



Supplement of

Enhancement of ammonium nitrate aerosol in the Northern Hemisphere lower stratosphere linked to Asian summer monsoon outflow

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S1 Flight path overview of the PHILEAS campaign 2023

Figure S1 provides an overview of the flight tracks conducted during the PHILEAS campaign in 2023. The figure complements the description of the air mass selection used for the analysis of AMA filament air masses in the ExLS. In addition to the six flights used for the Early and Late Phase comparison in the main text, the filament analysis also includes measurements from flights F08 to F18. These flights sampled air masses over the western Pacific, Alaska, northern Canada, and northern Europe, where AMA filament were identified based on enhanced CH₄ mixing ratios following Köllner et al. (2026). The flight path overview is therefore included to provide spatial context for the broader flight selection used in this part of the analysis.

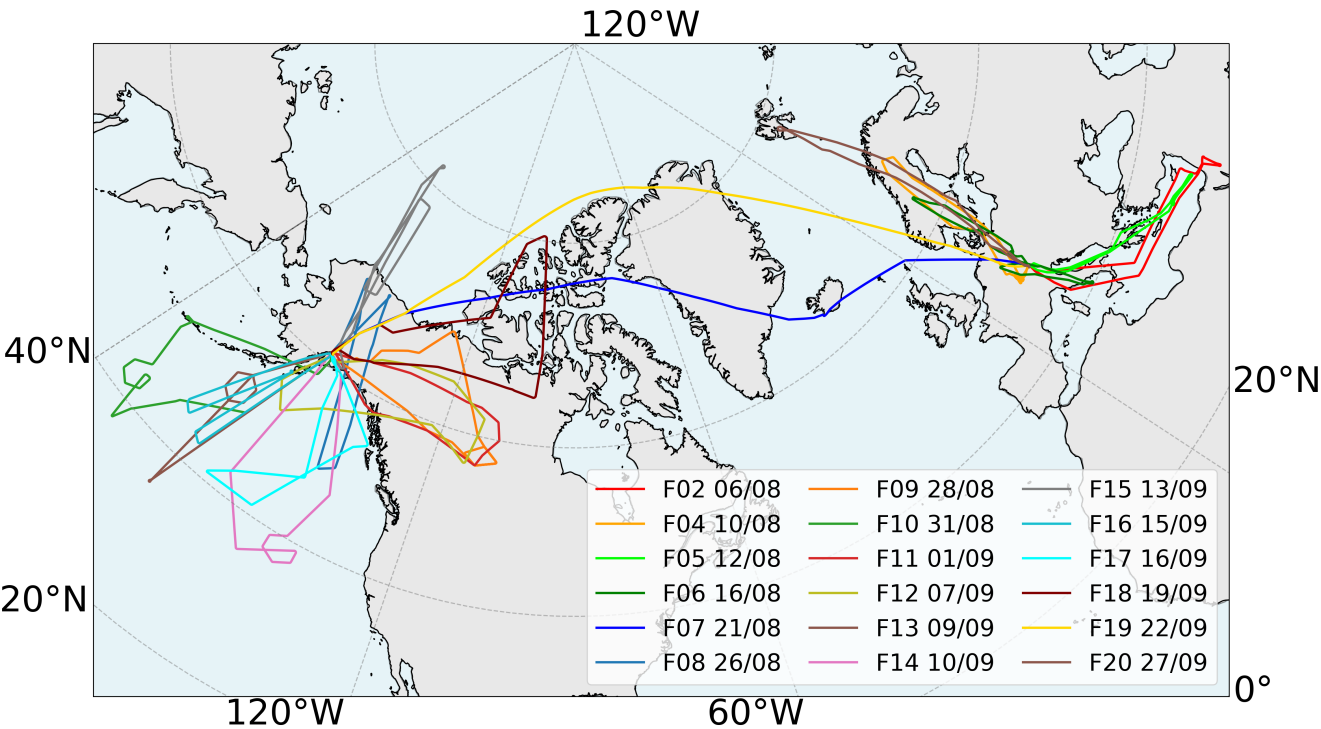


Figure S1. Overview of the PHILEAS flight tracks conducted between 6 August and 27 September 2023. The colored lines show individual research flights from F02 to F20, with the corresponding flight dates given in the legend. This overview provides spatial context for the selection of flights F08 to F18, which were used for the analysis of AMA filament air masses in the ExLS.

