

Dear reviewer,

we thank you for your valuable feedback to our manuscript, which we believe makes it more valuable to the readers. Within the letter, we commented on and replied to all suggestions and requests. The changes made to the manuscript are written italicized in quotation marks within the reply. Within the manuscript, we marked all changes with track changes.

Reply on “Comment on amt-2022-206” of Anonymous Referee #1

The submitted manuscript by Pikmann et al introduces a new, automated offline sampler for both aerosols and gases called the AERTRACC, which is part of the mobile laboratory platform MoLA. The stated aim in its design is to allow for more efficient source separation when sampling complex source environments, specifically for the analysis of organic aerosol (OA) and their precursors. The manuscript describes the hardware and control software in detail, and then demonstrates its operation with a (static) single source experiment. That includes an in-depth analysis of gas and particulate phase tracers detected by their analyzer of choice (an TD-CIMS) and the source-specific contrast ratios observed. The authors conclude with a detailed discussion of the optimal choice of input parameters to control the sampler, in order to increase source contrasts for this particular case. So while there is no data shown from actual mobile sampling, the reader is reasonably reassured that it will in fact work for that scenario.

The overwhelming majority of offline samplers operate on some type of predefined timegrid, which leads to different airmasses and hence sources and chemistries being integrated into one sample. For mobile sources where air mass variability is higher this can limit the usefulness of offline analysis significantly. Hence, on airborne platforms, most offline samplers (such as whole air samplers) are operated based on some type of expert assessment of air mass change, which in (some, rare) cases is automated. While aircraft payloads are highly variable from mission to mission, that is obviously not the case for the MoLA platform, which has a well-defined instrument payload. Therefore, it makes sense to not only build a “smart” offline sampler for MoLA, but to automate it based on all the possible ancillary measurements available. So while this type of sampling has been done before, this paper shows a technically proficient, well-executed implementation of it for a platform that will certainly make good use of it in the future. So this is well within the scope of and of general interest to the AMT audience. However, I have some concerns about the way the work is framed and about the details of the analysis, which are described in the following:

Unless I am completely misunderstanding the work presented, the key aspect of this sampler is that it switches between “source” and “background” conditions many, many times over the course of the experiment. This is quite different from most offline samplers where only one continuous sample is taken. I would recommend making this much clearer in the description, and possibly illustrating this by e.g. showing the actual sample times on top of Figure S5. It would also be good if the authors discussed what the minimum sample time (per valve switch) actually is, and how this could possibly impact the overall performance once MoLA is actually moving and hence the source sector segments become smaller.

Answer:

Yes, this is correct. Thank you for your suggestions to clarify the operation principle. We added the actual sampling intervals for the source and background aerosol to Figure S6 (previously S5) and changed the figure caption accordingly. We also added a sentence about the sampling periods and the switching between the sampling paths based on the evaluation (Section 4.3.1):

“Time intervals for sampling of source emissions and background are highlighted. Depending on the evaluation of the data, the sampling was frequently (often after only a few seconds or at most minutes) switched between source and background aerosol paths.”

Further, we added a short description in the section on sampler operation (Section 2.3) in which we describe that during an experiment the sampler typically switches multiple times between different sampling paths, based on which aerosol type conditions are fulfilled, and discuss the impact on mobile sampling experiments.

“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. 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.”

Related to the last item, can the authors please discuss what the limitations are on leaving the “source” channel idle for long periods between source interceptions? My specific concern is that any type of filter substrate has issues with loss of volatiles (e.g. Heim et al, 2020), and while during active sampling these “losses” will likely end up in the TDTs, once the line is idle they will simply evaporate and possibly diffuse/deposit to the “background” channel. And there is also, specifically for CIMS measurements, obviously the oligomerization problem (e.g. Lopez-Hilfiker et al, 2015), which should at least be acknowledged.

