Author response to all referees' comments on "Measurement report: 30 years of monitoring aromatic hydrocarbons (BTEX) at a suburban site in Europe"

We would like to thank the two reviewers for their time reviewing our manuscript and their valuable comments, which significantly enhanced the clarity of the paper. We have considered all comments carefully and present our point-by-point responses below (reviewer comments are in blue and author responses are in black).

Response to Referee #1

Major remarks

Based on the title of the paper I had the impression that the paper would be about BTEX only, but major parts of the paper deal with the relative contribution of BTEX with regard to the overall burden of VOCs in ambient air, for instance contribution to OFP and SOA formation (chapter 3), while marginal comments are made on the NMHC measurements beyond BTEX.

In response to the reviewer's remark, we changed the title to "Measurement report: 30 years of BTEX monitoring at a suburban site in Switzerland supported by additional urban VOC observations" for more clarity.

Neither their measurement details nor their speciation is mentioned. This is a major drawback of this paper, as it seems that OVOCs might have replaced BTEX, at least with regard to OFP.

Thanks for pointing this out. A dedicated subsection has been added in the Material and Method section: "VOC measurement with GC-FID in ZUE" with the following text:

" In addition to the BTEX measurement conducted with the GC-FID, VOC sampling with 1-hour resolution was conducted in ZUE using a GC-FID. Before 2023, OVOC monitoring was not routinely conducted in ZUE, thus a complete dataset including all VOCs quantified with our analytical system is only available for the years 2005, 2015, 2023, and 2024. An overview list with the VOCs measured in Zurich and their corresponding class is available in SI, Table S1. The sampling and analytical procedures used for the 2005 dataset are described in Lanz et al. (2008). The procedure for subsequent years is very similar to that for the 2005 dataset and is described below. The GC is equipped with two capillary columns connected via a Deans Switch (Restrictor DB-1, 2.48 m x 0.25 mm) and two FID detectors, enabling the simultaneous detection of alkane, alkene, alkyne, BTEX, terpene and OVOCs.

300 mL of ambient air from the main inlet passes through a glass trap maintained at -43°C to remove residual water and is subsequently trapped onto a multi-sorbent trap (U-T17O3P-2S, Markes international Ltd). The trap is then heated to 250°C for 5 min and the desorbed VOCs are transferred to the GC (7890B, Agilent Technologies). Alkane, alkene and alkyne are separated on a PLOT column (Al_2O_3, Na_2SO_4; 50 m × 0.53 mm x 10 µm) while BTEX, terpenes and OVOCs are separated on an OxyPLOT column (30 m × 0.53 mm x 10 µm). Calibration and QA/QC procedures follow the same protocol as described in section 2.2. If no standard is available for a given compound, its concentration is calculated according to the response factor of benzene in the calibration tank and to its effective carbon number (ECN) given in Sternberg (1962)."

Also, as the authors used full-fledged VOC data, at least for the years 2005, 2015, 2023, and 2024, they could perform source apportionment analysis and yield information about the change of potential emission sources for toluene.

We thank the reviewer for this remark. The focus of this manuscript is the long-term trend of BTEX in Zurich area. Source apportionment analysis, such as positive matrix factorization analysis, has previously been conducted in more detail in Zurich, using the 2005 dataset (cf Lanz et al., 2008) and compared to a dataset collected in 1993-1994. To highlight this long-term series on BTEX, we have chosen not to include source apportionment analysis. Currently, another publication focusing solely on Zurich's emissions using source apportionment analysis is in preparation, including an in-depth analysis of the VOCs measured in Zurich over different years.

In the subsection "T:B ratio changes over the years", a discussion point has been added referring to Lanz et al. (2008) as follows: " In the study of Lanz et al. (2008), a source apportionment analysis of VOCs was conducted in ZUE using data collected between 2005 and 2006 and the results were compared with source apportionment findings from 1993–1994. The increase in the T:B ratio has been notably attributed to the restriction of benzene content in gasoline between 1993 and 2006 (Lanz et al., 2008). Furthermore, toluene was mostly explained by the solvent use factor. Between 1993–1994 and 2005–2006, the relative contribution of the road traffic factor to total sources declined from 40 % (9.9 ppb) to 26 % (3.5 ppb), while the contribution from solvent use increased slightly from 18 % (4.5 ppb) to 20 % (2.7 ppb), highlighting the significant reduction in traffic-related emissions in ZUE over this period (Lanz et al., 2008). "

In L71 the authors mention measurements of total NMHC concentrations, NO_x and CO. Why do the authors not incorporate that wealth of data to support their findings? It would be interesting and easy to do to use these data sets to analyze for temporal trends during the same time period of the BTEX measurements. It would allow to determine how the fraction of BTEX vs NMHC changed from year to year, and whether trends of NO_x and CO showed the same degree of reduction as the BTEX and whether they support the authors' statement why the toluene/benzene ratio changed over time.