S2 HALO Aerosol Submicrometer Inlet (HASI)

S2.1 S2.1 Description of HASI System

10 The HASI (HALO Aerosol Submicrometer Inlet) is designed to sample submicrometer aerosol particles for in-situ measurements onboard the research aircraft. It provides a controlled airflow of up to 30 liters per minute, distributed among four sam-

pling lines that supply aerosol measurement instruments inside the aircraft with sampling air. The inlet is mounted on top of the aircraft fuselage to ensure representative sampling of ambient aerosols, avoiding disturbances from the aircraft boundary layer. The HASI system decelerates incoming airflow by a factor of ~40 through a three-stage process comprising a front shroud, a main diffuser, and smaller diffusers at the tips of the sampling tubes. An optional backward-facing sampling tube is also available for alternative measurement configurations. The design minimizes the entry of large cloud droplets and ice crystals, reducing potential measurement artifacts (Minikin et al., 2017; Andreae et al., 2018). During the PHILEAS campaign in 2023, the HASI system was used for the ERICA and the FASD (Fast Aerosol Size Distribution; Curtius et al. (2024)) instrument for submicron aerosol sampling. To maintain accurate aerosol sampling, the HASI system is operated under isokinetic conditions, where the airflow velocity at the inlet matches the aircraft's airspeed. The so-called HASI Flow Control Unit (HASI-FCU) regulates the sample flow rate during flights, using pumps and bypass lines to ensure consistency. During PHILEAS, in certain instances, the HASI-FCU malfunctioned, failing to provide sufficient bypass flow for isokinetic sampling. This issue was attributed either to software problems and/or the failure of the by pass pumps. In Table S1 all measurement events that were affected by this are listed and analyzed in Sect. S2.2.

Table S1: HASI-FCU Shutdown events: All listed measurement events correspond to when the bypass flow responsible for isokinetic sampling dropped.

Flight	HASI-FCU operation problems (start time – end time)
F01	2023-07-25 10:27:47 – 13:22:14
F02	2023-08-06 06:25:18 – 06:48:07; 2023-08-06 07:11:47 – 08:17:59
F04	2023-08-10 07:39:50 – 07:42:24; 2023-08-10 07:52:53 – 07:57:43; 2023-08-10 08:20:23 – 08:32:36; 2023-08-10 13:42:34 – 14:16:36; 2023-08-10 14:21:24 – 14:31:34
F05	2023-08-12 06:23:11 – 07:19:18; 2023-08-12 07:20:40 – 07:25:02
F07	2023-08-21 10:05:36 – 10:09:25; 2023-08-21 18:53:36 – 19:24:35
F09	2023-08-28 22:16:10 – 22:36:53; 2023-08-28 23:04:49 – 23:09:34; 2023-08-29 01:00:13 – 01:09:39; 2023-08-29 02:59:46 – 03:18:01
F14	2023-09-10 20:59:28 – 21:21:35; 2023-09-10 21:44:57 – 21:56:19
F15	2023-09-14 01:18:37 – 02:15:33
F16	2023-09-15 22:05:21 – 22:10:23
F17	2023-09-16 21:56:13 – 22:54:10; 2023-09-17 05:43:44 – 06:27:59
F18	2023-09-19 18:00:01 – 18:34:18; 2023-09-20 01:15:49 – 01:32:56; 2023-09-20 01:36:39 – 02:16:09
F19	2023-09-22 21:39:58 – 21:48:51; 2023-09-22 21:50:32 – 21:54:21; 2023-09-22 21:59:16 – 22:03:49; 2023-09-22 22:13:21 – 22:15:53; 2023-09-22 23:19:42 – 23:39:46; 2023-09-23 00:00:55 – 00:12:16; 2023-09-23 00:34:32 – 00:52:24; 2023-09-23 01:40:08 – 01:56:13; 2023-09-23 02:16:30 – 02:21:49; 2023-09-23 02:32:14 – 02:40:54; 2023-09-23 04:49:11 – 04:52:05; 2023-09-23 05:43:33 – 06:08:00

