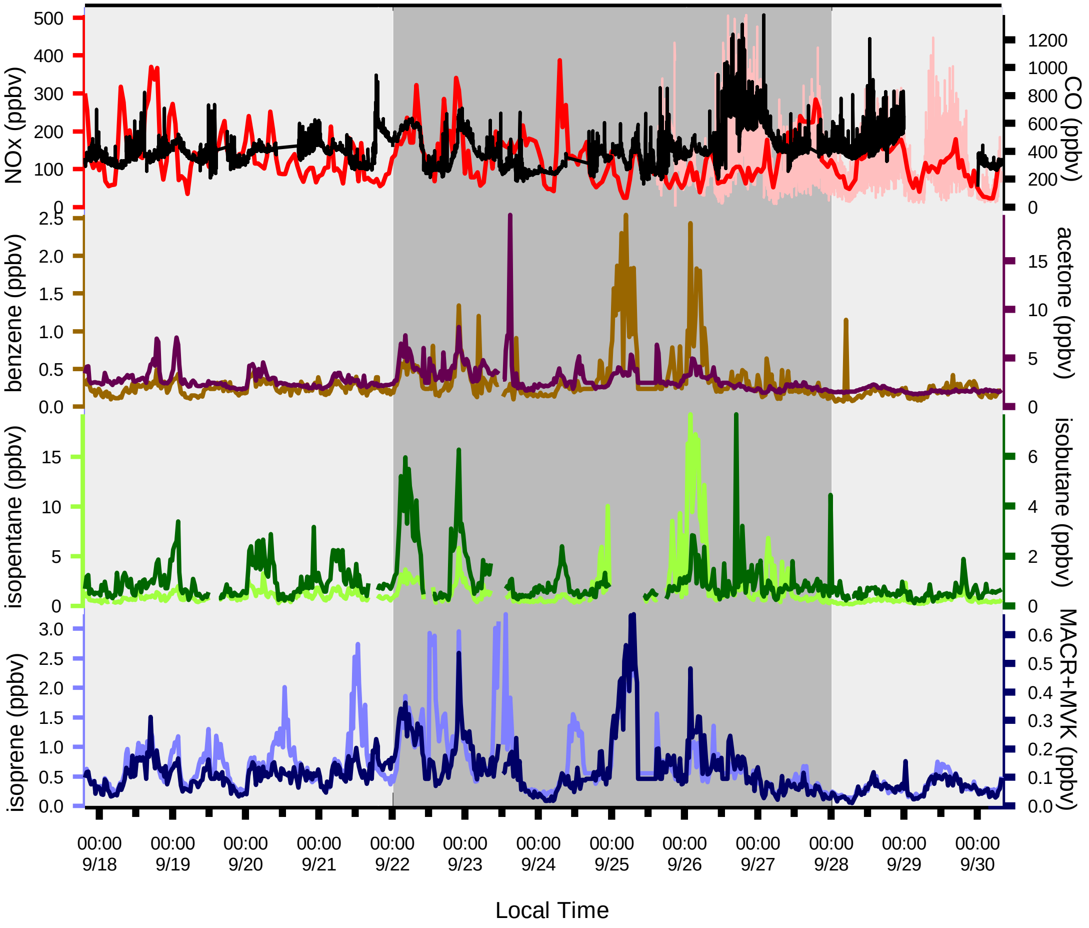


Figure 4: VOC composition at various locations in Istanbul from tubes (a) and canister (b) sampling.



1075

Figure 5: Time series of NO$_x$, CO and few VOC. Background colors represent the different periods relative to meteorological conditions (light grey period 1 and 3 and dark grey: period 2). Time series of NO$_x$ data from the super site are in pink and the ones from Besiktas site are in red.

