REVIEWER 1: This study presents a comprehensive investigation into the distribution, sources, and biogeochemical drivers of alkylamines in Antarctic surface waters, offering novel insights into polar marine nitrogen cycling and microbial ecology. The authors employ a high-sensitivity analytical method (HS-SPME-GC-NPD) to quantify dissolved and particulate alkylamines, addressing long-standing challenges in measuring these reactive, low-concentration compounds. These findings are timely, given the climate relevance of alkylamines in aerosol formation and their underexplored roles in polar microbial food webs.

Authors: We thank the reviewer for his/her positive comments and appreciations.

Key Concerns:

1. In the introduction, lines 57-60, the authors have elaborated extensively on aerosol-related content and cited relevant references. However, no discussion on aerosol is present in the discussion section. It is recommended to include a discussion on aerosol in this section. Incorporating wind speed/SST data could further quantify their climate relevance.

Authors: We agree with the reviewer and we have added the following sentences at the end of the discussion "These findings also highlight the necessity of increasing alkylamine determinations to be incorporated into future biogeochemical and climate models, given the Southern Ocean's abundance of aerosol precursor gases and the pivotal role of alkylamines in both marine and atmospheric systems. Biogenic emissions influence atmospheric chemistry through primary and secondary pathways, potentially enhancing CCN concentrations and modulating cloud albedo, thereby impacting regional radiative forcing (McCoy et al., 2015). The contribution of low-molecular-weight alkylamines to aerosol mass, particularly from air masses passing over melting sea ice (Dall'Osto et al., 2017), underscores the critical role of marine plankton and sea-ice melt in particle formation and Antarctic climate regulation (Brean et al., 2021). Our results emphasize the need for an understanding of ocean–atmosphere interactions in pristine polar environments and, more broadly, of aerosol processes that likely play a major role in climate dynamics.". We are unable to calculate amine fluxes because, although we have sea surface temperature and wind speed data, we lack the concentrations of amines in the air.

McCoy et al., 2015: 10.1126/sciadv.1500157. The other references are already cited in the text.

2. The hypothesis that phytoplankton directly produce DMA via TMAO demethylase (Lines 691–693) lacks direct evidence. While the authors cite fish tissue studies (Kimura et al., 2000), extrapolating this to microalgae requires genomic or enzymatic validation.

Authors: Thanks for allowing us to clarify. TMAO is a cellular osmolyte and is present throughout marine ecosystems, from surface seawaters to deep sediments (Fitzsimons et al., 1997; Gibb et al., 1999; Carpenter et al., 2012, Mausz et al., 2019) and also in polar diatoms (Dawson et al., 2020, Fitzsimons et al., 2024). The fact that eukaryotic cells like those of some fish have the capability to enzymatically transform TMAO to DMA allows us to speculate that this may also occur in phytoplankton. We know this is just speculation and we are trying to provide an explanation for the relationship between DMA and phytoplankton. We have modified the sentence: "Although the specific enzymatic pathways are unknown, it is plausible that phytoplankton could directly release DMA or indirectly through bacteria attached to the outer membrane or residing in the phycosphere."

Dawson et al., 2020: 10.1093/icb/icaa133; Fitzsimons et al., 1997: https://doi.org/10.1016/S0146-6380(97)00062-4; Gibb et al., 1999: https://doi.org/10.1016/S0967-0645(98)00119-2; Carpenter et al., 2012: https://doi.org/10.1039/c2cs35121h.

3. Despite measuring viral abundances (V1–V3), the discussion overlooks viral lysis as a potential amine source. Given the correlation between Factor 1 and V1–V3 (Table 1b), a brief analysis of virus-phytoplankton interactions (e.g., *Phaeocystis* lysis) would strengthen the narrative.

Authors: We agree with the reviewer; however, in lines 743-744 we had written "Notably, the factor most strongly linked to mortality, viruses, did not appear to influence alkylamine pathways." Factor Analysis enabled us to numerically visualize the correlations between variables. Although Factor 1 is associated with V1–V3, no amines appeared to be linked to the virus populations. From the Factor Analysis, the only correlation between viruses and amines has already been stated in lines 652–654. We have added this sentence "However, incorporating viral lysis as a key phenomenon in Antarctic phytoplankton dynamics is essential for advancing the understanding of microbial interactions and improving the accuracy of organic matter flux estimations in this climate-sensitive region (Biggs et al., 2021)."

Biggs et al., 2021: https://doi.org/10.1038/s41396-021-01033-6.