Answer:

We agree that losses of volatiles from filters are always possible and that those volatiles will likely be adsorbed by the TDTs during sampling, if the types of molecules can be adsorbed by the adsorption media. During times when the sampling line is idling, volatiles will diffuse away from the filter. A fraction of those will end up in the TDT. Diffusion and deposit into other sampling lines, however, is not possible, as the aerosol would have to diffuse against the non-sampling path flow (which is active during non-sampling conditions, see Figure 1) up to the next flow split.

To clarify this, we added the following sentence to Section 2.2:

“Further, for non-sampling conditions, diffusion of volatiles from one sampling path to another is avoided as the volatiles would have to diffuse a short distance upstream the flow persisting through the non-sampling path.”

We agree that oligomerization might occur during the analysis, however this was not observed for our measurements. We added this information to the manuscript as suggested (Section 2.5).

“Oligomerization during analysis with CIMS might occur (Lopez-Hilfiker et al., 2015) but was not observed within this study.”

I do not think that the current introduction does the best job in framing the significance and applicability of AERTRACC. First of all, I think the sampler needs to be separated more clearly from the specific application (in this cases, molecular OA composition). So by way of example, the current AERTRACC, with a simple change in filter media would surely be of high interest to single-particle TEM folks, a field where optimizing contrast for the source-specific aerosol types of interest (and not necessarily organic ones) can be extremely challenging. So framing AERTRACC as an efficient way of solving the contrast issue for any type of off-line analyzers will better illustrate its potential.

Answer:

We agree that it would be better to focus more on the AERTRACC sampler and to stress that the application of the sampler is not limited to molecular OA composition analysis but applicable to all kinds of offline analysis methods. Therefore, we changed the last paragraph of the introduction accordingly.

“AERTRACC collects samples of different aerosol types for subsequent in-depth analysis on separate sampling media which can be quickly and simply exchanged.”

and

“While online instruments for in-depth chemical analysis with high temporal resolution are limited to the respective analysis methods, the AERTRACC sampler enables the use of the full potential of analytical chemistry and microscopic analysis for the investigation of such aerosols beyond these specific approaches. For this work, TD-HR-ToF-CIMS (thermal desorption high resolution time-of-flight chemical-ionization mass spectrometry) was chosen as analysis method offering high resolution mass spectra combined with high sensitivity and low sample fragmentation as well as minimized sample preparation effort (Aljawhary et al., 2013; Mercier et al., 2012; Yatavelli et al., 2012).”

In addition, we added a short sentence in the beginning of Section 2.4 that the choice of sampling media was suitable for the CIMS but is not limited to it.

“Generally, the sampling media used are dependent on the subsequent offline analysis method. The choice of the sampling media for this study was based on the selection of thermal desorption as sample introduction method for the subsequent analysis using TD-CIMS, which reduces the chances of potential contamination through sample preparation.”

Furthermore, we added a sentence in the beginning of Section 2.5 to stress that AERTRACC can also be used for other offline methods.

“The AERTRACC sampling can be used with various kinds of sampling media and consequently can be used in combination with a broad variety of offline analysis methods.”

The summary was also adjusted based on the reviewer’s suggestion.

“Up to four samples can be taken in parallel; in this study, each sample was taken onto a filter and a thermal desorption tube (TDT) for the particle and gas phase, respectively.”

and

“Apart from TD-CIMS, a broad variety of chemical, physical, and microscopical analysis methods could be used in combination with AERTRACC to acquire the desired kinds of information from the samples.”

More importantly, this statement (L79-80) “Currently, no instrument offers detailed chemical analysis of aerosols in real-time for the analysis of individual sources (Parshintsev and Hyötyläinen, 2015)” which is the linchpin of the current introduction, is simply incorrect. There are real-time, 1 Hz capable molecular OA detectors, such as the EESI-ToF (Lopez-Hilfiker et al, 2019, Pagonis et al, 2021) or the CHARON-PTR-MS (Eichler et al, 2015, Piel et al, 2019). None of them are perfect (no instrument is), but the point is that molecular identification of OA from mobile sources can be accomplished in many different ways, and AERTRACC+TD-CIMS is just one of many, and not really the main reason (in my view) for AERTRACC.