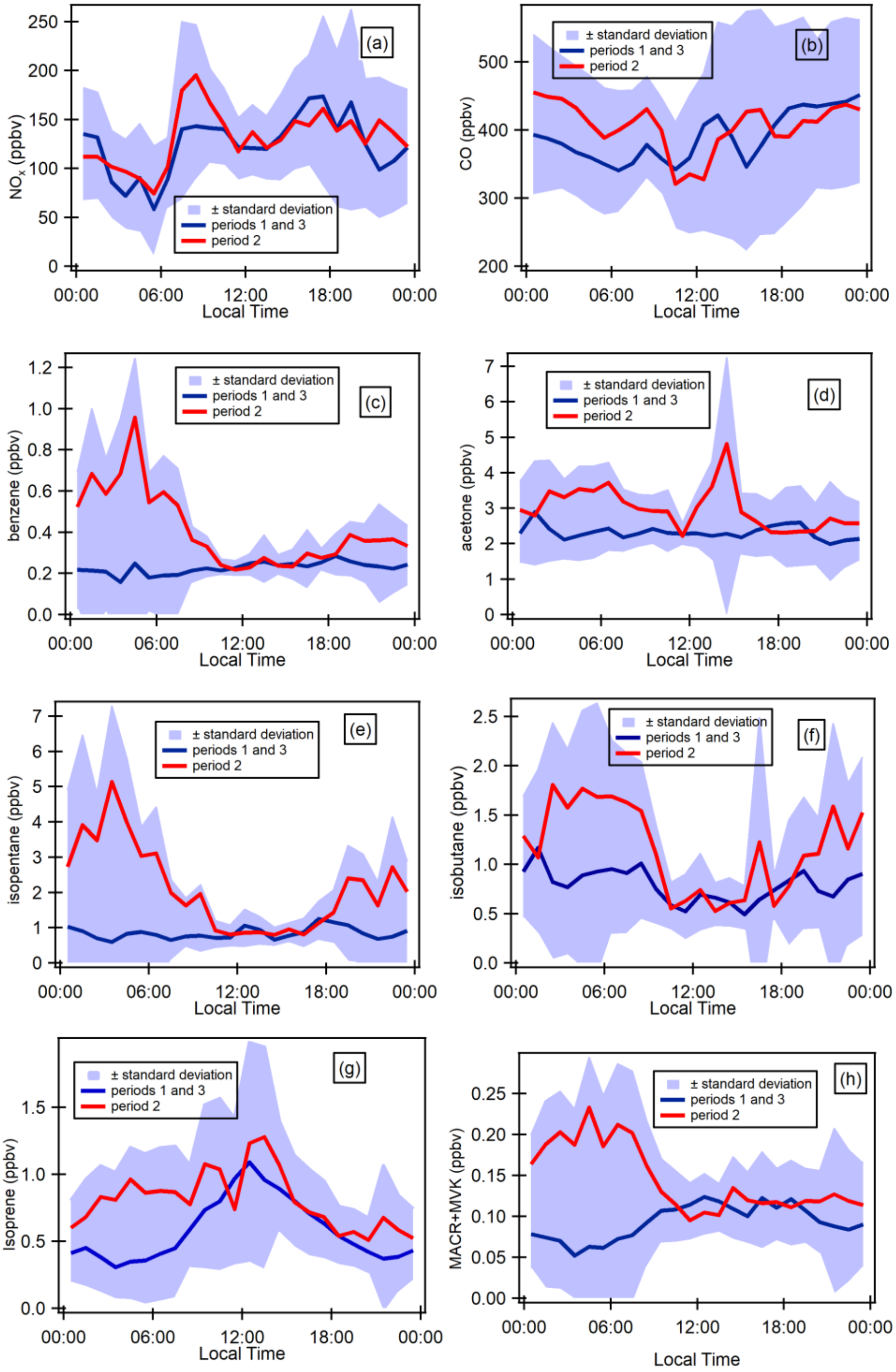


Figure 6: Diurnal profiles of some selected gaseous species (ppbv). Blue shaded-areas represent the minimum and maximum diurnal concentrations over all the measurement periods, blue lines, the average diurnal concentrations during period 1 and 3 and red lines the average concentrations during period 2.