In response to this remark, total NHMC concentrations, NO_x and CO datasets have been used for the results and discussion section of this manuscript. We agree that those datasets have not been properly introduced. Thus, we added a description of the measurements in the Material and Methods section in the "BTEX measurement and ancillary data" subsection with the following text:

Ancillary data, including ambient temperature, total NMHC, nitrogen oxides (NO_x) and carbon monoxide (CO) concentrations are available from NABEL. Data from NABEL can be made available on request. Total NMHC concentration (ppm C) refers to the difference between total volatile hydrocarbons and methane concentrations measured simultaneously at the station with dedicated FID instruments (APHA-360 and APHA-370; HORIBA, Ltd.). As the carbon contribution of the oxygenated volatile compounds to total NMHC is lower than 1:1 due to the presence of oxygen, the same effective carbon number as the FID's response of the GC-FID analysis is used to calculate their contribution to total NMHC concentration. NO_x and CO measurements are performed using type-approved instruments in accordance with European Standards EN 14211 and EN 14626, respectively. CO observations at DUE are missing for the years 2000-2009.

Additionally, the yearly trend in total NHMC concentrations in parallel to those of BTEX has been added to Fig.1, panel B.

Fig, S4 has been added showing the yearly trends of CO and NO_x in ZUE and DUE. A description of yearly variations of CO and NO_x concentrations has been added in the subsection "Decrease in BTEX concentration from 1994" in the results and discussion section.

Potential reductions in combustion related emission processes should reflect in the NO_x and CO data. As CO is unrelated to solvent emissions, CO could be a better parameter than benzene or at least an additional approach to determine the supposed increasing contributions from solvents for toluene.

We thank the referee for this comment. We included the CO data in the T:B ratio change discussion with an additional figure in the SI as follows: "This seasonal shift is further supported by the relationship between T:B ratio and CO concentrations shown in Fig. S11, with elevated T:B ratios that diverge from CO concentrations in summer after 2000".

Minor remarks

L20-25: Some updated thorough NMHC source apportionment analysis have been done in complex urban areas using online NMHC measurement techniques and should be incorporated. You may want to consider some of these:

- Leuchner and Rappenglueck (2010): VOC Source-Receptor Relationships in Houston during TexAQS-II, Atmos. Environ., 44, 4056-4067, doi:10.1016/j.atmosenv.2009.02.029
- Ahmed et al. (2021): Source Apportionment of Volatile Organic Compounds, CO, SO_2 and Trace Metals in a Complex Urban Atmosphere, Environ. Adv., 6, DOI: 10.1016/j.envadv.2021.100127
- Sadeghi et al. (2022): Influence of seasonal variability on source characteristics of VOCs at Houston industrial area, Atmos. Env., 277, DOI: 10.1016/j.atmosenv.2022.119077

We agree with the reviewer that NHMC source apportionment analysis is an important asset for gaining further information on source emissions in urban areas, especially when many VOCs are available, as is the case with the VOC dataset of Zurich introduced in this manuscript. As mentioned above, we are currently conducting a thorough analysis of the NHMC source apportionment analysis in Zurich and decided not to include this analysis in this current manuscript. Nevertheless, we added the results from the study of Lanz et al. (2008), concerning the traffic-related and solvent use emissions conducted in Zurich, with the following text:

" Furthermore, toluene was mostly explained by the solvent use factor. Between 1993–1994 and 2005–2006, the relative contribution of the road traffic factor to total sources declined from 40% (9.9 ppb) to 26% (3.5 ppb), while the contribution from solvent use increased slightly from 18 % (4.5 ppb) to 20% (2.7 ppb), highlighting the significant reduction in traffic-related emissions in ZUE over this period (Lanz et al., 2008)."

L29: Ozone events are not necessarily confined to heatwaves. Wintertime ozone events have also been observed. Ozone events are primarily driven by the amount and kind of ozone precursors and the availability of solar radiation in combination with stagnant weather conditions.

In response to this remark, we changed this sentence for more precision to "Higher tropospheric ozone events, driven by abundant ozone precursors under stagnant meteorological conditions and sufficient solar radiation, can cause severe damage to human health and vegetation (Lippmann, 1991, Edwards et al., 2014)."

L59: What is really meant by “non-continuous sampling” here? Is it a different measurement technique and/or different temporal resolution, for instance once every day or once every week?

We agree that the sentence was not clear and that the non-continuous sampling was referring to sampling campaigns conducted at specific moments. As the years given in the same sentence suggest that the instrument was not running all the time at this station, we changed the sentence to:

"In addition, sampling of BTEX has been conducted in Zurich city at Kaserne Zurich, considered as an urban background site (ZUE, 47.378°N, 8.530°E; 409 m a.s.l.) from 1993 to 1994, from 2001 to 2017 and since 2022 with a GC-flame ionization detector (GC-FID) with 1-hour resolution." for more clarity.

L71: I did not see NO_x, CO or O_3 data incorporated in the discussions of the paper. So there is no real reason to mention them, unless they would be used in the data interpretation, which would strengthen the statements made in the paper. I assume that total NMHC data was used (e.g in L81). If this is true, the specifications of the total NMHC measurements should be described.

We incorporated the NO_x, CO and total NHMC data in the discussions of the paper as described in response to a previous comment above.

L81: It would be informative to see the long term trend of NMHCs in a similar way the authors present the BTEX data in Fig 1.

We agree with the reviewer that the long-term trend of NMHC can help to further understand the BTEX dataset in Dübendorf. Thus, a plot showing the long-term trends of total NMHC with the BTEX fraction has been added in Fig.1, panel B.