Flight	HASI-FCU operation problems (start time – end time)
F20	2023-09-27 07:22:55 – 07:40:25; 2023-09-27 07:41:53 – 07:49:15; 2023-09-27 07:51:35 – 07:56:45; 2023-09-27 08:05:09 – 08:18:43; 2023-09-27 09:18:32 – 09:20:48; 2023-09-27 10:57:17 – 11:01:22

25 S2.2 Analysis of Isokinetic Flow Regulation and Impact on Measurements

To assess the impact of the HASI-FCU issues on the aerosol mass concentration measurements with ERICA, Flight F18 was analyzed as a representative case. This flight was chosen because the HASI-FCU outage occurred at particularly high altitudes in the UTLS region, the primary region of interest for this study. The measurement conditions during F18 are thus well-suited for evaluating potential sampling artifacts under the most relevant atmospheric conditions.

30 A malfunction of the HASI-FCU interrupts the bypass flow necessary for maintaining isokinetic sampling at the aircraft inlet. Sampling theory distinguishes between isokinetic, sub-isokinetic, and super-isokinetic conditions, depending on the relationship between the sampling flow (V_0) and the velocity of the surrounding airstream (V_1). Under isokinetic conditions ($V_1 = V_0$), the sampled particle population is representative of the ambient aerosol. In sub-isokinetic conditions ($V_0 > V_1$), as expected when the bypass pumps are off due to HASI-FCU issue, larger particles are preferentially enriched in the inlet
35 system. This is because large particles, owing to their momentum, cannot easily follow the streamlines and are more likely to enter the inlet, potentially resulting in artificially increased mass concentrations. In contrast, under super-isokinetic conditions ($V_0 < V_1$), small particles are preferentially sampled (Kulkarni et al., 2011).

Despite these theoretical considerations, analysis of the ERICA-AMS and ERICA-SkyOPC (model Sky-OPC, Series 1.129, GRIMM Aerosol Technik Ainring GmbH & Co. KG) data for Flight F18 (Fig. S2) reveals no evidence of sudden or artificial
40 increases in aerosol mass and/or particle number concentrations during periods of the HASI-FCU issue. Both the ERICA-AMS and the -SkyOPC show consistent values throughout the HASI-FCU outage, indicating that the HASI-FCU issue did not impact the measurements. This result is likely attributable to the aerosol size distribution in the UTLS, which is dominated by particles smaller than $1\ \mu\text{m}$. At high altitudes, larger particles are generally absent, and thus the bias expected from sub-isokinetic sampling does not materialize. All HASI-FCU failure events across the UTLS dataset were systematically examined,
45 and no significant artifacts or changes in AMS and/or SkyOPC concentrations were observed during any of these events. These findings underscore the robustness of AMS and SkyOPC measurements in the UTLS, even in the presence of temporary inlet control failures.

