Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., author comment AC2
https://doi.org/10.5194/amt-2020-482-AC2, 2021

Reply on RC2

Johannes Passig et al.

Author comment on "Detection of ship plumes from residual fuel operation in emission control areas using single-particle mass spectrometry" by Johannes Passig et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2020-482-AC2, 2021

Response to Anonymous Reviewer #2
We thank the referee for reviewing our manuscript and the valuable comments. Please see our reply below.

Note:
Reviewer comments are in italics.
Author responses are in normal format.
Changes that were made to the manuscript are in **bold face.**

Review of Passig et al., Detection of ship plumes from residual fuel operation in emission control areas using single-particle mass spectrometry
This manuscript describes single particle composition measurements that identify ship exhaust using iron and vanadium in such particles. It is a nice study, and I don't think the authors would be surprised for me to say it is not earth-shattering news. In particular, the Ault et al. papers (properly cited here) already show the use of vanadium to see ship exhaust in single particles. What is new is being a little further from the ships and more important, that a different laser wavelength resonantly ionizes iron, making its signals large enough to be paired with the vanadium as a tracer.
I think this manuscript has a place but probably should be much shorter. It is always hard, especially for young authors, to leave out that nice bit of analysis you have done but that doesn't really contribute to the flow of the paper. There is a lot here that isn't on the rather more focused topic of "this is what we can do that isn't in previous papers". The descriptions of the background particles and their behavior in 3.1, 3.2, and 3.3 are much too long. The discussion of hygroscopicity isn't required – it isn't part of the tracking of ship exhaust. Further, some of the material actually detracts. Here are two examples: (1) I was questioning how much of the diurnal behavior (near line 235) is due to boundary layer influence. Then I realized that a paper about V and Fe in ship exhaust doesn't really need to discuss diurnal variation of OC-EC particles. (2) There are many other reasons than water that negative ions might appear (near line 155) and was about to write some review comments on this, but since V and Fe are only in the positive ion spectra the manuscript would be better off just not discussing negative ion spectra at all. These are just two examples.
Overall, I would suggest aiming for a manuscript about half as long rather than cutting a few sentences here and there.

We thank the referee for the comments and the vital discussion. Comments on the issues raised by the reviewer:
- There are several more new aspects in the paper: (I) We could prove that ships under scrubber operation can still be detected by the metal emissions, although the majority of particles is removed by the scrubber. Moreover it is the first SPMS study on plumes from scrubber operation and reveals substantial sulphur emissions, showing how malfunctions and compliance issues can be detected. (II) The distance to the ships is about 10-fold larger than in previous papers (e.g. the mentioned Ault et al. papers), fulfilling a prerequisite for open-sea monitoring. (III) Mass spectral signatures to distinguish individual plumes from background ship emissions are introduced and discussed. **(IV) For the new manuscript, additional experiments were performed to better demonstrate the enhancements for metal detection which are a keystone for pushing the limits single plume detection to larger distances.**
- We agree with the referee that parts of the manuscript are too long and detailed. However, claiming the detection of individual plumes from such distances in a complex and variable environment required us to provide the full picture. We are happy to convince both referees that such plume detection is possible. **To improve the manuscript, we moved the mass spectra and discussion of all particle classes but the ship particles to the supplement, provided a smaller Fig. 2 and shortened the manuscript wherever possible. Of note, reviewer #1 asked for some more discussion and data on the individual plumes, which reduces the margin for shortenings a bit.**
- Our analysis shows that the mass spectral signatures of both positive and negative ions from ship emission particles can provide valuable information on the particle aging and the distance to the source, a key aspect for potential open-sea monitoring. We showed that the clustering of mass spectra separated events of transient nature (ship plumes) from background shipping emissions. These differences in positive and negative mass spectra belong therefore to the key findings of our study and need some discussion. **To follow the referee's advice, we rephrased the discussion on ageing and avoid to attribute it only to water uptake.**

Some technical points:
1) Figure 4 is a good use of ART-2a. Too often, people just use ART-2a cluster as simple quantitative tracers, something they are actually not that well suited for. I like the way the manuscript manually combines and separates the Fe-V clusters to see different behavior.
We thank the referee for the honouring words.

2) The manuscript could use some suggestions for a non-cluster algorithm of tracking ship exhaust. Something along the lines of "If Fe greater than x, V greater than y, some other ion less than z" you have a pretty good idea a particle is ship exhaust. Other researchers are not going to be able to duplicate your ART-2a categories.
We added a plot in former Fig. 3e that shows the timeline of particles with Vanadium and Nickel signatures without a clustering analysis. This plot also illustrates some effects of the Fe-enhancement.

3) Line 61 the mixing contrast between particles and gases is confused. In turbulent mixing and wind-driven transport particles and gases are carried together. Particles may be easier to measure at large distances because the compositions are more unique than a generic gas-phase tracer like carbon monoxide, not because gases "rapidly mix". The particles rapidly mix, too.
We corrected this sentences, focusing only on the conservation of signatures in an externally mixed particle ensemble.

4) If feasible consider putting the zones with special fuel requirements overlaid on Figure 1.

Unfortunately, this is not possible as the complete North Sea and Baltic Sea belong to this zone, an area much large than that one depicted in Fig. 1.

5) Near line 184 I disagree that V+ and VO+ are obscured by organics – that is possibly but not at all usual.
We agree that interferences occur more easily when the Vanadium signals are weak or when the threshold for V-signals are too low. **We added the V-Ni-timeline in Fig. 3e, which indicates some ambiguity for periods of strong organic signals if only a marker-ion approach is used instead of a cluster algorithm.**

6) Near line 190 and Figure 21. If the mean aerodynamic diameters for all of the accumulation mode particle classes are above 500 nm then either you don't have efficient optical detection down to 150 nm or your aerodynamic lens is not working well for smaller particles. The concentrator alone doesn't explain that.
The optical detection efficiency as well as the aerodynamic lens system was well-proven for particles down to 100 nm and even below (Li et al., 2011). The inlet design resembles the UF-ATOFMS by (Su et al., 2004) In our experiments, the concentrator reduced the particle count rates below 500 nm size. However, we could not find the cause so far.

7) Near line 314. It is better to delete the speculation about sulfate-driven dissolution if you can't measure it.
Statement removed correspondingly.

References

Li, L., Huang, Z., Dong, J., Li, M., Gao, W., Nian, H., Fu, Z., Zhang, G., Bi, X., Cheng, P., and Zhou, Z.: Real time bipolar time-of-flight mass spectrometer for analyzing single aerosol particles, Int. J. Mass Spectrom., 303, 118–124, https://doi.org/10.1016/j.ijms.2011.01.017, 2011.

Su, Y.; Sipin, M. F.; Furutani, H.; Prather, K. A. Development and Characterization of an Aerosol Time-of-Flight Mass Spectrometer with Increased Detection Efficiency. Anal. Chem. 2004, 76, 712−719