L85-86: What do the authors exactly mean by “strongest decrease”: (1) absolute decrease, (2) relative decrease, (3) annual decrease, or (4) the point when the annual decrease of BTX tends to become smaller? Depending on the definition, different years could be defined. From what I see is that the annual decrease of BTEX is about the similar magnitude until 2004, afterwards there is less annual decrease, for instance.

Thank you for raising that point! The description and discussion concerning Fig. 2 have been changed for more clarity with the following text:

"To visualize the evolution of BTEX concentrations in DUE over three decades, we grouped the data into four representative periods: the late 1990s (1994–2000) before the restriction of benzene content in gasoline and the introduction of the VOC incentive tax (Swiss Confederation, 1997), the early 2000s (2001–2010), the 2010s (2011–2020) and the most recent year available (2024) as shown in Fig. 2. Overall, a clear decrease in BTEX concentrations is observed since 1994 with the most significant reduction in concentrations occurring between the 1994-2000 and 2001-2010 periods, notably due to the regulations on VOC emissions implemented since 2000."

L88-89: I suggest to remove "calculated according to the territorial principle", as the information is thoroughly described in the subsequent part of this sentence.

This sentence has been corrected in the new version of the manuscript.

Fig 2 shows overall stronger seasonal variation for all of the BTEX compounds in the time frame 1994-2000 compared with the subsequent time periods. Why would this be the case? Apart from this I am not sure about the value of showing all the individual annual variations in these plots. It only makes the plots hard to decode.

We agree with the reviewer that in Fig. 2, due to the large span concentration over the years coupled with the overall low concentration measured in the last few years, the seasonal variations after 2000 are not well represented. To account for this, we added Fig. S9 to the SI where the monthly average values for the different periods selected in Fig. 2 are normalized to the maximal value of each period. In Fig S4, the seasonal pattern did not vary a lot with the typical winter peak and relatively low concentrations in summer. For more clarity, we removed the annual variations from Fig. 2. In the manuscript, Fig. S9 is mentioned as " Seasonal patterns remain consistent across all the periods as shown in Fig. S9 with the normalized BTEX concentrations with the typical winter peak and relatively low concentrations in summer."

L90-92: How do the authors know the specific source contributions for benzene? In case it is from the Swiss inventory, then please insert a corresponding reference. Otherwise, please justify these assumptions. Also, the statement made in this sentence should be accompanied by a statement about the overall trend in NMHC emissions. Otherwise, the reader would be misguided that emissions from wood combustion increased in absolute terms, unless this is what has happened.

Thank you for pointing this out. The specific source contributions for benzene are available from the Swiss inventory but we agree that the reference to this inventory was not well introduced. The reference was indicated as "(Bundesamt fur Umwelt (BAFU), 2023)" but it lacked clarity. It has been changed to the English abbreviation (FOEN) and was included more precisely in the revised manuscript. We changed this part to make it clearer and included the overall trend in NMHC emissions from the Swiss inventory as follows.

"Total NMHC emissions from the Swiss emission inventory, considering all emissions emitted within Switzerland from industry, households, transport and agriculture/forestry sectors, decreased by 75% between 1994 and 2022, from 220'232 t y^{-1} to 72'515 t y^{-1}. Over this period, the contributions from industry and transport declined from 56% to 47% and from 25% to 11%, respectively (FOEN, 2024). NMHC compounds subject to the Swiss incentive tax, including BTEX, and representing on average 46±2% of the total NMHC emissions during the same period, are dominated by the industry sector which contributed 87% in 1994 and remained stable after 2003 at 77±1%.

Benzene emissions reported in the Swiss emission inventory declined by 85% between 1994 and 2022, from 3'656 t y^{-1} to 564 t y^{-1} (Fig. 3; A; FOEN (202)). Benzene emissions are dominated by the transport sector, accounting for 70% in 1994 and 65% in 2022. Although emissions from the industry and household sectors have remained relatively stable since 2014 at 86 ± 5 t y^{-1} and 136 ± 11 t y^{-1} respectively, the decrease in transport emissions has increased the relative contribution of the household sector (including wood combustion) from 11% in 1994 to 20% in 2022 (FOEN, 2023)."

Fig 3: I guess the unit should be [t/year] for the x-axis in the left plot. I suggest to remove "calculated according to the territorial principle" in the figure caption.

Thanks for pointing out the units. The labels and the caption for Fig. 3 have been modified as suggested by the reviewer.

L93: It is either "concentrations" or "emissions", but not "concentrations emitted".

The wording has been changed to "concentrations measured at the suburban DUE station".

L95-96: I suggest the authors do some seasonal analysis similar to the plots shown in Fig. 2 to explore whether there might have been any significant seasonal deviations between these two sites, which eventually could help to explain the deviations.