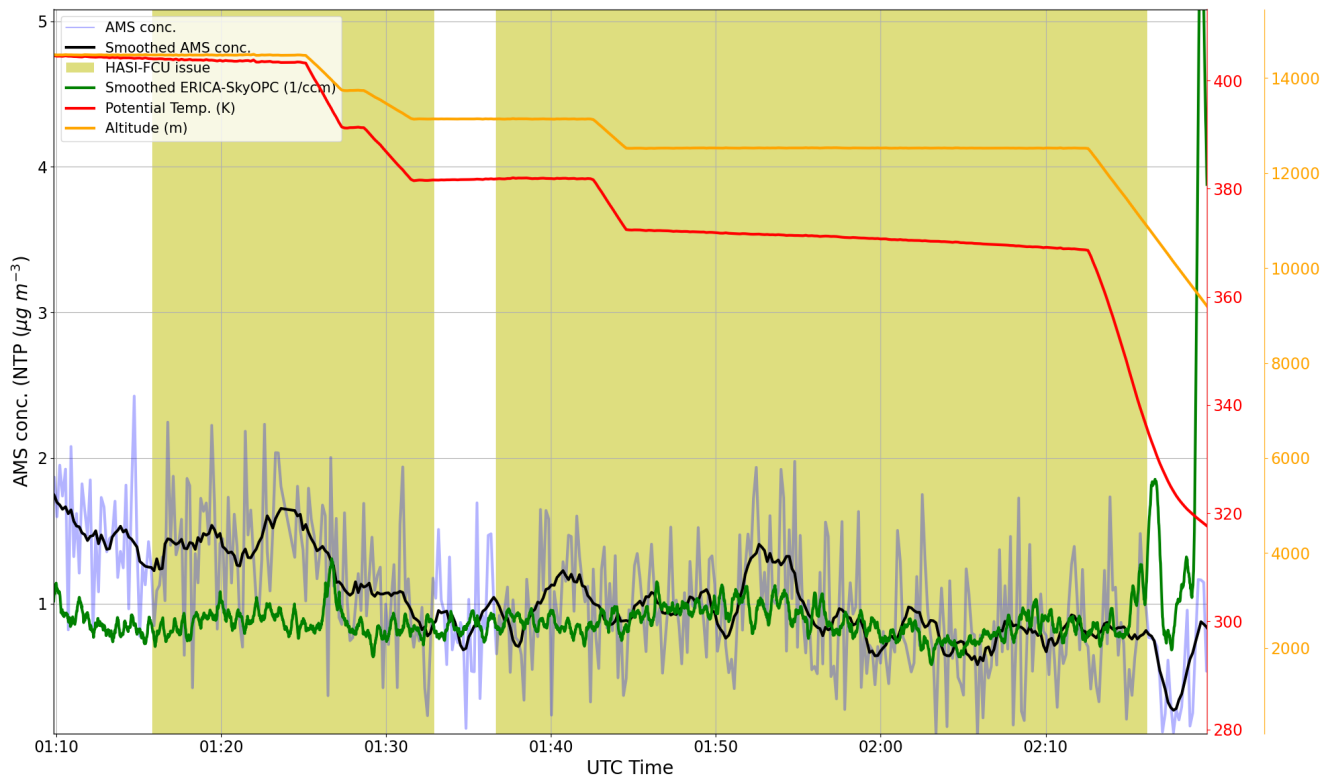


Figure S2. Time series of AMS total aerosol mass concentration (gray, smoothed in black; in $\mu\text{g m}^{-3}$) and smoothed ERICA-SkyOPC particle number concentration (green; in ccm^{-1}) during HASI-FCU issues for Flight F18. Yellow-shaded regions mark periods of HASI-FCU malfunction. Altitude (orange; in m) and potential temperature (red; in K) are shown for reference. Despite HASI-FCU control outages at high altitudes, neither AMS nor SkyOPC data exhibit sudden increases or artifacts, indicating no measurable impact on aerosol measurements. These findings are consistent with all other HASI-FCU events in the UTLS analyzed in this study.

S3 ERICA-LAMS: Data Evaluation

S3.1 Data Post-Processing

- 50 In the following, we will present the post-processing steps necessary to analysis ERICA-LAMS single particle spectra. First, a zero-offset correction was applied to eliminate baseline signals, followed by a threshold of 1 mV for both cations and anions to differentiate real particle from noise spectra (see Tab. S2 'Noisy-Spectra'). This was done immediately after the flights in order to remove the empty spectra that contained only noise. Second, the HASI inlet used for particle sampling during flights was not suitable for measurements inside clouds. Therefore, particle spectra obtained inside clouds were excluded from the further
- 55 analysis by using a cloud flag derived from the BCPD instrument (Backscatter Cloud Probe with Polarization Detection; Lucke et al. (2023)) (see Tab. S2 'Cloud-Spectra'). The cloud flag was provided by Johannes Lucke (DLR). After these steps, the

remaining particle spectra (referred to as 'Flight-Spectra', Tab. S2) were mass calibrated using the software package CRISP (Klimach, 2012). As a last step, particle spectra with a maximum bipolar ion peak intensity lower than a 5 mV*sample (determined in Sect. S3.2) were not further analyzed. Thus, the number of spectra analyzed in this study is given in Tab. S2 with 'Valid Spectra'. Finally, all particles that are present in the ExLS background air masses after filtering with N₂O (< 336 ppbv) and CO (< 40 ppbv) are listed in the column 'ExLS background Spectra'.

