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Reply on RC1

Eric Förster et al.

Author comment on "Chemical and dynamical identification of emission outflows during the *HALO* campaign EMeRGe in Europe and Asia" by Eric Förster et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-455-AC1, 2022

Author response on anonymous referee #1 (R1), acp-2022-455

The manuscript by Förster et al. provides an insight into measurements conducted as part of the EMeRGe campaign. The analysis is thorough and convincing. I recommend publication after addressing comments below

Answer: First of all, we would like to thank R1 for carefully reading the manuscript and for the generally positive, helpful comments. We have followed all suggestions for change and have modified the manuscript and Supplementary Information accordingly. Below we provide point by point responses to the *comments* with given lines of changes (if applicable) and highlighted the corresponding changes made in the manuscript (supplement file) in yellow. Changes corresponding to comments of R2 are highlighted in blue.

Author response

Define MPC – what size, what criterium?

Answer: We specified the definition in lines 63-65: "…, we will use the term MPC to describe megacities with more than 10 million inhabitants as well as metropolitan areas or converging urban conurbations with more than four million inhabitants (e.g. metropolitan area of Rome or Madrid)."

However, like the definition of megacity (the only criterion is more than 10 million inhabitants) the term MPC can just be loosely defined.

Line 110- 120: The authors mention emissions extensively throughout the manuscript, however they do not quantify nor measure emissions directly. Typically emissions as opposed to concentrations are defined as g/s or g/m2/s or similar. Whenever appropriate I suggest to rephrase these statements. The overarching measurement approach was not designed to specifically quantify emissions (a typical aircraft setup for monitoring emissions for example: Yuan et al., 2015 (doi: 10.1002/2015JD023242 and Baray et al., 2018: doi: 10.5194/acp-18-7361-2018). Rather I would call the measurement approach

to characterize and interpret atmospheric concentrations (e.g. aged composition rather than aged emissions). What is actually promoted here is the use of the chemical composition of certain tracer VOC as a relative fingerprint of pollution sources.

Answer: We agree that the term "emission" was used in two ways throughout the manuscript: First as term for a general description of "release of trace gases" from various sources, e.g. biogenic or anthropogenic, without a quantitative statement. And second, as modeled CO emission uptakes, with a quantitative indication.

For the first case (related to measured trace gas enhancements), we mostly changed the term "emission" to "pollution" or "composition" throughout the manuscript as suggested by R1. We added also a short paragraph defining pollution as emission impact (lines 101-105):

"In general, localised (intensive) trace gas emissions of urban areas rapidly increase corresponding volume mixing ratios in affected air masses. Chemical conversion and dilution can attenuate such emission driven enhancements of tracer volume mixing ratios in a given air mass. However, in most cases emission impacts can be clearly detected by measuring relative enhancements of volume mixing ratios and here we will to refer to such enhancements as pollution (events)."

Since the modelled emission uptake is given as a mass, we kept the term for the modelling of the anthropogenic CO uptake. However, we tried to be more precisely and using now mostly the terms "emission uptake" or "modelled emission" throughout the modelling discussion.

Line 151: this is true on a global scale, however in the northern hemisphere the anthropogenic contribution is much larger (up to 50%). This has also been shown recently by a number of VOC measurements in urban areas (e.g. Karl et al., 2018, doi: 10.1073/pnas.1714715115; Gkatzelis et al., 2021: doi : 10.1021/acs.est.0c05471). The regional distribution of VOC should be discussed in this manuscript.

Answer: We thank R1 for the remark. The text has been modified accordingly (lines 158-163):

"Globally, the vast majority of VOCs in the atmosphere are emitted by biogenic sources (Guenther et al., 1995; Sindelarova et al., 2014), thus from vegetation or biomass fires (Ciccioli et al., 2014). However, the regions with the largest biogenic emissions are the rain forests in South America and Africa. In the northern hemisphere, biogenic VOCs are only emitted during the vegetation phase with overall smaller emissions rates (Guenther et al., 1995). Accordingly, recent urban measurements indicate that anthropogenic emissions account for about half of the VOC flux into the atmosphere of the northern hemisphere (Karl et al., 2018). Inside urban agglomerations, anthropogenic VOC emissions will even dominate (Amodio et al., 2013)."