As suggested by the reviewer, we conducted a seasonal analysis for benzene in DUE and ZUE to highlight the differences between both datasets. Discrepancies observed between datasets have been highlighted in Fig. S10 for more clarity. We removed the months from ZUE that were not overlapping between both stations to have a representative yearly average for comparison, which was the case in 2001 in January and February. The following text has been added in the manuscript:

"Discrepancies are observed between the modeled benzene emissions and measured benzene in Dübendorf between 2000 and 2005. Based on the long-term correlation between Zurich and Dübendorf since 1994 (Fig. 3, B), higher benzene concentrations would have been expected during the summer period in 2003 and 2004 in Dübendorf, as shown in Fig. S10."

L105 and following lines: There are some BTEX datasets from a similar central European city taken in years 1993-1997, including diurnal variations of BTEX ratios. Also references to other cities are made in this paper. It could be worthwile to compare the datasets and to see how both datasets agree for the early period of the Zurich time series.

- Rappenglueck and Fabian (1999): Non Methane Hydrocarbons (NMH,C) in the Greater Munich Area/Germany, Atmos. Environ., 33, 3843-3857

We agree with the reviewer that a comparison with other BTEX datasets collected in Europe since the 1990s is beneficial for this manuscript. Thus, we added a description of the BTEX series conducted in Germany at a traffic station and in UK at a suburban station as follows:

"The reduction in BTEX concentrations at DUE was also observed at other European monitoring sites for the same period. Long-term monitoring at the Augsburg Königsplatz traffic station in Germany has been conducted since 1995 (Bayerisches Landesamt für Umwelt, 2025). Between 1995 and 2023, the decrease in benzene and toluene concentrations was comparable to that observed at DUE, decreasing by 96 % from 3.6 ppb to 0.11 ppb and from 7.4 ppb to 0.27 ppb, respectively. A similar trend was observed at the London Eltham suburban station, where BTEX concentrations decreased on average by 90 % between 1995 and 2022, with benzene decreasing from 1.2 ppb to 0.12 ppb, toluene from 2.5 ppb to 0.20 ppb, ethylbenzene from 0.45 ppb to 0.043 ppb and xylene from 0.83 ppb to 0.086 ppb (Defra, 2025)"

L112: Why would biomass burning be negligible during winter between 8 and 9 am? It sounds like during other daytime hours in winter it would be non-negligible.

We agree that this sentence was misleading. For more clarity, we changed it to: "Thus, the winter T:B ratio was determined for each year during the morning rush hour in the winter (8-9am), when road traffic peaks and the morning CO concentrations are the highest. This time window provides a T:B ratio representative of traffic emissions with minimal influence from photochemical degradation. The contribution of biomass burning to T:B ratio at DUE is in general negligible, given the station’s proximity to the road and that biomass burning emissions occur predominantly in the evening (Qi et al., 2019)"

Equation 1: during what time of the day is the benzene data taken in the summer? Is it also between 8 and 9 am?

Thank you for raising this question! In the summer, the hourly benzene concentration is used to calculate the theoretical toluene concentration. As it lacked clarity, we added the following information: "Here, $\text{benzene}_{\text{summer}}$, corresponds to the hourly benzene concentration in summer and was used to estimate $\text{toluene}_{\text{th, summer}}$ from the winter T:B ratio."

L121-122: I think this could be further analyzed, when CO data is being considered in addition. I assume that traffic regulations would have an impact on both, CO and toluene, while solvent toluene emissions would be unrelated to CO.

Thank you for the suggestion. We had a closer look at the T:CO ratios in the summer and winter and T_{th}:CO as well. We added Fig. S13 with the following text: "For the period 1994-2000, the solvent contribution to toluene concentrations was estimated at 18 ± 14% and approximately doubled afterwards to 44 ± 17% for the period 2011-2020 as shown in Fig. 5. Since 2021, a lower solvent contribution has been observed (39 ±19 %), although this reduction is not statistically significant relative to 2011-2020. Future observations are required to confirm the decrease in solvent contribution after 2020 and may reflect either more controlled solvent-related toluene emissions or a shift in the dominant summertime sources of toluene at DUE. To investigate if $\text{toluene}_{th,summer}$ represents well toluene emitted from traffic emissions, the summer and winter T:CO ratios were investigated as shown in Fig. S13. Winter and summer ratios T:CO ratios are significantly different with 2.5-3.5 10^{-3} and 4.5-6.9 10^{-3}, respectively. The $\text{toluene}_{th,summer}$:$\text{CO}_{summer}$ ratio, which should be largely related to traffic emissions, shows significant differences across the periods: 4.9 ± 0.28 10^{-3}, 2.2 ± 0.15^{-3} and 3.1 ± 0.17 10^{-3} for 1994-2000, 2011-2020, > 2020. The difference in $\text{toluene}_{th,summer}$:$\text{CO}_{summer}$ ratios between 1994–2000 and the later periods is consistent with the implementation of VOC emission regulations for vehicles, as a larger decrease was observed for toluene relative to CO concentrations (Section 3.1). Additionally, $\text{toluene}_{th,summer}$:$\text{CO}_{summer}$ ratio is similar to the winter CO:T ratio, indicating that $\text{toluene}_{th,summer}$ concentrations represent well the toluene emissions from car exhaust."

L131-137: I was confused to see all of a sudden the availability of continuous measurements of speciated VOCs, including OVOCs. This dataset was not introduced at any point in the “Material and methods” sections. It appears that there have been four specific years for these measurements (2005, 2015, 2023, 2024). As those are continuous measurements, why just these four years? Are these complete years? It is a critical dataset and should be introduced accordingly. Also, in case you have full-fledged VOC data, you could do VOC emission source apportionment and elucidate the potential change in toluene emissions.