Answer:

Thank you for this comment. We agree and removed the mentioned statement. Instead, we added the mentioned instruments as current high time resolution instruments.

“A few instruments with high time resolution in the order of seconds, sufficient for the analysis of transient aerosol occurrences, combined with detailed analysis were developed in recent years, such as the EESI-ToF (electrospray ionization time-of-flight mass spectrometer) (Lopez-Hilfiker et al., 2019; Pagonis et al., 2021) and the CHARON-PTR-MS (chemical analysis of aerosol online proton-transfer-reaction mass spectrometer) (Eichler et al., 2015; Piel et al., 2019).”

What both the introduction and the rest of the paper do not discuss are detection limits, which are typically one of the main design criteria for samplers. This needs to be addressed, since currently there is not context whatsoever on what a reasonable total sample time would be (and hence how practical the use of AERTRACC is for typical urban source applications). Based on the description, under typical polluted urban conditions ($\sim 10 \mu\text{g m}^{-3}$ OA), it would take about 2 hours to sample $1 \mu\text{g}$ of material, which given typical DLs for organic compounds in the FIGAREO ($\sim 0.5 \text{ ng sm}^3$ from filter blanks) seems sensible. But that seems like a long sampling time for a local source, so a discussion of the possible tradeoffs would be appreciated.

Answer:

Thank you for this comment, we agree that this needs further discussion. Indeed, for CIMS analysis we aim to sample in the order of $1\text{--}2 \mu\text{g}$ of material to avoid overloading the CIMS (as stated in Section 2.4). For other chemical analysis methods, the desired amount of sample material is in a similar order of magnitude, while for microscopic analysis it could be much lower. At an ambient concentration of $10 \mu\text{g m}^{-3}$ with a sample flow of 7.5 LPM, this translates to a sampling time of 13 min, which needs about two hours of measurements if only 10% of the time (as during our validation experiment) the emissions are sampled. Therefore, to collect sufficient sample material, it must be possible to probe the air in the vicinity of the source over sufficiently long time. This also means that both, the source emissions and the ambient transport conditions must prevail over this time. The chemical analysis of

single events, short or very weak emissions is therefore likely not possible with this setup. The use of microscopic methods for the analysis of the samples, however, might strongly reduce the necessary sampling times or source concentrations, for successful analysis.

We added a discussion on this issue at the end of Section 2.3 on sampler operation:

“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 10 µg m⁻³, 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 hours would be needed to collect enough material for analysis. Therefore, the probed source must emit over sufficiently long times to allow a successful chemical characterization of their emissions. Higher emission concentrations, more stable transport conditions, and lower detection limits of the applied analysis method can reduce sampling times significantly. Especially when using microscopic and single particle techniques, which might need extremely low amounts of sample, sampling times could be reduced further and also single transient emission events might provide sufficient material for successful analysis.”

The (nicely done) PMF analysis of the AMS measurements seems a bit underutilized at the moment. Its sole purpose currently is to show the wind dependence for the OA sources, which could certainly be showcased with less work. Obviously it is an ancillary measurement, and not part of AERTRACC, but Figure S1 shows a lot of high-time resolution, high contrast data that could be certainly utilized to assess what ideally AERTRACC can achieve. So I would encourage the authors to add the PMF factors to Figure 5 (and Tables S3-S5), and the sampling periods to Figure S1, which should make current trends clearer, at the very least. In that context (assuming the AMS is a regular instrument on MoLA), the authors could also consider adding some discussion of to what extent the ancillary variables used in the last section could be augmented by using the f43, f55, f57, f60 from the AMS real time feed.

Answer:

We agree that we underutilized the PMF analysis and therefore added the PMF factors to Figure 5 and Tables S3-S5, as well as the sampling periods to Figure S2 (previously S1). In addition, we included further hypothetical sampling scenarios based on sampling conditions using AMS data as suggested and also added them to Figure 5. These additional sampling scenarios are based on the fractional contribution of individual marker ions to the total AMS organics signal. We used f60 as a marker for biomass burning OA and f55 as well as the ratio f55/f57 as markers for cooking-related OA.

