Response to Anonymous Reviewer #1
We thank the reviewer for his/her work and the valuable comments. We are convinced that addressing the issues raised by the reviewer helped to improve the manuscript. 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 to "Detection of Ship Plumes from Residual Fuel Operation in Emission Control Areas using Single-Particle Mass Spectrometry" by Passig et al., AMT-2020-482

This paper reports on the detection of individual ship plumes over distances of several (ten and more) kilometers by single particle mass spectrometry. The authors use laser ablation ionization with resonance-enhanced detection of iron which increaes the sensitivity to iron-containing particles. Such iron-containing particles (together with vanadium and nickel) are then used to identify ship plumes. Furthermore, a concentrator was used to increase the concentration of particles. I have some issues with the scope and the overall goal of the paper. I don't see why it was submitted to AMT. ACP or Atmospheric Environment would have been a better choice, because the measurement technique is not the main focus of the paper. The technique of resonanced-enhanced detection of metals has been described by the authors in an ACP paper (Passig et al., 2020), which to my opinion should have been an AMT paper.

We thank the referee for carefully reviewing our manuscript and the valuable comments. The paper has several key aspects that are all technical: (I) The application of the generic resonance effects in SPMS to detect ship plumes from the distance. (II) Determination of mass spectral signatures for remote ship traffic and for individual plumes in a typical situation with complex aerosol background. (III) The first detection of plumes from scrubber-operated ships and (IV) by far the largest distance to the ships, thus illustrating the open-water monitoring capabilities. **In order to improve clarity on the key aspects of the study, we shortened and refined the manuscript, e.g. by moving the discussion on particles of other origins than ships to the supplement and putting the focus more on the particle's metal signatures. Moreover, we performed additional laboratory experiments, showing enhancements in detection efficiency also for Vanadium and Nickel.**

In the present work, neither the resonance-enhanced detection nor the application of the concentrator (which is done in Passig et al, 2020, supplement) are described and discussed. I suppose the authors consider the detection of ship plumes using the enhanced detection efficiency for iron-containing particles as the technical aspect in this work. But I guess the decision whether this manuscript fits into the scope of AMT or not has already been taken by the editor.

We agree with the referee that the iron-enhancements are a suitable technical aspect. However, quantifying the improvements for plume detection would require a direct comparison of the mass spectral signatures with and without the resonance for ambient air experiments on transient ship plumes. This would require two SPMS systems operated at the same time. **To strengthen the aspect of resonance- and wavelength effects and to provide**

an estimate on the improvements in detection capabilities, we performed new experiments using a research ship engine. Thus, we could demonstrate a much more efficient detection of V, Ni and Fe with resonant ionization compared to non-resonant ionization. In order to prevent the manuscript from becoming too long (see comments of Reviewer II), we added these experiments in the Supplement and refer to it in the manuscript. Furthermore, to better illustrate the role of Fe-resonances and clustering for plume detection, we added a new graph to Fig. 3 that allows a comparison to a conventional ion marker approach for V without Fe-signals.

I am somewhat impressed by the finding that ship plumes can still be detected by single-particle analysis over such long distances, but the authors have to admit that this was also a good piece of luck and that they are strongly dependent on wind direction. If fact, the authors admit that in the conclusions section. It has also to be noted that the idea of analyzing ship plume particles by aerosol mass spectrometry is not new. A very similar study by Ault et al (which is referenced here) identified about 12 ship plumes in 5 days. Diesch et al. (2013, not referenced) identified and analyzed 139 ship plumes in 5 days, using a similar setup, but being located much closer to the shipping route. Furthermore, a recent ship-based study (Celik et al., 2020, not referenced) detected more than 250 ship plumes during a 2 month cruise and were therefore able to provide a large data set on ship plume characteristics.