We agree with the reviewer that this dataset is not well introduced. Thus, we added in the introduction the following sentence: "Furthermore, this study integrates VOC measurements collected in parallel with BTEX monitoring in Zurich to relate BTEX concentrations to the overall composition of ambient VOCs.". A dedicated subsection in the Material and Methods section has been added with the title: " VOC measurements with GC-FID in ZUE"

In the past, OVOC measurement was not systematically conducted. For more clarity, we added the following text in the subsection mentioned above: "Prior to 2023, OVOC monitoring in ZUE was not routinely performed. Consequently, a complete dataset of all VOCs quantified with our analytical system is available only for April–December 2005 and the complete years 2015, 2023 and 2024."

L134-135: Why did the yearly NMHC average ambient air concentration increase from 2005 to 2024? At this point there was a lot of discussions about efficient BTEX reductions. Why would have OVOC concentrations increased drastically? What are those specific OVOCs?

The increase in the last few years in OVOC concentration has been observed at the few monitoring stations monitoring OVOCs. The discussion of the OVOC increase was not further extended in this manuscript to focus on the contribution of BTEX to the VOC mixture. Nevertheless, we added the details of the OVOC monitored in ZUE (Table S1), the concentration of each single OVOC measured and their contribution to OFP in ZUE (Fig. S14). References to the literature of the large contribution of OVOC to total VOC concentration has been added in the manuscript as follows: " Recent studies have shown that OVOCs are emerging as the predominant class of VOCs in ambient air across many regions (Ma et al., 2025; Borbon et al., 2024). This increase in OVOC concentrations is likely driven by a shift in source dominance with vehicle emissions decreasing while solvent and product use emissions have become a major source of OVOCs in (sub)urban areas (FOEN, 2024; Lanz et al., 2008; Legreid et al., 2007)."

L149: I think, it is either “low volatile” or “condensable”, but not “low-condensable”.

Thanks for pointing this out, we changed the wording to: "condensable organic vapors".

L160: The supposed ”significant increase in the contribution of solvent to the toluene concentrations” requires some more analysis.

For more clarity, we extended the discussion on the contribution of solvent to toluene concentrations and referred to the study from Lanz et al., 2008 mentioning the change in solvent use in ZUE, as mentioned above. Additionally, in the conclusion section, we changed the sentence to: "Changes in the T:B ratio, particularly in the summer following the restriction on benzene content in gasoline in 2000, indicate an increasing relative contribution from solvent use to toluene."

L162-164: Given the significant decrease in OFP by BTEX, which seems to be even less than for alkanes in 2024, it seems that BTEX are not a critical quantity for ozone formation any longer, whereas OVOCs are. And this looks like an important finding.

We agree with the reviewer that the importance of OVOCs in OFP has increased since 2015. We added an additional figure showing the single contribution of the OVOCs to OFP in Fig. S14 as well as the importance of OVOC monitoring which has been acknowledged in the conclusion section with the following sentence:

"In addition, OVOCs are becoming predominant in ambient air. Despite their relatively low MIR values, the cumulative contribution of individual OVOCs can significantly enhance ozone formation potential. Including OVOCs in addition to BTEX in the air quality monitoring programs is therefore essential for a representative composition of (sub)urban VOC mixtures in ambient air."

References

Bayerisches Landesamt für Umwelt: Messwertarchiv Luft – Immissionsmessungen, https://www.lfu.bayern.de/luft/immissionsmessungen/300messwertarchiv/index.htm, licensed under Creative Commons Attribution 4.0 International (CC BY 4.0), 2025

Borbon, A., Salameh, T., Sauvage, S. & Afif, C. Light oxygenated volatile organic compound concentrations in an Eastern Mediterranean urban atmosphere rivalling those in megacities. *Environmental Pollution* **350**, 123797 (2024).

Defra: UK Air Quality Archive, https://uk-air.defra.gov.uk/, © Crown 2025 copyright Defra via uk-air.defra.gov.uk. Licensed under the Open Government Licence (OGL), 2025.

Edwards et al., High winter ozone pollution from carbonyl photolysis in an oil and gas basin, Nature, 514, 351–354, https://doi.org/10.1038/nature13767, 2014.

Lanz, V. A. *et al.* Receptor modeling of C_2-C_7 hydrocarbon sources at an urban background site in Zurich, Switzerland: changes between 1993–1994 and 2005–2006. *Atmos. Chem. Phys.* **8**, 2313–2332 (2008).

Legreid, G. *et al.* Oxygenated volatile organic compounds (OVOCs) at an urban background site in Zürich (Europe): Seasonal variation and source allocation. *Atmospheric Environment* **41**, 8409–8423 (2007).

Ma, X., Liu, G. & Chen, J. PTR-QMS observation of OVOCs in an urban suburb of Guangzhou: seasonal characterization, source apportionment and regional transport. *Atmospheric Environment* **362**, 121589 (2025).