As shown in Figure 5, BBOA as well as COA show strongly enhanced concentrations in the source-related sampling intervals, independent on the definition of the sampling scenarios, while OOA concentrations are very similar in the source-related and the background sampling intervals. When the sampling scenarios were defined on the basis of AMS marker ions, an effective enhancement of the respective source-to-background concentration ratio was observed for several of the measured variables. This enhancement is especially large for those variables, which are directly associated with the applied marker ions, used for definition of the sampling scenarios, e.g. enhanced BBOA source-to-background ratio when f60 is included in the sampling scenario definition.

We added a discussion of these additional results to Section 4.3.3, which also includes a discussion on the limitations of this approach, due to the relatively low time resolution of the AMS measurements with typically 15-60 s, which does not allow the reliable sampling of the source aerosol under quickly fluctuating wind conditions.

"The combination of PNC measured by CPC and wind direction was evaluated as additional sampling scenario (Wind+CPC). Further sampling conditions were defined based on the AMS data using fractions of the organic signals at single m/z , e.g. at m/z 55 as f_{55} , to test whether a potential use of the AMS for AERTRACC control could improve aerosol separation. The selection of a combination of wind direction and f_{55} (Wind + f_{55}) as well as f_{55} and the ratio f_{55}/f_{57} (Wind + $f_{55} + f_{55}/f_{57}$) was based on known markers for COA while the combination of wind direction and f_{60} (Wind + f_{60}) was based on the known marker for BBOA. The limit values in the sampling condition definitions were chosen from literature values for these aerosol types (Elser et al., 2016; Mohr et al., 2009; Mohr et al., 2012; Saarikoski et al., 2012; Sun et al., 2011; Xu et al., 2020)."

and

"The mass concentrations of black carbon (BC), polyaromatic hydrocarbons (PAH), organics measured by AMS, the AMS PMF factors BBOA, COA, and OOA, PM_{10} as well as PNC measured by CPC and OPC were used to compare how well different sampling scenarios separate between source emissions and background."

and

"The largest ratios for almost all variables besides the AMS-based ones, and consequently the most effective separation of source-related and background aerosol, were achieved when elevated PNC measured by OPC additional to the right wind direction were used as sampling condition (Wind+OPC)."

and

"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. For COA, higher source/background ratios were achieved with the Wind + f_{55} sampling scenario, compared to the other scenarios, and even higher ones with the Wind + $f_{55} + f_{55}/f_{57}$ 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 + f_{60} scenario enables the most effective separation for BBOA combined with potential sampling times comparable to the Wind+OPC scenario."

and

"Therefore, for scenarios like Wind stable and Wind + $f_{55} + f_{55}/f_{57}$, longer overall measurement periods in the vicinity of the source are necessary to reach sufficient sampled aerosol mass."

In the summary, a sentence regarding a potential addition of the AMS for AERTRACC control and its benefits was added.

"A future addition of AMS for AERTRACC control would offer the possibility to define specific sampling conditions for certain aerosol types, like BBOA and COA, derived from AMS measurements, using known markers."

Minor comments:

The manuscript often uses “aerosol” when it really means “aerosol type”, suggest rephrasing.

Answer:

We agree with the reviewer and revised the whole manuscript accordingly.

L29: “Within multiphase processes aerosol interacts with atmospheric gases forming new substances”. While this is certainly true, in many (most) cases the chemistry happens in the gas phase and the products end up in the particle phase by simple partitioning, so consider rephrasing.

Answer:

Thank you for the suggestion. We rephrased the sentence. (L1).

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

L36: Seasalt (as well as dust) is by far the largest primary aerosol type by mass, consider revising.

Answer:

We rephrased the sentence (L35).

“Primary particles can be related to anthropogenic sources like combustion processes of fossil fuel and biomass as well as natural sources emitting e.g. sea salt and dust.”