Table S2. Overview of number of ERICA-LAMS spectra for all PHILEAS flights used in this study (F04, F06, F07 and F18-F20). The number of usable spectra for each flight is called Flight-Spectra. It represents the number of spectra before the classification for each event (as described in Sect. S5). It includes usable spectra with information about particles without bipolar noise or cloud interactions. Noisy-Spectra are spectra filtered by a threshold of 1 mV for cation and anion signals. Cloud-Spectra are spectra taken during cloud sampling during the flight.

Flight	ExLS background Spectra	Valid Spectra	Flight-Spectra	Noisy-Spectra	Cloud-Spectra
F04	3149	22666	24381	41	4693
F06	3423	18568	19901	44	1617
F07	3837	33128	33818	316	1130
F18	6295	26769	28427	251	1493
F19	11687	30988	32595	44	171
F20	9010	25800	27090	6	579

S3.2 Ion Peak Area Threshold

The ion peak area threshold was introduced by Köllner et al. (2017) in order to distinguish ions signals from background noise. The following criteria were used to determine this threshold: First, all single particle mass spectra sampled during the PHILEAS mission were taken into account. Second, it is assumed that certain m/z values are not occupied by ions from ambient particles by the laser ablation and ionization process. Specifically, $m/z +2$ to $+6$ for the positive polarity and $m/z -2$ to -11 for the negative polarity were considered here. Finally, the threshold was determined at the intersection of the normalized cumulative abundance curve crossing the 99% of the cumulative value, as shown in Fig. S3. Although the results indicated slightly different thresholds for cations (under 5 mV*samples) and anions (under 4 mV*samples), the proximity of these values led to the adoption of a unified threshold of 5 mV*samples for both polarities.

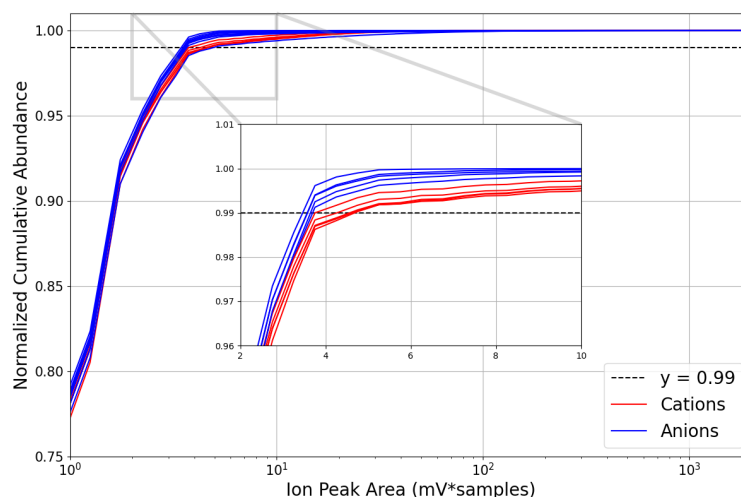


Figure S3. Normalized cumulative abundance of ion signal intensities for of the positive (red) and negative (blue) ion peak areas at m/z +2 to +6 and m/z -2 to -11 (assumed non-occupied m/z values based on Köllner et al. (2017)). The black dashed line indicates the horizontal line for 99%. The inset highlights the region where 99% of the cumulative ion abundance is reached, corresponding to an intensity threshold of approximately 4 mV*samples. To ensure a conservative filtering of noise and retain chemically meaningful signals, we adopted a stricter threshold of 5 mV*samples as the lower limit for ion inclusion in the analysis.

S3.3 Particle Classification: NO^+ –rich and potassium-dominated

The classification method described by Appel et al. (2022a) was used to identify NO^+ -rich particles, and the approach outlined by Köllner et al. (2017) was applied to classify potassium-dominated particles. In total, 37,401 particle spectra from flights F04, F06, F07, F18, F19, and F20 were analyzed, restricted to number of particles within ExLS background air masses (as defined in Sect. S5) and with diameters between 200 and 500 nm (defined in Sect. S3.4)