Qi, L. *et al.* Organic aerosol source apportionment in Zurich using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) – Part 2: Biomass burning influences in winter. *Atmospheric Chemistry and Physics* **19**, 8037–8062 (2019).

Author response to all referees' comments on "Measurement report: 30 years of monitoring aromatic hydrocarbons (BTEX) at a suburban site in Europe"

Response to Referee #2

The title: this work is solely based on measurements from Zurich (and surroundings) urban sites, so I think saying "Europe" is too vague and misleading, since there isn't any evaluation on the representativeness of Zurich over a large EU domain characterized by a high variety of urban settlements.

We changed the title to "Measurement report: 30 years of BTEX monitoring at a suburban site in Switzerland supported by additional urban VOC observations" for more clarity.

L43: "their background concentrations" I would mention that is referring to "urban background" since most of the data are from the DUE, ZUE and BER urban /sub-urban station; moreover it's not clear if and where the data from Bern and Beromunster have been used in the discussion.

We replaced the wording with "urban background concentration". A comparison with the other Swiss sites has been added as follows:

"At all the Swiss stations monitoring, a decrease in BTEX concentrations is observed (Fig. S8). Toluene remains the most abundant BTEX compounds. In ZUE, very similar BTEX concentration ranges and reduction as in DUE are observed between 1994 and 2024 with toluene concentration decreasing by 86% (from 2.5 ppb to 0.36ppb) and benzene concentration by 81% (from 0.91 ppb to 0.17 ppb). Between 2001 and 2024, ethylbenzene decreased by 82% (from 0.30 ppb to 0.05 ppb) and xylene by 78% (from 1.1 ppb to 0.26 ppb) in ZUE. BTEX concentrations in BER were overall higher due to the station's proximity to a busy road. In 2023, yearly average concentrations at BER reached 0.16ppb for benzene, 0.35ppb for toluene, 0.04ppb for ethylbenzene, and 0.20 ppb for xylene. Average BTEX concentrations at BER decreased by 71% between 2011 and 2023. Over the same period, benzene and toluene concentrations at DUE declined by 50% and 60%, respectively. In contrast, the rural BRM site showed much lower concentrations in 2024, with yearly average of 0.09 ppb for benzene, 0.17 ppb for toluene, 0.01 ppb for ethylbenzene and 0.04 ppb for xylene."

L75: even though is reported later, I would specify clarify here too that the "longest time series in Dubendorf" is actually only for BT and not EX;

Thank you for pointing this out! We agree that this sentence is misleading, therefore we changed the sentence to "At the suburban Dübendorf station, BTEX monitoring began in 1994. The longest continuous time series is available for benzene and toluene, while monitoring of ethylbenzene and xylenes was discontinued in 2011 due to their low concentrations."

L 80: "..for both compounds " I'll clarify again that you are looking for a correlation from the available measurements for the period 1994-2010, if I understood correctly the points reported on the graphs S3; in addition why in fig S2 only data from 1994 to 2000 are reported? Is the correlation evaluated based on this short time frame? could you explain better how the relative contribution is evaluated, I mean against which compound exactly? or the sum of the two BT? or what else?

We agree with the reviewer that the calculation was not well explained, thus we rephrased it to:

"Since no measurements of ethylbenzene and xylenes are available after 2011, their concentrations from 2011 onwards were estimated based on their average relative contributions to total BTEX concentrations derived from the measurement period 1994–2010 (Fig. S2). For this estimation, the yearly sum of benzene and toluene was used together with the known average relative fractions of ethylbenzene and xylenes determined before 2011."

We also noticed a mistake in Fig. S2 (now Fig. S3), where we considered data from 1994 to 2010 and not to 2000. The caption has been changed accordingly in the new version.

L81: authors mention the total NMHC concentrations but there isn't any other reference in the text about these measurements (at least in the supplementary?)

We agree that the information on total NHMC concentrations was not well introduced. Thus, we added a description of the measurements in the Material and Methods section in the "BTEX measurement and ancillary data" subsection with the following text:

"Total NMHC concentration (ppm C) refers to the difference between total volatile hydrocarbons and methane concentrations measured simultaneously at the station with a dedicated FID (APHA-370; HORIBA, Ltd.). As the carbon contribution of the oxygenated volatile compounds to total NMHC is lower than 1:1 due to the presence of oxygen, the same effective carbon number as the FID's response of the GC-FID analysis is used to calculate their contribution to total NMHC concentration."

Additionally, the yearly trend in total NHMC concentrations in parallel to those of BTEX has been added to Fig.1, panel B.

L81-84: the two long measured compounds B and T show a similar decrease trend (87 and 89%) : how do you explain in terms of the implementation of the Swiss policies that put stringent targets for toluene -as I understood- but a complete ban of benzene? In terms of the timing of the policies, could this be a source of variability on the ratio of the emissions over the years (and so on the evaluation of EX concentrations after 2010)?

