

Dear editor,

we wrote a short reply to the reviewer's comments to help you to understand our reactions to them. The changes as suggested by the reviewer are written italicized in quotation marks. If we disagreed with the reviewer, we wrote a short reply. Within the manuscript, we marked all changes with track changes.

Major comments:

The authors have certainly made a major effort to address the comments from the first round, and the resulting manuscript is certainly a lot clearer now. I have a few small comments on the response, detailed below. I have also reread the manuscript and I added a few minor comments that mostly address readability. Overall, I think this manuscript will be ready for publication once these comments are addressed.

- The clarification regarding the multiple valve switching nature of the sampler is appreciated. One additional question comes to mind, which is a) what is the minimum sampling interval the software could do (and why?) and b) is that interval (2s per L328?) really desirable/appropriate for ambient sampling?. On the latter point, each valve switch introduces the possibility of either sample contamination (from stuff absorbed on the valve ball) and sample volatilization (from turbulence introduced by the pressure fluctuations). Both of these are admittedly very hard to quantify, but I would be curious what the authors' thoughts are on this subject.

Section 2.3:

"During measurements when air masses containing different aerosol types reach the inlet, the sampler switches automatically between the according sampling paths based on the evaluation of the sampling conditions each second. The evaluation is performed each second based on the highest available time resolution of the instruments, hence the valves can be switched on a 1s-base as well. While frequent switching of the valves introduces frequent flow and pressure disruptions in the sampler, these are not expected to produce enhanced sampling artefacts by e.g. re-volatilization of material from the tube surface or the filters, compared to less frequent switching scenarios. Therefore, switching between different sampling paths typically occurs multiple times within an experiment of hours of duration, which is in contrast to conventional continuous sampling. Although the AERTRACC is primarily designed for stationary measurements, it is also possible to sample during mobile measurements if the air mass segments are large enough to differentiate between them on a few seconds time scale. The flowrate sub-window contains information on the flow setup of the AERTRACC sampler (Fig. 2b). Here, the user enters the flow rates, which are adjusted with the individual needle valves. The graphical user interface automatically provides the combined flow rates at critical devices, such as the inlet cyclone, and thus supports the correct selection of the individual flow rates in order to match their required flow conditions. Furthermore, in this window the MoLa inlet height is entered. This information is used to select the correct delay times between registration

of the sampling status, i.e. sampling or non-sampling, and the activation or de-activation of flows through the individual sampling paths (see Sect. 3.2)."

Reply:

As mentioned in the added text, we do not expect enhanced sampling artefacts due to the frequent switching of the valves. Furthermore, the valves are located downstream the sampling media to avoid any contamination from the valves.

- Regarding the discussion of volatilization of the analyte, I suppose what the authors are trying to say is that at worst it will lead to biased partitioning data (although given the complications in the calibration of gases and aerosols, these are likely not distinguishable in the data from the "true" partitioning). So this could be stated explicitly. Furthermore (and I might be overinterpreting the author's intentions here, this is just my reading of it), typically (e.g. see the recent Tong et al, 2022 paper) it is a given that the results from the molecular technique are not really used for absolute quantification, but for molecular ID'ing. Advanced statistical techniques (e.g. constrained PMF in the Tong et al example) can then be used to further constrain the actual sensitivity/quantification on a molecular PMF basis, bypassing to a large extent the need for single molecule calibrations as requested by Reviewer #2. Up to the authors if they want to make this case explicitly in the paper, but realistically it seems that routine analysis of AERTRACC sampled TD-CIMS data is probably going to be handled in a similar fashion, and that hence both absolute sensitivities and, to a lesser extent, the aforementioned quantification biases can be addressed that way.