For NO^+ -rich particles, spectra with the dominant ion peak at m/z +30 (NO^+) were identified, yielding a total of 12,108 particles of this type. As a subsequent step, the ion marker method was employed to further classify the NO^+ -rich particles, determining whether they contain primary compounds such as silicates and potassium (see Tab. S3). The presence of primary marker species in the NO^+ -rich particle spectra was assessed by evaluating whether at least one of the following ion signals exceeded a peak area threshold of 5 mV*samples: Si, P, Na, Mg, V, Fe, K, Cr, Zn, Ti, Cu, Li, or Pb. Spectra that met this criterion were classified as 'primary' NO^+ -rich particles (1,624 spectra), while those without any of these marker ions above the threshold were categorized as 'secondary' NO^+ -rich particles (10,484 spectra). This study focuses on 'secondary' NO^+ -rich particle types to be consistent with the analysis in Appel et al. (2022b). The analysis for this study was carried out using this particle type, as according to Appel et al. (2022a), they correspond to particles formed in the ATAL without inclusion of 'primary' compounds. Figures S4a and b show the typical mean spectra of NO^+ -rich particles for different air mass periods. Figure S4a is a comparison of the Late Phase and the AMA filaments into the ExLS. Figure S4b is a comparison of the NO^+ -rich particle spectra between the AMA filaments into the ExLS and the lower ATAL regime measured during StratoClim (< 370

K potential temperature). The NO^+ -rich particles represent a particle type whose properties correspond well with the signature of the particles measured within the ATAL described by Appel et al. (2022a). Therefore, this particle type is treated as being related to the sources and formation processes of the ATAL throughout this work. However, it is not possible to completely exclude other sources, as we are currently unaware of any other sources for this specific particle type.

For other particle types such as potassium-dominated, the remaining spectra were analyzed using a fuzzy c-means clustering method in CRISP with specific parameters:

- *Ion type*: **Cation**;
- *Preprocessing*: **power each m/z by 0.5**;
- *Normalization*: **Sum**;
- *Distance metric*: **Correlation**;
- *Initialization Startcluster Number/Difference*: **10/0.9**;
- *Fuzzifier/Fuzzy abort*: **$1.3/1\text{e}^{-5}$** .

This clustering yielded four particle types: meteoric material containing particles (7,642 spectra) dominated by m/z +24/+25/+26 (Mg^+) and +54/+56 (Fe^+); potassium-dominated particles (5,151 spectra) with dominant signals at m/z +39/+41 (K^+) (Fig. S4 c); mixed-type particles (4,838 spectra) containing organics, sulfur oxides, and other components; and undefined particles (7,662 spectra) that could not be assigned to the other types.

Table S3. Particle classification by marker species and associated ion markers applied in this study (ion peak area threshold > 5 mV*samples (see Sect. S3.2)).

Ion markers	Marker species (Threshold > 5 mV)
m/z -76 (SiO_3^-); m/z -60 (SiO_2^-); m/z +28 (Si^+)	Si (Silicon)
m/z -79 (PO_3^-); m/z -63 (PO_2^-)	P (Phosphorus)
m/z +23 (Na^+)	Na (Sodium)
m/z +24/+25/+26 (Mg^+)	Mg (Magnesium)
m/z +51 (V^+); m/z +67 (VO^+)	V (Vanadium)
m/z +54/+56 (Fe^+)	Fe (Iron)
m/z +39/+41 (K^+)	K (Potassium)
m/z +40 (Ca^+)	Ca (Calcium)
m/z +52/+53 (Cr^+); m/z +68 (CrO^+); m/z +84 (CrO_2^+)	Cr (Chromium)
m/z +64 (TiO^+); m/z +48 (Ti^+)	Ti (Titanium)
m/z +63/+65 (Cu^+)	Cu (Copper)
m/z +7 (Li^+)	Li (Lithium)
m/z +208; m/z +207; m/z +206 (Pb^+)	Pb (Lead)
m/z +202; m/z +199; m/z +200 (Hg^+)	Hg (Mercury)
m/z +64; m/z +66; m/z +68 (Zn^+)	Zn (Zinc)