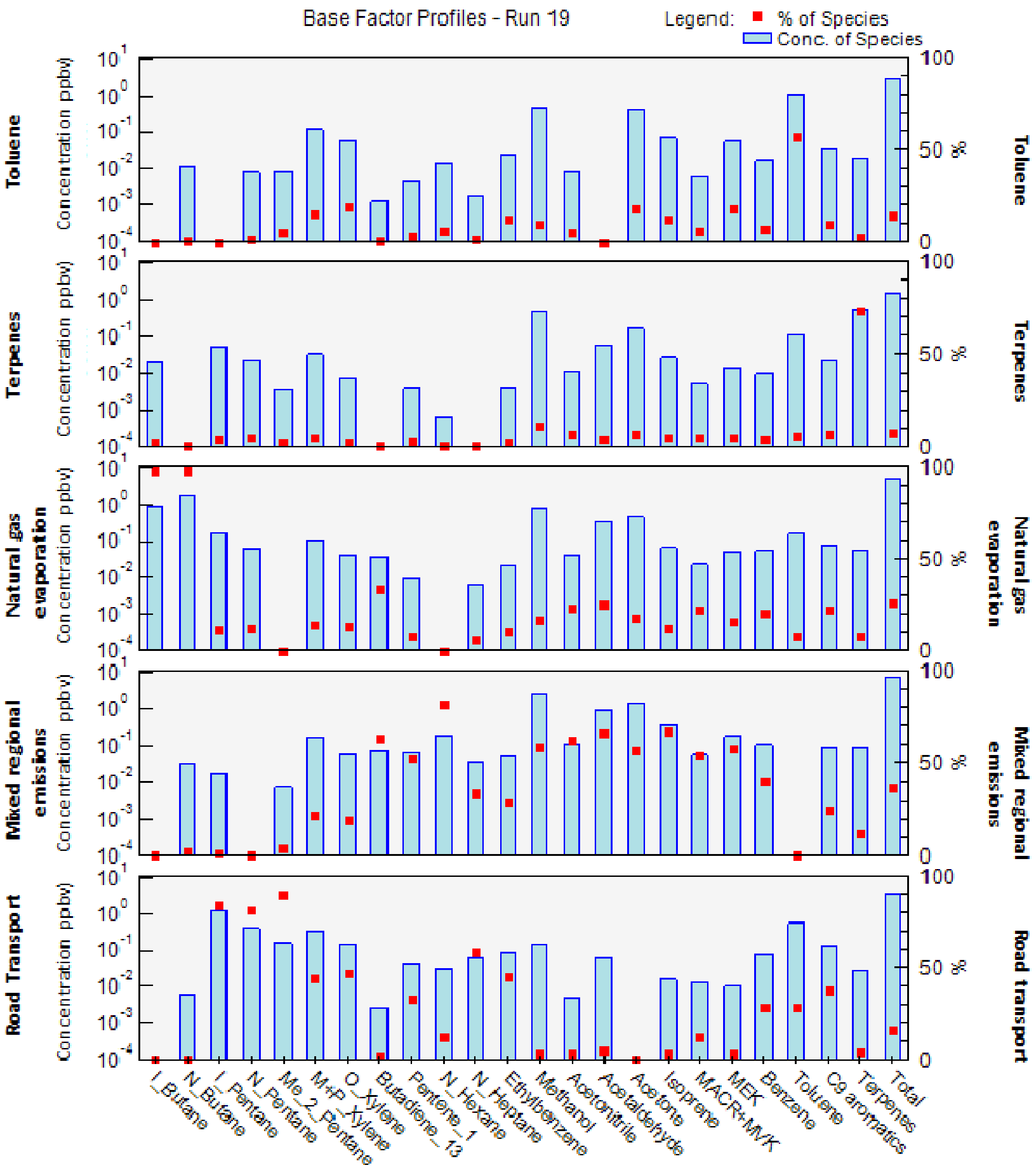


Figure 7: Source composition profiles of the PMF factors. The concentrations (ppbv) and the percent of each species apportioned to the factor are displayed as a pale blue bar and a red color box, respectively.