Section 5:

Section 4.3.2:

"The ratio of the ion signal intensity for selected identified species from the pizza oven and the background samples was calculated for the filter and the TDT samples (Fig. 4), respectively, to show which of the species mainly originate from background and which ones are associated with the source emissions. Additionally, the average ratio for all species assigned to only background (aged/traffic) and oven emissions (biomass burning/cooking – BB/C) as well as both groups (mixed) were calculated for comparison. The assignment to the sources must be regarded as a rather preliminary one, as the apportionment is only based on a literature search. The list of identified species and used acronyms is shown in Table 2 and Table 3 for the filter and TDT samples, respectively. Substances found on the filters and TDTs differ mainly due to gas-particle partitioning and the selectivity of the TDT adsorbents. Volatilization of material from the filters and subsequent sampling in the TDTs could lead to biased information on the partitioning of substances, however, within the uncertainties of the analysis, this effect is presumably not significant."

Section 4.2:

"Signal intensities for individual compounds were determined semi-quantitatively as a calibration for each compounds was not feasible. This allows determination of relative concentrations in separate samples as well as supporting PMF analysis for quantitative determination of aerosol type concentrations (similar to the approach by Tong et al., 2022). Independently of the sampling media, the ion signal intensities during desorption of the samples exceeded the limit of detection (three

times the standard deviation of the molecular background) for all reported samples and ions, with the majority of samples and ions showing an excess by at least an order of magnitude."

- Having said that, I am not clear how you determined that "oligomerization...was not observed in this study". A comparison of the CIMS TD profile with other volatility methods (e.g. bulk TD) would be required for this, and I do not think these data were recorded. It is probably ok to write that "the effect of oligomerization appears minor in our testing", but everything beyond that seems unsupported.

Section 2.5

"The reproducibility of the integrated ion signal intensity of different calibration compounds, determined through laboratory experiments, was found to be 10% for filter and 62% for TDT samples (details see Sect. S4). Oligomerization during analysis with CIMS might occur (Lopez-Hilfiker et al., 2015) but ~~was not observed within this study~~ appeared minor in our testing."

- While adding the programming language of the control software is appreciated, I believe it would still be appropriate to mention, either in the paper or in the data availability statement, if the software is publicly available. If so, it would be good to specify under which license and if not, if there are plans to make it available in the future.

Section 2.3:

"The AERTRACC control software (ACS) is the interface between the MoLa online measurements and the sampling system and is integrated into the MoLa data acquisition software for simple and direct access to the data. It was developed in Igor Pro (Version 6.3, WaveMetrics, Inc., USA) and is available from the authors upon request."

- L241: I used 10 $\mu\text{g m}^{-3}$ as a (US-centric) typical number in my review. You could use something more typical of West German urban conditions, and add a reference to support it. Regardless, your subsequent statement covers it.