4. The speculated role of iron in regulating alkylamine distributions (Lines 588–589, 644–646) lacks supporting Fe concentration data.

Authors: We are trying to discuss possible explanations for the differences in amine concentrations in the Antarctic Peninsula versus the Weddell Sea. However, we agree with the reviewer that point to iron when there is no measurement may be going too far, and have made changes in the revised manuscript: "Given the similarities in phytoplankton abundances and composition of the two areas, this difference can likely be attributed to the potential effect of light stress, since waters of the Weddell Sea were clearer and more stratified (data not shown), hence more exposed to excess of damaging sunlight." The other sentence has been deleted.

5. Contrasting Antarctic alkylamine levels with prior Arctic or temperate studies would highlight polar-specific processes.

Authors: Thanks for the suggestion. Indeed, reviews by Poste et al., 2014 (including freshwater studies) and more recently by Fitzsimons et al. (2023 and 2024) report alkylamine data. Amines have been detected in various marine environments such as the Arabian Sea (Gibb et al., 1999a, b), the North Atlantic, and Cape Verde waters (van Pinxteren et al., 2012, 2019), as well as in the ice-associated waters of the Southern Ocean (Gibb et al., 2004, Dall'Osto et al., 2017, 2019). Notably, there is currently a lack of studies on alkylamine detection in (polar) seawater, with more extensive research on alkylamines conducted in the (polar) atmosphere (Köllner et al., 2017, Brean et al., 2021). We have added these sentences: "Amines have been measured in seawater in polar regions primarily by Gibb et al. (2004), who used a flow-diffusion gas chromatography method with selective nitrogen detection in Marguerite Bay, Antarctica, and by Dall'Osto et al. (2017, 2019), with subsequent methodological improvements introduced by Akenga and Preston (2024). Gibb et al. (2004) reported maximum dMMA concentrations of 36 nM, while Dall'Osto et al. (2017, 2019) observed concentrations of total methylated amines (3–10 nM) that were significantly lower than those measured in the present study."

Gibb et al., 2004: https://doi.org/10.1016/j.marchem.2004.04.005; Gibb et al., 1999a,b: https://doi.org/10.1016/S0967-0645(98)00119-2 and https://doi.org/10.1029/98GB00743; van Pinxteren et al., 2012: dx.doi.org/10.1021/es204492b.

> 6. The particulate amine protocol (Lines 166–172) lacks critical details: (i) filter storage duration before analysis, (ii) CPA spike recovery rates, (iii) NaOH volume for amine liberation. Clarify to ensure reproducibility.

Authors: We agree with the reviewer. We have improved the section accordingly: "We also measured amines in particulates retained on GF/F filters after seawater filtration (section 2.2). Analyses were conducted ~6 months after sample collection. Prior to extraction, each filter was placed in a 20 mL autosampler glass vial and allowed to thaw inside the vial (one filter per vial). Subsequently, we added 250 µL of CPA (20 nM final concentration) as internal standard and 500 µL of 10 M NaOH, to liberate gaseous amines, and the vial was tightly sealed. This treatment was assumed to volatilize the target analytes into the vial headspace in a manner analogous to dissolved samples. Particulate amine concentrations were quantified using standard amine solutions, as described previously.". Recovery data for CPA in particulate samples are not available. We assume that the volatilisation of amines from the NaOH-treated filter is the same as that from NaOH-treated solution. Particulate amine concentrations were calculated using the same standards as for dissolved amines. This procedure was most suitable and applicable for particulate quantification. Note that this is the first time that particulate amines are analyzed in seawater.

7. Inconsistent use of "nanophytoplankton" and "phytoplankton" (2–20 µm in Methods vs. 2–7 µm in Results). Standardize definitions or justify size-class divergences.

Authors: Nanophytoplankton encompasses all phytoplankton within the size range of 2 to 20 µm. Therefore, referring to phytoplankton in the range of 2 to 7 µm still classifies them as nanophytoplankton although we wrote phytoplankton "cells 2–7 µm in size". When we consider the nanophytoplankton from 2 to 20 µm, we refer to the sum of the abundances or biomasses from 2 to 20 µm (sum of biomass or abundances between 2–7 µm, 7–15 µm and 15–20 µm). We have revised the sentences throughout the text for improved clarity.

In summary, the paper by Rocchi et al. (2025) presents valuable data and insights into the distribution and sources of alkylamines in Antarctic surface waters. With some revisions to address the issues outlined above, the paper has the potential to make a significant contribution to the field of marine biogeochemistry.