Measurement report: Vanadium-containing ship exhaust particles detected in and above the marine boundary layer in the remote atmosphere–reviewer comments

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We would like to thank the reviewers for their insightful comments and suggestions, which have enhanced the quality and clarity of the paper.

In addition, changes requested by the reviewers, we have made the definition of the Saharan Air Layer more consistent between figures in the manuscript. The changes are minor and do not affect the discussion or conclusions.

REVIEWER 2

‘**General comments:**

The authors present data on the distribution of vanadium-containing ship exhaust particles in the atmosphere, measured during regular flights over large areas of the world's oceans at different altitudes. This is a unique dataset and the authors report on the prevalence of these particles also in remote regions and high altitudes. Ageing mechanisms and the chemistry of vanadium-containing particles are discussed in the context of the altitude-dependent particle number fractions and their chemical composition.

The study provides valuable insights into the distribution of ship emission particles, prerequisite for a better understanding of their climate impact. The manuscript is technically sound and interesting. There are a few points that could help to further improve the manuscript:

Specific comments:

- When emphasizing the importance of ship emissions, the authors could consider to also provide some newer literature, that also addresses the current changes due to the fuel regulations, e.g. Kuittinen et al. Environ. Sci. Technol. 2021, 55, 1, 129–138, Jonson et al., Atmos. Chem. Phys., 2020, 20, 11399 —11422, Anders et al., Environ. Sci.: Atmos., 2023, 3, 1134-1144 etc.

We have added the Anders et al., 2023 reference to line 48. Although the other citations you have mentioned are insightful, they are less relevant to this manuscript. We do cite newer literature on vanadium-containing ship exhaust particles near line 71:

"These methods can also result in a reduction in the total number of vanadium-containing particles emitted by ships (Yu et al., 2021; Xiong et al., 2023); however, the reductions are not complete as vanadium-containing ship exhaust particles are still detected in ECAs (Passig et al., 2021; Xiong et al., 2023)."

- line 30: In the abstract, the -mount of annual PM emissions was given as 1.2 Tg/y, here as 1.67 Tg/y PM.10. Also, please provide a reference.

This abstract text was changed to 1.67 Tg in line 9. The following reference was added to line 30:

Additionally, the combustion of heavy fuel oil from ships contributes to approximately 1.67 Tg y-1 of particulate matter with an aerodynamic diameter of 10 µm or smaller (PM10) (Eyring et al., 2005).

- line 110: Traditionally, the particle's sulphur content is evaluated by the negative charged sulphate ions and sulphuric acid. I understand that the compact aircraft-deployable design of PALMS only allows for unipolar measurements, but could the authors provide a brief statement on the evaluation of sulphur content via S+ and SO+, particularly regarding potential interference with carbon cluster from soot at m/z=48?

Although soot can appear at m/z=48, soot spectra can be distinguished by the presence of C_n, C_nH, and C_nH2 (n = 1, 2, 3, etc.), which were not observed in the vanadium-containing particle spectra identified in this work. This is now stated in the manuscript on line 118:

"SO+ at m/z = 48 can be distinguished from C4+ from soot by the absence of peaks such as C3+ and C4H+."

- line 113-115: The strong NO+ signal compared to e.g. Ault (2010) and Passig (2021) can be attributed to the wavelength of the used ArF-Excimer laser. In a direct comparison of a 248 nm KrF-laser with a 193 nm ArF laser, it could be shown that the 248 nm laser is much more sensitive to iron and transition metals due to a resonance effect, but the 193 nm laser is more effective in ionizing NO+ and nitrogen-containing organics, see Passig et al., ACP, 20, 7139–7152, 2020. Ault et al. used Nd:YAG lasers at 266 nm, a wavelength more comparable to the KrF excimer laser than to the ArF laser.

We have amended the text on line 121 to include the following text from your suggestion:

"The strong NO^+ signals observed in this work may be a result of using a 193 nm excimer laser, which is more effective at ionizing nitrogen containing species compared to the 248 nm (Passig et al., 2021) and 266 nm laser (Ault et al., 2010) used in the other studies, which are more sensitive to iron and transition metals due to a resonance effect. Finally, this could also be indicative of atmospheric aging processes."

- lines 159-162: Anthropogenic particles in the respective size mode are subject to long-range transport. So, why exclude particles detected over land and in polar regions? While shipping activity is much lower in the polar regions, the particles there are important for climate impacts, e.g. through deposition on ice and albedo changes. Were there not enough V-containing particles detected? The exclusion of these areas should be better justified.

Almost all the ATom data is over the ocean, and the very few flights over land (for example, transits across northern Alaska) were not representative of larger areas. The polar regions are a different category than the open oceans. Not only is there essentially no shipping, the boundary layer and wind transport are different over ice than over open ocean. Finally, near Antarctica the flight patterns were different. It would considerably complicate the manuscript to include the polar regions. We have added a brief mention of the different boundary layer to the caption of Figure 4.

- lines 163-170: The conservative determination of V particles from shipping is appropriate. An important consideration is the ageing of these particles. Both an increase and a decrease in the organic carbon content of the particles is possible during ageing and would have a direct effect on particle identification using the criteria of V+/VO+ peak intensity relative to neighbouring peaks. This is discussed later in the manuscript, but may be briefly mentioned already here.

The criteria of V+/VO+ peak intensity relative to neighbouring peaks, is to distinguish vanadium from organic peaks. Although an enhancement in organics could affect this interpretation, the organic content increase would have to be significant, which we do not expect to see during the atmospheric aging of vanadium-containing ship exhaust particles. We have added the near on line 179 in the manuscript:

"In addition, vanadium signals could be obscured by larger organic signals as particles age, although the organic peaks do not get so large (section 3.5) for this to noticeably affect classification."

- General comment: I am missing the total number of V-particles in the respective measurements/flights. I may have overlooked it, but this information would give an estimate of the statistical quality.

This is now stated near line 210 during the discussion of Figure 4:

"Each ~12° latitude bin in Figure 4 includes about 1000 to 4000 particles in the MBL and about 4000 to >10000 particles above the MBL during each deployment. With about 1% of particles in the MBL containing vanadium and less than that above the MBL, each point in **Fig. 4** represents tens of vanadium-containing particles."

- lines 201-214: Could the authors provide an example of these diluted plumes? For example as a plot in the supplement?

We have added Figure S5.

- Figure 5: Again, I am missing absolute particle numbers. If the feature in the tropical Pacific is attributed to a single ship plume, as stated in the main text, I assume the particle numbers to be relatively low. Since sampling time is limited and particle concentration in the free remote atmosphere is low, low particle numbers are an inherent problem of such measurements and not a drawback of the study.

Particle numbers are now stated near line 210 during the discussion of Figure 4:

- line 255: Did you really observe a sufficient signal of oxalate in positive mode? I cannot see this signal in the mass spectra (Fig. 2).

Oxalate is indeed difficult to see in positive mode. We have removed mentioning it here.

Finally, we apologize for the slow response to reviewers. The lead author started a new job during the review process, which led to some delays in our response times.