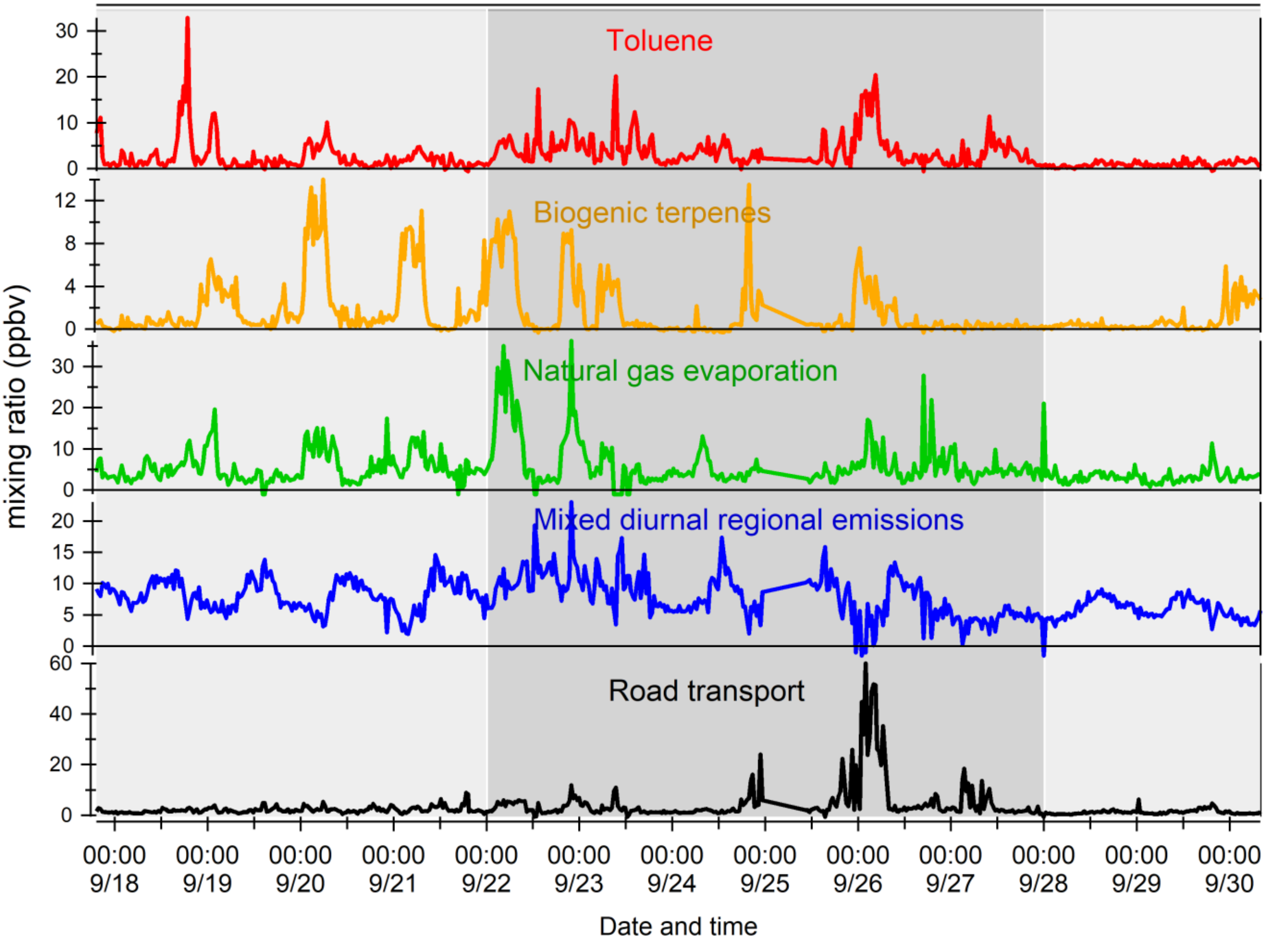


Figure 8: Time series of factors contributions (in ppbv) extracted from the PMF.