Line 166: for E/N of 142 I would expect that a large fraction on the 'benzene' mass can potentially originates from fragmentation of higher aromatics (e.g. ethylbenzenes) – the authors should give constraints on this interference

Answer: This remark is now included in the text (lines 187-191):

"Furthermore, the mass of benzene (m/z=79) can potentially experience signals from the

fragmentation of higher aromatics, e.g. from C8 aromatics like ethylbenzenes (m/z=107), due to the operation of the HKMS with a relatively high E/N value (de Gouw and Warneke, 2007). Nevertheless, higher aromatics originate mostly from anthropogenic sources as well, why we consider the signal of m/z = 79 still as suitable tracer for anthropogenic activities."

Line 194: Acetonitrile has been used as a biomass burning marker, however the magnitude of acetonitrile and HCN emissions depends on the fuel N content – urban burning events for example are often not captured adequately

Answer: This remark is now included in the text (lines 185-187):

"However, it should be noted, that the magnitude of acetonitrile emissions depends on the nitrogen content of the burned fuel, showing lower concentrations in residential wood burning and hence, acetonitrile may not be a suitable tracer for domestic burning in urban areas (Coggon et al., 2016)"

Line 201: It should be noted that there are also isoprene (and furan) emissions from biomass burning, which could dilute the specificity of this tracer.

Answer: Therefore, we consider for the source signature "only biogenic" just isoprene enhancements without the simultaneous enhancement of acetonitrile and benzene, to filter out possible fresh BB sources of isoprene. We try to make it clearer in the manuscript (lines 220-221):

"This source signature denotes only a biogenic signal without enhancements of benzene and acetonitrile (filtering out BB induced isoprene emissions, e.g. Müller et al., 2016)."

Line 240: emissions from the RCP (residential, commercial and public) as well as industrial sector do not only happen during daytime. The analysis of FLEXPART could therefore suffer from that assumption.

Answer: The text has been accordingly modified to consider the nighttime emissions and the possible influence on the analysis due to higher PBL uncertainties (lines 267-268):

"However, emissions from the RCP (residential, commercial and public) as well as industrial sector can also arise during the night, where larger PBL height uncertainties might have an influence on our analysis."

Line 289: I understand the influence of chemistry here for the degradation of CO, but not transport- Shouldn't Flexpart handle dilution as well

Answer: For our analysis, we did not use the dispersion model FLEXPART itself but "only" the trajectory model FLEXTRA (that does not handle dilution). The main reason why we used FLEXTRA (+ ERA5 PBL + EDGAR) is that most of our measurements (80%) are outside the PBL and nearly half of the probed air masses (45%) haven't been in the PBL (where the emissions are) during the last 10 days. In the free troposphere above the PBL "simple trajectories" are sufficient to identify the mean transport pathways, mainly due to

less turbulence/shear compared to the PBL.

Source-receptor-relations between emission sources at the ground and airborne observations can only be calculated by dispersion models like FLEXPART. This would be needed to quantify source contributions of pollution plumes, i.e. calculating the enhancement of CO mixing ratios by the different sources (at the ground) at the location of the aircraft. However, this quantification is not the intention and beyond the scope of this paper. Our intention is to identify and characterize in a first step all air masses probed during EMeRGe in an efficient way. The results allow then further analysis, e.g. dispersion modelling for specific cases.

We added a short paragraph in the manuscript for clarification (lines 256-262).

Fig4. I would rather call this a source signature rather than an emission signature. Background air is NOT an emission signature – this refers again to my comment at the beginning -> I would be more concise about the actual meaning and definition of emissions throughout the manuscript.

Answer: The term "emission signatures" was changed to "source signatures" throughout the manuscript. We agree that this is a more suitable term.

Section 3: The authors classify aged and non aged emissions. To that end the ratio of Toluene/benzene could help to verify their assumptions for airmasses without a large influence of biomass burning. Do the aged ratios agree with the estimated calculations from back trajectories assuming typical OH densities (e.g. from CMIP climatology models)?

Answer: The ratio of TOL/BEN was investigated in earlier data analyses to estimate air mass ages over a chemical clock. Unfortunately, due to the lack of ratios near the emission sources (climatological emissions does not help here, because we are looking mostly at specific events) and the strong mixture of different anthropogenic sources (with different air mass ages), the clocks lead to no clear age estimation. Therefore, the ratio of TOL/BEN is for EMeRGe in general not suitable to verify the transport time given by the trajectories. However, with the TOL/BEN ratios itself, fresh and aged air masses have been estimated for plumes with toluene enhancements in an earlier analysis (Förster et al., 2018).

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Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2022-455/acp-2022-455-AC1-supplement.pdf