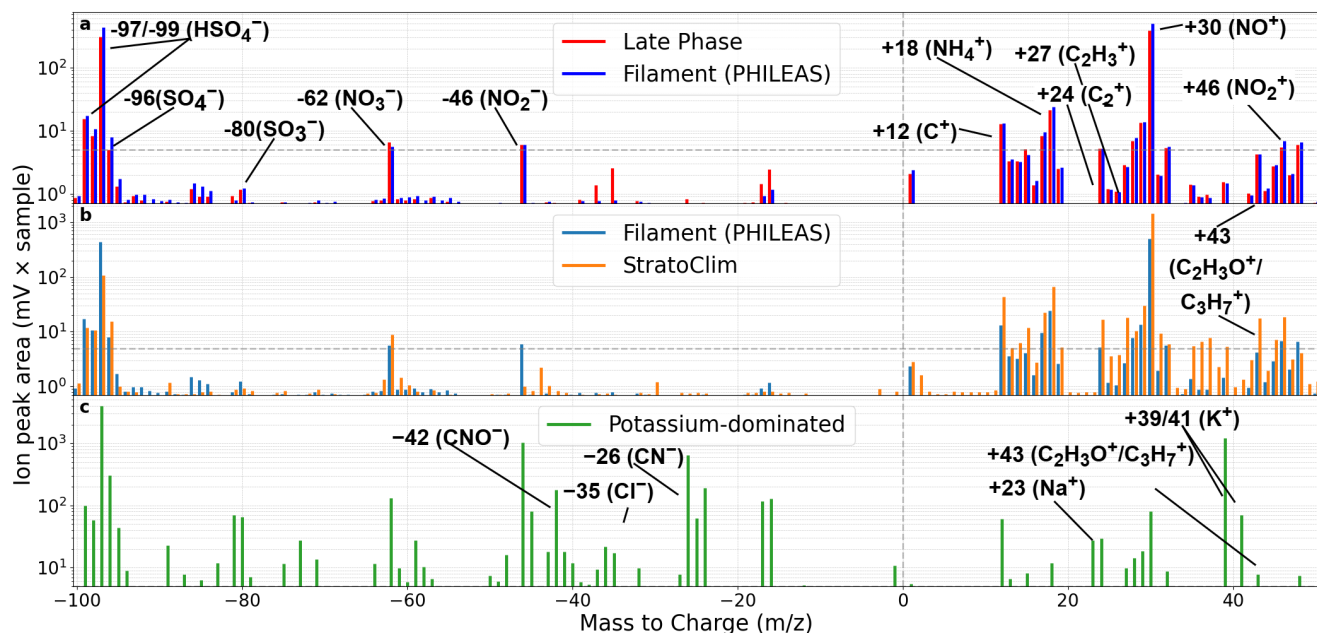


Figure S4. Bipolar mean spectra of the ERICA-LAMS NO^+ -rich particle type: (a) Comparison between the Late Phase (red average over 9,182 spectra) and AMA filament (blue, average over 11,145 spectra) events in the ExLS. Key peaks include $-97/-99$ HSO_4^- , -96 SO_4^{2-} , -80 SO_3^- , -62 NO_3^- , -46 NO_2^- , $+30$ NO^+ , and $+18$ NH_4^+ . (b) Comparison between the AMA-Filaments and lower ATAL regimes measured during the StratoClim campaign (orange, average over 4,769 spectra), showing similar spectral patterns. (c) Mean spectrum of potassium-dominated particles (green, average over 5,151 spectra), characterized by dominant signals from $+39/+41$ K^+ , along with $+23$ Na^+ , -35 Cl^- , -26 CN^- , -62 NO_3^- , $-97/-99$ HSO_4^- , and -42 CNO^- .

S3.4 Size dependence of particle mass spectra characteristics

105 The laser ablation process using ERICA-LAMS can yield varying mass spectra characteristics for different particle sizes even within the same particle type. To minimize this size-dependent effect and to ensure comparable mass spectral characteristics across different measurement phases and campaigns (e.g., from the center of the AMA (during StratoClim) to the ExLS (during PHILEAS)), only particles with diameters between 200 and 500 nm were selected for this analysis. This selection was supported by an analysis of the relative frequency distributions of particle sizes for NO^+ -rich particles measuring during StratoClim and PHILEAS, as described in the main text. The results indicate that the majority of NO^+ -rich particles, approximately 94% for StratoClim and 86% for PHILEAS, are within this size range.