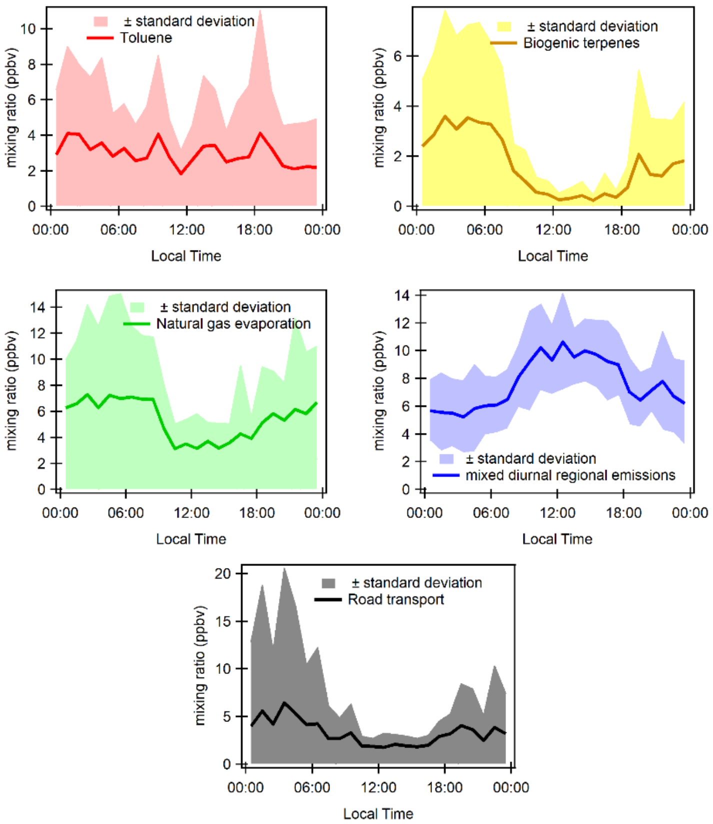


Figure 9: Diurnal variation of sources contributions (in ppbv)

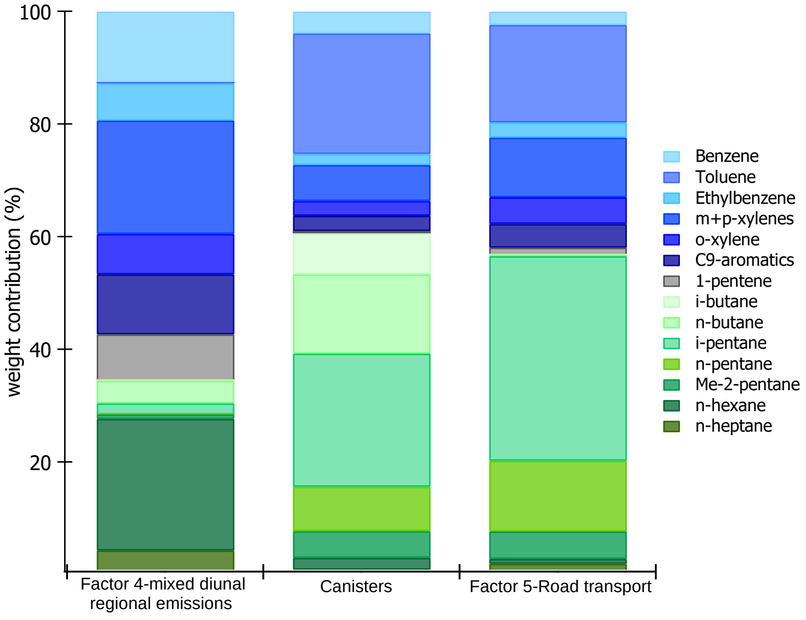


Figure 10: Comparison of speciated profiles issued from canisters (traffic source) and Factor 4 and 5 of PMF simulations. The species contributions are expressed in percentage volume