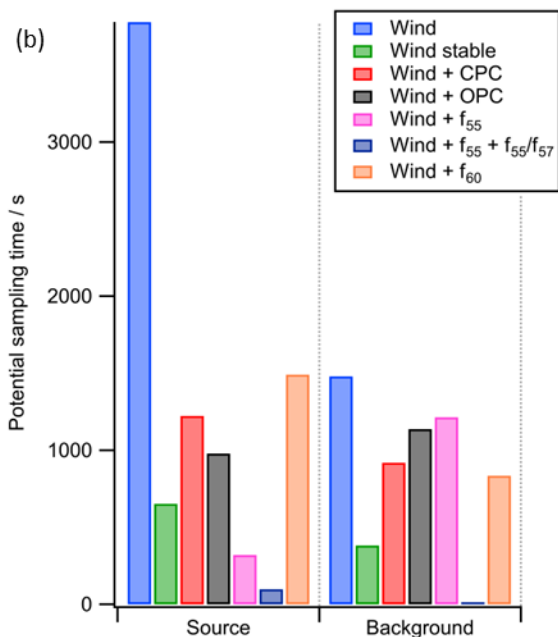
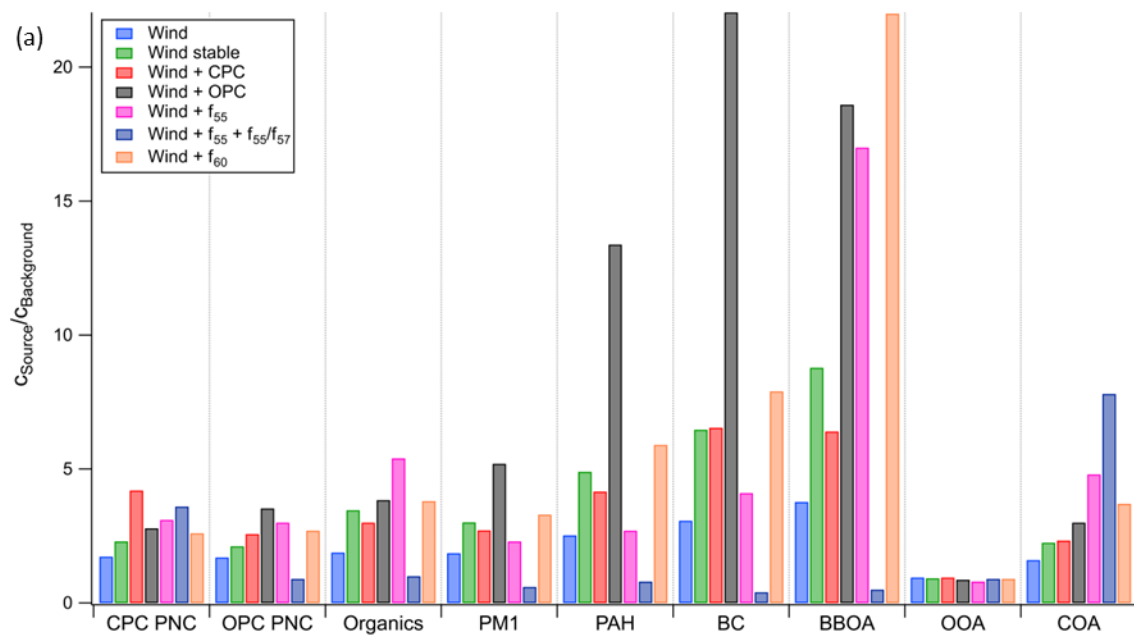
"The chemical analysis of aerosol samples (like e.g. when using FIGAERO-CIMS measurements of organic compounds) typically requires sampled mass in the order of 1 μg in order to exceed instrumental detection limits, depending on the specific analysis method. In ~~polluted~~-urban conditions with organic mass concentrations of 5-10 $\mu\text{g m}^{-3}$ (Chen, et. Al, 2022), with a sample flow rate of 7.5 L min⁻¹ and with approximately 10 % of the time sampling source emissions (like in our validation experiment, see Section 4), a total sampling time in the order of ~~two~~ 1-2 hours would be needed to collect enough material for analysis."

- L425: DL=3xsigma Background is a conservative DL definition by some practitioners' standards, so overall it does look like all your compounds were actually roughly above DL. The large SD of the TDT, however, is notable. Is this an issue with the much higher concentration of these compounds in the background, or rather was less material collected on the TDTs compared to the filters? As noted by Reviewer, a little bit more detail on how exactly the combined error bars in Figure 4 come about would be helpful.

Reply:

This issue is explained in more detail in the Supplemental Material (Section S4) of the revised version. Apparently, likely because no tracked changes version could be submitted for the SI, the reviewer has missed this information in the revised SI.

- Revised Figure 5: This is very nice, thank you for making it! Please consider adding a vertical grid, the plot is pretty busy and this might improve readability. I would also note that the S/B for the AMS cases might improve if you ever chose to operate the AMS at 0.5 Hz or something like that.



Section 4.3.3

“Inclusion of the AMS data in the AERTRACC control using the fractional signal intensity of known marker m/z could improve specific sampling for certain aerosol types. This is especially the case if the AMS is operated with shorter averaging intervals to capture short-time variations of air masses containing different aerosol types. For COA, higher source/background ratios were achieved with the Wind + f55 sampling scenario, compared to the other scenarios, and even higher ones with the Wind + f55 + f55/f57 scenario as it is more specific for COA. Regarding the potential sampling times especially within the latter scenario, the times are quite limited due to the very specific conditions and possibly due to shorter COA emission periods compared to the more dominant BBOA. The Wind +

f60 scenario enables the most effective separation for BBOA combined with potential sampling times comparable to the Wind+OPC scenario."