In 2000, a restriction of benzene content from 5% to 1% as well as the regulation of solvent emissions via the incentive tax have been introduced in Switzerland. Since both measures aimed at limiting benzene or toluene emissions, their individual impacts are challenging to separate. Interestingly, so far as we know, such regulations for toluene have been first introduced in 2007 under the REACH regulation in Europe. By comparing the long-term BTEX monitoring in other European countries, very similar decreases are observed for toluene and benzene. A comparison with those European stations has been added in the manuscript as follows:

"The reduction in BTEX concentrations at DUE was also observed at other European monitoring sites for the same period. Long-term monitoring at the Augsburg Königsplatz traffic station in Germany has been conducted since 1995 (Bayerisches Landesamt für Umwelt, 2025). Between 1995 and 2023, the decrease in benzene and toluene concentrations was comparable to that observed at DUE, decreasing by 96 % from 3.6 ppb to 0.11 ppb and from 7.4 ppb to 0.27 ppb, respectively. A similar trend was observed at the London Eltham sub-urban station, where BTEX concentrations decreased on average by 90 % between 1995 and 2022, with benzene decreasing from 1.2 ppb to 0.12 ppb, toluene from 2.5 ppb to 0.20 ppb, ethylbenzene from 0.45 ppb to 0.043 ppb and xylene from 0.83 ppb to 0.086 ppb (Defra, 2025)"

L85: could you better define/quantify the amount of the “strong decrease” in the short time period of the implementation of the restriction policies?

In response to the reviewer's comment, this section has been rewritten for more clarity including the values of the decrease observed for the different BTEX compounds with the following text:

"The most pronounced year-to-year reduction in benzene concentrations occurred between 1999 and 2000 with concentrations decreasing by 33% from 0.89 ppb to 0.60 ppb linked to the reduction of benzene content in gasoline. Ethylbenzene and xylene decreased by 75% (from 0.42 ppb to 0.10 ppb and from 1.7 ppb to 0.46 ppb, respectively) between 1994 and 2010. For toluene, ethylbenzene and xylene, the most significant decrease in concentrations occurred between 2003 and 2004 with an average reduction of 40%. Nevertheless, no regulations on VOC emissions were implemented in Switzerland during this period, nor any exceptional meteorological conditions were observed that could explain these low concentrations. A comparison with the time series from ZUE showed significant lower concentrations in DUE in 2004, whereas in other years both sites have comparable seasonal patterns with similar concentration ranges (Fig. S6-7). Besides the discrepancies observed in 2004, a significant decrease in concentrations of these compounds was observed in 2001 with an average decrease of 28% after the introduction of the VOC incentive tax.

L89: you will compare results for DUE: what is meant exactly with the “territorial principle”? Do you mean the total emission is redistributed by population?

Thank you for pointing this out! Here, "territorial principle" refers to the emissions emitted within Switzerland. For more clarity, it has been removed from the manuscript.

L90: could you provide a reference for the reported emission categories? or is this information derived from some source apportionment exercise not better defined in the manuscript?

The reference was indicated as "(Bundesamt fur Umwelt (BAFU), 2023)" but it lacks clarity. In response to the reviewer's remark, it has been changed to the English abbreviation (FOEN) and better included in the manuscript.

L93: should be “benzene concentration MEASURED” and not “EMITTED” ; figure 3 would add a label “DUE” on panel A.

Thanks for pointing it out. We changed the text and the figure according to the remarks.

L-95: did the authors evaluate the reason for the lower values? I think it is worth reporting whatever results they have got even though inconclusive. Have the low values for the cited years been used for the following analysis or have been rejected?

As suggested by the reviewer, we conducted a seasonal analysis for benzene in DUE and ZUE to highlight the differences between both datasets. Discrepancies observed between datasets have been highlighted in Fig. S10 for more clarity. We removed the months from ZUE that were not overlapping between both stations to have a representative yearly average for comparison, which was the case in 2001 in January and February. As QA/QC procedures have been regularly conducted in the past, we kept the low values observed in 2003 and 2004 at DUE. The following text has been added in the manuscript:

"Discrepancies are observed between the modeled benzene emissions and measured benzene in Dübendorf between 2000 and 2005. Based on the long-term correlation between Zurich and Dübendorf since 1994 (Fig. 3, B), higher benzene concentrations would have been expected during the summer period in 2003 and 2004 in Dübendorf, as shown in Fig. S10."

L109: authors have attributed the change in T:B ratio to " a shift in source dominance": but could there be other explanations for this that could be discussed and compared? ie. the implementation of the policies cited in the introduction, line 36; or a change in the formulation of gasoline that is quite common in low temperature countries

We agree that this section lacks clarity and did not highlight the impact of the regulations on the T:B ratio. This section has been rewritten and a reference to the implementation of the benzene content restriction has been mentioned in the text:

"In the study of Lanz et al (2008), a source apportionment analysis of VOCs was conducted in ZUE using data collected between 2005 and 2006 and the results were compared with source apportionment findings from 1993–1994, the increase in the T:B ratio has been attributed to the restriction of benzene content in gasoline."

L111: I know modelers sometimes require to simplify the world and tend to make such kinds of assumptions but the choice should be discussed and justified a bit more: the ii sound reasonable, less the other two. At least provide some literature for those

For more clarity, this section has been modified, and the following text has been added:

"Thus, the winter T:B ratio was determined for each year during the morning rush hour in the winter (8-9am), when road traffic peaks and the morning CO concentrations are the highest. This time window provides a T:B ratio representative of traffic emissions with minimal influence from photochemical degradation. The contribution of biomass burning to T:B ratio at DUE is in general negligible, given the station's proximity to the road and that biomass burning emissions occur predominantly in the evening (Qi et al., 2019)."

