Free and combined amino acids in Antarctic aerosol particles. Insights from molecular-level size-resolved field measurements during PolarChange.

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Marine aerosol particles over the Southern Ocean can be a model for pristine atmospheric conditions, yet their molecular organic composition remains insufficiently resolved. This study presents a comprehensive analysis of free amino acids (FAA), combined amino acids (CAA), and nucleobases in size-segregated Antarctic marine aerosol particles and associated seawater samples collected during the PolarChange ship campaign around the Antarctic Peninsula. Using a unified UHPLC-HILIC-QTOF-MS approach, atmospheric particle extracts and dissolved and particulate ocean waters were quantified, enabling direct comparison of oceanic sources with atmospheric composition.

Amino acid concentrations in this study fall within previously reported polar ranges but represent the first molecularly resolved CAA dataset for this region. CAAs systematically exceed FAAs in concentration and exhibit a pronounced submicron enrichment, contributing up to 10% of ultrafine particle mass and up to 35% of organic carbon. In contrast, FAAs contribute less to particle mass and display stronger variability with meteorological parameters. Size-resolved molecular analysis reveals distinct partitioning behavior, suggesting selective enrichment during sea spray aerosol formation and/or secondary production processes for certain analytes.

Chemical signatures indicate predominantly fresh marine influence, supported by strong Na^+-Cl^- correlations and hydrophilic dominance. Molecular patterns further reveal dominance of proteinogenic, water-soluble amino acids (e.g., Gly, Ser in CAAs; Gln in FAAs), episodic nucleobase occurrence, and enrichment of acidic amino acids. Correlation analyses demonstrate that FAAs respond analytically to humidity, wind speed, and inorganic ions, whereas CAAs appear largely decoupled from inorganic variability.

Overall, the results highlight differential transfer, transformation, and stabilization mechanisms governing FAAs and CAAs in Antarctic marine aerosol. These findings provide new molecular constraints on organic nitrogen cycling, secondary processing, and ocean-atmosphere exchange in the climatically sensitive and comparatively pristine polar environment.