- While again exact quantification is not the goal, in my view, I wonder, also in the context of the PM1/PM10 comparisons, if adding a gravimetric filter analysis of both denuders and filters as a routine step prior to the thermal desorption would be a helpful addition for general QC of the data.

Section 4.3.2:

"In conclusion, for the filter samples the chosen sampling conditions for the background and source emissions proved to be suitable to sample the source emissions separately while the background emissions are found in approximately equal concentrations on the source and background filters at least based on the identified compounds. A gravimetric analysis of the samples could be performed in addition to the chemical analysis to extend the general information on the sampled aerosols. For the TDT samples the shown ratios indicate a weaker separation of source and background emissions, likely because most of the identified compounds can originate from both, background and source emissions, and no distinct markers were found for the source emissions. "

- The SI does not seem to have been revised; hence, I have not reviewed it.

Minor comments:

L21: Replace "(PM1 and PM10)" with "(with PM1 and PM10 cutoffs, respectively)"

"Particle and gas phase of each aerosol type, e.g. source emissions and background, are sampled onto separate filters with PM₁ and PM₁₀ cutoffs, respectively, and thermal desorption tubes, respectively."

L30: is "permanent" necessary here?

"Various chemical and physical processes lead to ~~permanent~~ changes of the aerosol properties, like the particle size and composition."

L42: Consider "are generally classified into" instead of "consist"

"Atmospheric aerosol are generally classified into ~~consists of~~ two major chemical fractions, the inorganic one with substances like ammonium, nitrate, sulfate, metal oxides, mineral dust, and sea salt ~~(Fuzzi et al., 2015)~~, while the organic aerosol, the other fraction, constitutes the more complex part (Fuzzi et al., 2015)."

L45: Citation needed. Nault 2021 or Southerland 2022 could be used, there are others.

“Especially fine particulate matter, which has a relevant effect on climate and health, contains usually a large organic fraction (Zheng et al., 2020). These particles consist of many individual components but only a small fraction of them are identified 45 by state-of-the-art instruments (Fuzzi et al., 2015; Johnston und Kerecman, 2019; Zhou et al., 2020).”

Reply:

The Fuzzi et al., 2015 citation was placed too early in the sentence. This review paper is a reference also for the statement about the organic aerosol fraction. We therefore moved it to the end of the sentence (see answer to comment before). For the following sentence a refence was added that supports the statement that organics are an important fraction of fine particulate matter and its negative health effects.

L73: Citation needed for EC/OC sampler

“A semi-continuous online bulk analysis can be performed with the thermal-optical EC/OC analyzer measuring the hourly concentrations of elemental carbon (EC) and organic carbon (OC) (Zhou et al., 2015).”

L92: "and quick online methods do not provide in-depth chemical analysis capability". Not sure what "quick" is trying to qualify here, but in terms of "capability" the EESI or CHARON (or VIA) will provide it, I suppose the question is how cumbersome both ops and analysis are... So at a minimum please replace "quick" with "most". The authors could add a half-sentence about offline methods typically providing more detail regardless, and hence being preferred.

“Offline and semi-online methods offering highly resolved speciation data do not provide the required temporal resolution and quick-high-time resolution online methods typically do not provide in-depth chemical analysis capability.”

L106: "probing the emission of a pizza oven"

“Here, we present the design and characteristics of AERTRACC and demonstrate its capabilities in a field experiment, probing the emissions of a pizza oven in a semi-urban environment.”

L132: Please rephrase: "up to either 10 µm (PM10) or". More generally, it would probably read better if you removed this detail up here (could replace with "variable aerosol size cuts") and discussed the size cuts in detail further down. Also, both here and below, it seems that adding "nominal" in front of PM10 would be advisable. I mean, the fact that the plumbing can pass PM10 does still not mean that at say, 60 km/h in turbulent urban BL conditions PM10 sampling can really be achieved...And you write in Section 3.1 (which should probably explicitly be referenced here) that you have calculated significant plumbing losses above 3.5 µm. So something like "nominal PM10, in practice PM4-PM5" would seem appropriate.