New aspects beyond the literature are e.g. (I) the large distance individual plumes can be detected, even with considerable background (II) the detection of scrubber-operation (III) the identification of markers for the plume ageing. For example, most previous studies were conducted in harbour areas on short distance (e.g. Ault et al.: 0.5 km, Diesch et al.: 1 km). Furthermore, Diesch et al. and Celik et al. used an Aerodyne AMS. This is a very different approach without single-particle information, thus more affected by substantial background from other emission sources, especially in populated or urban areas. However, we thank the referee for indicating the new and impressive study of Celik et al. that was new to us and **we added both references. Moreover, we discuss the role of single-particle information to reduce the dependency on background levels and thus allowing plume detection both on open sea as well as in populated coastal areas.**

Overall, I am therefore not convinced that this method will be useful to monitor particle emissions from ships on a regular basis. Single-particle mass spectrometers are typically large, heavy, expensive and require a lot of maintenance (please correct me if I am wrong). This together with the difficulty in plume assignment to individual ships will make it very hard to use this setup in a kind of monitoring application.

Our SPMS can be installed in a car trailer and operated remotely for days. The difficulties in plume assignment are inherent to all fixed monitoring approaches and substantially eased by publicly available ship transponder and more accurate air trajectory data. **Furthermore, setting up two systems at opposite sides of a strait or region in the main wind directions facilitates monitoring. We comment on this in the new manuscript.**

Nevertheless, the paper presents some interesting data on selected ship plumes. I have two major comments that need to be addressed before publication, and several minor comments and technical corrections as listed below.

Major comments:
1) What I miss the most is a detailed analysis of all detected plumes. In Figures 4 and 5 I count about 12 "enhancements" of the V-Fe-Ni particle class, which (according to the argumentation of the manuscript) are likely ship plumes. In section 3.4, however, only the

plumes on June 28 are analyzed further. To be precise, they are assigned to ships but not analyzed. I suggest including (at least) a table with all events that qualify as a potential ship plume, list the possible assignment to a ship and the plume characteristic. Here, ion ratios averaged only over the plume times might be a useful indcator. V/Fe, Fe/Ni, Fe/S, for example. Additional graphs with averaged mass spectra for the plume periods or size dependend composition of the plume particles might also be helpful.

We thank the referee for this suggestion. Fig. 4 shows the distribution of particles with different chemical signatures over the individual plumes, providing most of the desired information. **However, we added table 2, listing the particle numbers, average particle size, ion ratios and sulfate signals for the individual plumes as suggested by the referee.**

A related question here is: Were there no accompanying data? No CPC, optical particle counter, CO/CO2/NOx dectectors, no black carbon instrument? All such parameters are usually required to better understand the plume characteristics and assignments.

We fully agree with the referee in that point. However, the plumes were accidentally captured in an experiment aiming on different aerosols in ambient air. Therefore, unfortunately, no further instrumentation was under operation.

2) It is not clear to me whether the resonance-enhanced iron detection is needed for this analyis. Would you find and identify the the same amount of ship plumes by:

- *applying the ART algorithm ignoring m/z 54 and 56, or*
- *using vanadium and nickel as marker ions without ART clustering? I mean, simply looking at the time series of mz 51 (V) and mz 58 and 60 (Ni)?*

I think that in an AMT paper that is supposed to be technical this should be shown and discussed.

We performed such analyses and found that the plumes can also be detected by their V-Ni signatures. However, dependent on the signal thresholds for V and Ni, this leads to either additional false positive results and lower contrast to background or to a reduced detection missing some features. **We added a timeplot for particles identified solely by their V-Ni signatures for comparison with the ART-2a result including the Fe signals in the former Fig. 3(e) (Fig. 2e in the revised manuscript). The discussion was extended correspondingly. Moreover, the new experiments on a ship engine further underline the importance of the resonances.**

Minor comments

Lines 56-57: UAVs are also limited in their payload

We thank the referee and added this comment.

Line 61: Gas and particle both mix with air and are transported. "in contrast" seems not to fit here.

We corrected this statement.