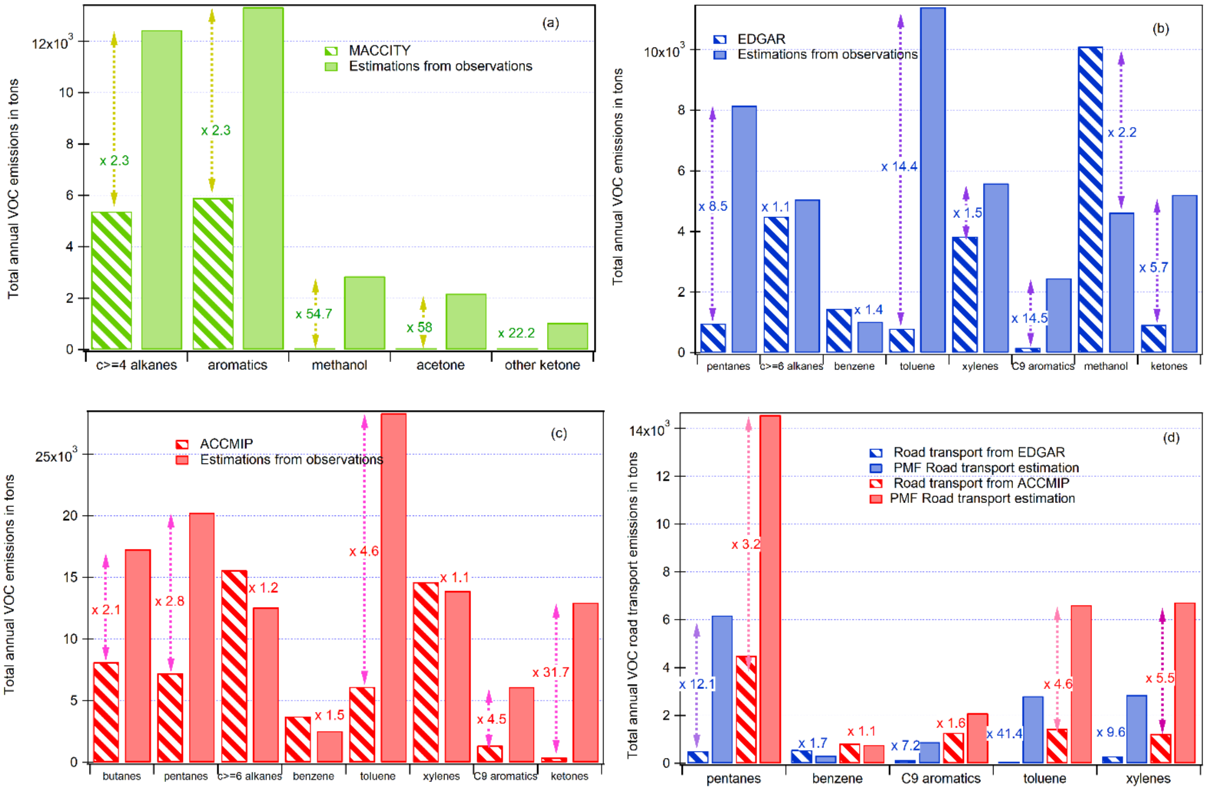


Figure 11: Comparison of the estimated emissions inventory from observations and PMF results and global emission inventories: a) MACCity, b) EDGAR, c) ACCMIP, d) Road transport for ACCMIP and EDGAR inventory.