Section 2.2:

"AERTRACC is designed to sample different aerosol types separately on individual sample carriers. The system is incorporated in MoLa with its own inlet and a flow path designed for minimal particle losses, minimizing non-vertical tubes and bends. With four available sampling paths up to four different aerosol types can be sampled separately. It is possible to sample particles ~~up to 10 µm in aerodynamic diameter (PM10) and up to 1 µm (PM1)~~ with two different size cuts on quartz fiber or PTFE filters as well as volatile compounds onto thermal desorption tubes (TDT) filled with adsorbent material (further details in Sect. 2.4). A control software for the AERTRACC sampler was programmed to accomplish separate sampling of different aerosol types based on the MoLa online data (see Sect. 2.3).

A schematic overview and a photograph of the sampling system installed in MoLa are shown in Fig. 1. The AERTRACC sampler has its own inlet line (ID = 48 mm), equipped with a PM₁₀ inlet head (Digitel, Switzerland, inlet flow rate 30 L min⁻¹) ~~for sampling nominal PM₁₀~~, which is mounted on the roof of MoLa. The inlet is located 0.5 m apart from the MoLa online instrument inlet and their heights are adjusted to each other to assure sampling of the same aerosol."

Additional reply:

We did not add the suggested statement that the PM₁₀ would in practice rather be PM₄-PM₅ because this is not what our inlet loss calculations suggest. Indeed, for particles larger 3.5 µm in diameter, significant particle losses were found. However, as shown in Figure S5 in the supplement, this does not mean that a majority of particles of this size is lost (it is rather a few percent). Even for 10 µm particles the loss in the tubing is well below 50%.

L285: I assume you "thune" when needed, since for a stationary instrument anything else would seem like overkill, so consider clarifying if you are describing your SOP or just the conditions of the text experiment.

"Tuning of the ion optics was performed before the first analysis procedure with formic acid and triiodide for signal intensity, mass resolution, and peak shape using the software Thuner (Tofwerk AG, Switzerland)."

L299: It is unclear how the concentration of individual species would be size-corrected if needed.

Reply:

We assume that, in agreement with the text in L299, the reviewer refers to a correction of the measured mass concentrations, not the particle sizes. Indeed, without knowing the size distribution for individual aerosol types, it would be very hard to correct for large inlet losses. However, due to the design of the inlet system, the transport losses are negligible and therefore no correction of the mass concentrations is needed – as stated in the text.

L375: Replace "occurrence in literature references" with "previous mention in the literature"

"The molecular formula of identified ions was determined for individual peaks; and individual species were identified through the molecular formula, detectability by Iodide-CIMS and previous mention in the literature ~~occurrence in literature references~~ (further details see Table S1)."

L376: Consider adding the single calibration compound you are using for scaling in parenthesis

"Signal intensities for individual compounds were determined semi-quantitatively in terms of detected ions as a calibration for each compounds was not feasible. Independently of the sampling media, the ion signal intensities during desorption of the samples exceeded the limit of detection (three times the standard deviation of the molecular background) for all reported samples and ions, with the majority of samples and ions showing an excess by at least an order of magnitude."

Reply:

No calibration was performed as stated in the text, hence no compounds were mentioned.

L502: The standard reference for f60 use in the AMS is Cubison et al, 2011, suggest adding it here.

"The limit values in the sampling condition definitions were chosen from literature values for these aerosol types (Cubison et al., 2011; Elser et al., 2016; Mohr et al., 2009; Mohr et al., 2012; Saarikoski et al., 2012; Sun et al., 2011; Xu et al., 2020)."

L578: "An in-house developed software package" would be clearer, not obvious who the "self" here is...

"An in-house developed ~~A-self-programmed~~ software is implemented in the MoLa data acquisition software for direct data access."

L582: Consider specifying the effective size range here again.

"The inlet and transport system was designed for minimal particle losses with typical estimated mass losses below 1 % for particles in the size-range 35 nm up to 3.5 µm."

References

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