Lines 107 - 118: This sounds like "normal" SPMS analysis. But the resonance-enhanced Fe detection will lead to an overweighting of Fe. Is this considered in the analysis? Please comment and discuss.

The increased Fe-signals have no limiting effect on the cluster analysis. Of note, also several particle-bound species are detected with much higher efficiency than others (e.g. alkali metals). This is a limitation for quantification in SPMS, but clustering algorithms only consider mass spectral differences between particles in the ensemble and the enhancement affects all Fe-containing particles. **We added a comment that the Fe-signals were not excluded from the clustering and discuss the particle identification by clustering via marker ion screening in the context of Fig. 3.**

lines 120-122: This should go into section 2.1 (line 98 ff)

We thank the referee and moved the sentence accordingly.

Lines 123 - 125: The HYSPLIT trajectory analysis is not sufficient. In the supplement, we see only single trajectories. It is necessary to use the "ensemble" option or to manually initialize more starting times and locations to get an estimation on accuracy and variability. On the other hand, the 0.5° resolution (see comment later) may lead to the conclusion that the trajectrories are not usefol here at all.

We agree with the referee that back-trajectory analyses without local wind data are generally not sufficient for plume assignment on such distances, which is discussed in our paper. **To fully exploit the trajectory data, we repeated the analysis engaging the "ensemble" option and changed the supplemental according to the suggestion of the reviewer.**

lines 161 - 153 and Fig 2: I would not term the second particle class "OC-EC", because it contains a lot of nitrate and sulfate. Something like "OC-EC + inorganic" or "EC + secondary" would describe this type better.

We changed the term accordingly. Please note that the mass spectra and discussion of all particle classes apart from the ship emission particles were moved to the supplement to meet the requirements of referee #2.

lines 171 - 174: But you measure close to the Balctic. I would therefore expect to see also fresh sea salt particles at times when the air arrives directy from the north. Why are there no fresh sea salt particles?

We thank the referee for studying the manuscript with so much care. Indeed, only few fresh sea salt particles were observed. The discussion on their ageing timescale would be speculative but we assume that the geographical situation with a relatively small distance of the trajectories over open sea at direct north winds play a role, as well as the comparable light winds. **We added a statement on this effect in the discussion on sea salt particles. Note that the discussion of particle types other than the ship emission particles has been moved to the supplement.**

Line 258: Why were only 12 out of 15 clusters used here?

The clusters are ordered with respect to their particle numbers. Clusters 13,14 and 15 contain less than 150 particles each, which is not sufficient for the plots with high time resolution.

Lines 274 - 279: The "transient group" is identified as ship plume particles. The question arises again: Would you get the same (or a similar) result without resonance-enhanced iron detection? What would happen if you use Vanadium as a marker ion?

We added a corresponding plot in Fig. 3e, illustrating the result for the use of Vanadium and Nickel without Iron as marker ions and discuss it there.

Fig 4 b) What are weight matrices? To me the plots looks like "averaged mass spectra". Why do panels b) and c) have different sizes?

Weigth matrices are a direct outcome of the cluster analysis and reflect the mass spectra in the respective cluster center, resembling the average spectra without being identical. **For clarity, we added a statement on this.** The panels have different limits of their m/z axes for clear recognition of relevant mass spectral signatures.

Lines 291 - 295 I don't agree that the absence of negative ions due to uptake of water is a sign of aging. It is more reflecting the actual humidity conditions and can therefore be a sampling issue. Drying the aerosol (intentionally by using a dryer or inadvertantly by drawing cold air from the outside into a warm laboratory) will remove the water from the particles again. Stratospheric particles which have presumably spent a long time in the atmosphere show large HSO_4^- signals (e.g. Murphy et al., 2014).