L120: conclusions of a shift in the source dominance toward solvent use should be reflected in the EX composition, at least for the other monitoring station: did the authors investigate this option?

As suggested by the reviewer, we integrated the analysis of the X/E ratio in DUE coupled with the measurements from Zurich in the discussion concerning the T:B ratio changes over the years as follows:

"The ratio (m,p-xylene+o-xylene)-to-ethylbenzene (X:E) can further indicate the age of the air masses, with low ratio indicating aged air masses and a X:E ratio between 3.8 and 4.4 suggesting fresh emissions from gasoline (Keymeulen et al., 2001). In DUE, X:E ratios are available only for 1994–2000 and 2001–2010, with average ratios of 4.2±0.13 and 4.6±0.06, respectively (Fig. S12, A). In ZUE, the average X:E ratio after 2000 was 4.8±0.32 (Fig. S12, B). Although the differences in X:E between the two periods are significant but small in DUE, they may indicate a shift after 2000 from predominantly fresh gasoline emissions towards the influence of more fresh local sources."

L131: here the authors introduced an additional dataset (MNHCs in Zurich) to expand the discussion: but shouldn't this part be introduced to the "material and methods" section? moreover I think it should be clarified in advance that the following discussion about OFP and SOAFP will be based on a different dataset from the nearby station, due to a completeness of the VOC measured compared to the DUE data

We agree that the VOC dataset from Zurich was not well introduced in this manuscript. We added this sentence in the abstract: "To complement the long-term measurements in Dübendorf, VOC data from the urban background station at Kaserne Zurich were analyzed to assess the contribution of BTEX to ambient VOC composition."

As well as at the end of the introduction:

"Furthermore, this study integrates VOC measurements collected in parallel with BTEX monitoring at the urban background station in Zurich to relate BTEX concentrations to the overall composition of ambient VOCs."

Additionally, in the Material and methods section, a dedicated section concerning the VOC measurement in Zurich has been added with the title: " VOC measurements with GC-FID in ZUE".

L134: is there any explanation for the increase in the total NMHC reported here for the Zurich station? maybe some additional information on the number reported other than the average value could help the discussion (a range of variation?), also the figure 6 could be reconsidered reporting some statistical distribution ? (a boxplot?)

The increase in the last few years in OVOC concentration has been observed at the few monitoring stations monitoring OVOCs. The discussion of the OVOC increase was not further extended in this manuscript to focus on the contribution of BTEX to the VOC mixture. Nevertheless, we added the details of the OVOC monitored in ZUE (Table S1), the concentration of each single OVOC measured and their contribution to OFP in ZUE (Fig. S14). References to the literature of the large contribution of OVOC to total VOC concentration has been added in the manuscript as follows: " Recent studies have shown that OVOCs are emerging as the predominant class of VOCs in ambient air across many regions (Ma et al., 2025; Borbon et al., 2024). This increase in OVOC concentrations is likely driven by a shift in source dominance with vehicle emissions decreasing while solvent and product use emissions have become a major source of OVOCs in (sub)urban areas (FOEN, 2024; Lanz et al., 2008; Legreid et al., 2007)."

L149: the term "low-condensable" doesn't sound appropriate: do they mean "low-volatile organic compounds"?

Thank you for pointing this out. We changed to condensable organic compounds.

L155: the discussion of the role of EX is very marginal and should be expanded, at least when discussing the role of the "solvent" sector in my opinion.

A discussion point on the X:E ratio has been included in the subsection "T:B ratio change over the years" as mentioned above.

L164: a missing conclusion should be related to the importance of the monitoring of all NMHCs rather than just BTEX due to the demonstrated shifting role of the different class of VOCs over the years to the ozone and aerosol formation.

We agree with the reviewer and added the following sentence in the conclusion:

"In addition, OVOCs are becoming predominant in ambient air. Despite their relatively low MIR values, the cumulative contribution of individual OVOCs can significantly enhance ozone formation potential. Including OVOCs in addition to BTEX in air quality monitoring programs is therefore essential for a representative composition of (sub)urban VOC mixtures in ambient air.

References

Borbon, A., Salameh, T., Sauvage, S. & Afif, C. Light oxygenated volatile organic compound concentrations in an Eastern Mediterranean urban atmosphere rivalling those in megacities. *Environmental Pollution* **350**, 123797 (2024).

Lanz, V. A. *et al.* Receptor modeling of C_2-C_7 hydrocarbon sources at an urban background site in Zurich, Switzerland: changes between 1993–1994 and 2005–2006. *Atmos. Chem. Phys.* **8**, 2313–2332 (2008).

Ma, X., Liu, G. & Chen, J. PTR-QMS observation of OVOCs in an urban suburb of Guangzhou: seasonal characterization, source apportionment and regional transport. *Atmospheric Environment* **362**, 121589 (2025).

Qi, L. *et al.* Organic aerosol source apportionment in Zurich using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) – Part 2: Biomass burning influences in winter. *Atmospheric Chemistry and Physics* **19**, 8037–8062 (2019).