It’s a minor point, but I find the distinction between the FIGAREO-CIMS and the “TD-HRToF- CIMS” not helpful and mostly distracting. It’s the same instrument, and per the AERTRACC description the authors are even using the FIGAREO inlet for their filter desorption. So it is the same instrument, and the authors are just using it in offline mode, no need to suggest that there is a difference beyond that.

Answer:

Thank you for pointing us to this potential source of confusion. We used “TD-HRToF-CIMS” as name for the analysis method not the instrument which is used for analyzing the filters and TDTs. As instrument, we used the HR-ToF-CIMS from Aerodyne with the FIGAERO inlet for the filters and a custom build inlet for the TDTs. We avoided using the term “FIGAERO-CIMS” because for the TDT analysis we used a different inlet.

To clarify the difference between method and instrument, we revised the manuscript and stated “TD-HR-ToF-CIMS” explicitly as analysis method in the abstract, introduction, and Section 2.5:

“Information on chemical compounds in the sampled aerosol is accomplished by thermal desorption chemical ionization mass spectrometry (TD-CIMS) as analysis method.”

and

“TD-HR-ToF-CIMS (thermal desorption high resolution time-of-flight chemical-ionization mass spectrometry) was chosen as analysis method offering high resolution mass spectra combined with high sensitivity and low sample fragmentation as well as minimized sample preparation effort (Aljawhary et al., 2013; Mercier et al., 2012; Yatavelli et al., 2012).”

and

“For analysis of the samples for this study the TD-HR-ToF-CIMS method was used with the HR-ToF-CIMS (Aerodyne Research Inc., USA) coupled to the FIGAERO inlet for filters and a custom-built inlet for TDT.”

L105: “non-refractory chemical composition of submicron particles”. This sounds as if the AMS is part of the standard MoLA suite, but that’s not what the Table reflects. Please make it consistent.

Answer:

Thank you for the hint. Actually, the AMS is part of the standard MoLa suite, however it was not used so far for controlling the AERTRACC sampler due to technical reasons. We included the AMS in Table 1 and, based on your last general comment, we added to the footnote that the AMS data are currently not used for AERTRACC control but might be implemented in the future.

Just a general comment: it seems that the flows are simply checked before startup and then left to their own devices. Given that a typical sample day is probably 4-6 h before the TDTs and filter holders are taken out, relying on the needle valves alone seems fine, but there could still be some variations that could potentially lead to turbulence while valve switching. So some monitoring equipment might be wise...

Answer:

Thank you for this suggestion. Indeed, it would be a valuable addition to AERTRACC to avoid any drifts and minimize uncertainties of the sample flows and to simplify flow settings by using mass flow controllers instead of needle valves. For cost reasons this was not implemented yet, but will be considered for future studies. We added to the manuscript in Section 2.2 that the flow rate did not change during control measurements and that mass flow controllers would avoid any fluctuations of the flows.

“No change of flow rates was observed during test measurements. Replacing the needle valves by mass flow controllers for future studies is planned to ensure constant flow rates and to simplify flow settings.”

Section 2.3: It should be stated in what language the software was developed (Igor Pro, I assume) and also what type of license is used for it.

Answer:

Thank you for the remark. It is correct, we used Igor and added this information to the text (Sect. 2.3).

"It was developed with Igor Pro (Version 6.3, WaveMetrics, Inc., USA)."

Section S1: What organic density is used? 1.4 g/cc or the variable one based on Kuwata et al (2012). For source studies the latter seems like the better choice

Answer:

We agree that the determination of organic density based on Kuwata et al (2012) is the better choice and used it for our study. We added this information to the SI together with a reference for further details on OPC data treatment.

"The PM1 mass concentrations were calculated from the combined particle number size distributions of FMPS ($dp = 5.6 - 560$ nm) and OPC ($dp = 0.25 - 32$ μ m) assuming spherical particles with a density calculated using the AMS and black carbon data based on the equation of Kuwata et al. (2012) for organic density and Salcedo et al. (2006) for overall density."

and

"Details on OPC data treatment like the conversion from optical diameter to geometric diameter are provided in Drewnick et al. (2020)."