The effect of particle ageing and secondary material on SPMS spectra was studied in great detail by Hatch et al. (2014) and the suppression of several peaks by particle-bound water was analysed by Neubauer et al. (1998). Our discussion is in line with their findings. Of note, a change in actual humidity conditions as well as a sampling artefact would affect the mass spectra of all particles in a specific period, which is clearly not observed (see e.g. the time plot of the sulfate signal in Fig. 5(b)) As discussed in the manuscript, the clustering algorithm separated events of transient nature (ship plumes) from background shipping emissions (further away, more aged) only by the particle's mass spectral signatures, without further assumptions. The differences in mass spectra are exactly the discussed features summarized in former table 1. **To accommodate the requirements of the referee and to leave the discussion open, we rephrased the discussion on ageing and avoid to attribute it solely to water.**

Line 297: By "in the plume" here you mean gas plume inside the MS after laser ablation, not the ship plume, or am I wrong?

exactly. **We removed this statement by shortening the manuscript.**

Line 313: "In contrast to negative ions and EC, OC as well as alkali cations". I suggest using consistenly either "positive and negative ions" or "anions and cations".

changed accordingly.

Line 315-317: I think that is clear that Fe is enhanced. How large is the enhancement compared to non-resonant ionization? Is there an enhancement factor? In Passig et al. (2020) you report an increase by up to a factor of 20 for ambient data. But is that particle detection efficiency or signal height? This should be be mentioned here.

We added a statement that refers to the approx. 20 times more frequently detected iron signatures in the direct comparison experiment in Passig et al. (2020). Furthermore, our new experimental data provides an estimate on the detection efficiency for all three metals, which is mentioned in the revised manuscript.

Lines 331 - 334: Would it make more sense to take only the "transient" clusters from Fig 4 (110, 150, 151, 161,164, 183)? Or show these clusters in separate time series?

I'm afraid this might be a little misleading because the sulfate signals are not discussed here as a signature to differentiate between plumes and background signal. We are confident that the differences in sulfate signals between the plumes are well recognizable and would prefer to leave the reader free to decide whether the sulfate signals can be attributed to an individual ship.

lines 354-369: I am certain that on such small local scales, wind direction is better than HYSPLIT with 0.5° resolution. The distance to the harbor was about 10 km, and 0.5° are in the Rostock region about 50 km in north-south direction.

We fully agree, discuss it in the paper and refer to the **changes in the HYSPLIT trajectories in the supplement.**

line 357: Refer to Fig 5 here instead of Fig 4d. Add markers (numbers) to the plumes in Fig 5 and refer to those.

changed according to the referee's suggestions.

line 364-369: See comment to 0.5 degree resolution above. You can't expect to see such local features.

We fully agree, discuss it in the paper and refer to the **changes in the HYSPLIT trajectories in the supplement.**

Lines 393 - 399: A more detailed plot of the time series for the individual plume would help a lot here.

The plots in the final manuscript will be high-resolution vector graphics with better detectable features that can also be easily zoomed.

Lines 434-435: I fully agree with this: local wind data and small scale models are absolutely needed.

This is one of the practical conclusions of the paper.

lines 437-439: Multiple stations? I think that would be a huge effort for single-particle mass spectrometers. A measurement site closer to the shipping route but in the main wind direction (e.g. Diesch et al., 2013) would improve the approach already a lot.

Our paper describes a route towards a long-range monitoring system with stationary SPMS setups, which can hardly be achieved with particle integrating/averaging approaches like the AMS used by Diesch et al. due to the lack of single-particle information. Our SPMS can operate autonomously for days to weeks in a car trailer. **We added a comment in the**

manuscript suggesting a setup of two instruments at opposite sides of a strait, covering two main wind directions. Indeed, we are already preparing such measurements.

Technical comments:

Line 48: However, "of" scrubber ooperation? Remove "of"

changed accordingly.

Line 56 + 411: please correct citation "Van Roy, W and Scheldemann, K., 2016"

citation corrected.

line 115 "if product" -> insert "the"

changed accordingly.

line 210: Insert full stop after S3

corrected.

line 268 "his" -> "this"

corrected.

References

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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 beyond the ones stated by the reviewer: (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.

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