An additional motivation stems from findings during a laboratory-based campaign (the SIA-campaign (SPMS Intercomparison campaign at AIDA 2023)) conducted at the AIDA chamber (KIT) with the ERICA aerosol mass spectrometer in November and December 2023. This experiment provided an opportunity to investigate the chemical properties of particles measured within the ATAL under controlled conditions simulating the AMA environment. It was observed that, for particle sizes above

500 nm, the ion signal intensity for single particles exhibited a dependence on particle size. The underlying mechanisms remain uncertain and is subject of ongoing research. The results of this laboratory campaign will be published separately.

S3.5 Uncertainty Calculation Methods: ERICA-LAMS Dataset

In this section, we describe the methodologies employed to calculate the uncertainties of three output variables by ERICA-LAMS: (1) the particle fraction (Eq. 1), (2) the difference of particle fractions (Eq. 2-4), and (3) the ratio of ion signal intensities (Eq. 5).

(1) Particle fraction

For the vertical profiles showing particle fractions versus potential temperature, the uncertainty in the particle fraction was determined using the standard formula for binomial proportions. This method evaluates the fraction of particles of a specific type relative to the total particle count within each bin of potential temperature. The uncertainty was calculated for each bin, incorporating the statistical variability inherent in particle counting by using the formula taken from Appel et al. (2022a):

$$\sigma_{PF}^{abs} = \frac{\sqrt{N_{total} \cdot f \cdot (1 - f)}}{N_{total}} \quad (1)$$

where:

- N_{total} is the total number of particles in a given bin,
- f is the particle fraction for the specific particle type, calculated as $f = \frac{N_{type}}{N_{total}}$,
- σ_{PF}^{abs} is the uncertainty of the particle fraction.

(2) Scaled number concentration with $N_0 \cdot PF$

The scaled number concentration was calculated by multiplying the particle fraction of a specific particle type PF with the averaged ERICA-LAMS particle number concentration at the first detection stage (N_0). The uncertainty was calculated following the method described in Appel et al. (2022a) and is presented here. The absolute uncertainty of N_0 is calculated using Poisson statistics:

$$\sigma_{N_0}^{abs} = N_0 \cdot \sigma_{N_0}^{rel}, \quad (2)$$

with the relative uncertainty given by:

$$\sigma_{N_0}^{rel} = \frac{1}{\sqrt{C_0}}, \quad (3)$$

where C_0 is the averaged ERICA-LAMS particle count at the first detection stage in the respective bin. The absolute uncertainty of the scaled number concentration was then calculated by Gaussian propagation of the uncertainties of PF and N_0 :

$$\sigma_{PF \cdot N_0}^{abs} = \sqrt{(PF \cdot \sigma_{N_0}^{abs})^2 + (N_0 \cdot \sigma_{PF}^{abs})^2}. \quad (4)$$

Here, σ_{PF}^{abs} is the absolute uncertainty of the PF calculated from binomial statistics as described in Sect. S3.5 (1), and $\sigma_{N_0}^{\text{abs}}$ is the absolute uncertainty of the averaged ERICA-LAMS particle number concentration at the first detection stage.

145 (3) Difference of particle fraction

To evaluate the uncertainty of the change in the particle fraction between two different air mass periods ('Early Phase' and 'Late Phase'), we used the binomial statistics. Figure S5 shows the uncertainties of the change in particle fraction between the Late and Early Phases of PHILEAS. The calculation was conducted as follows: The fraction of specific particle types in each period was computed as:

$$150 \quad f_{\text{Early}} = \frac{N_{\text{type, Early}}}{N_{\text{total, Early}}}, \quad f_{\text{Late}} = \frac{N_{\text{type, Late}}}{N_{\text{total, Late}}}, \quad f_{\text{Diff}} = f_{\text{Late}} - f_{\text{Early}}, \quad (5)$$

where $N_{\text{type, Early}}$ and $N_{\text{type, Late}}$ represent the number of specific particle types observed during the Early Phase and Late Phase periods, respectively, and $N_{\text{total, Early}}$ and $N_{\text{total, Late}}$ are the total particle counts during those periods. f_{Diff} is the difference in the particle fraction between the Late and Early Phase.

The uncertainty was calculated as follows:

$$155 \quad \sigma_{\text{Early}} = \frac{\sqrt{N_{\text{total, Early}} \cdot f_{\text{Early}} \cdot (1 - f_{\text{Early}})}}{N_{\text{total, Early}}}, \quad \sigma_{\text{Late}} = \frac{\sqrt{N_{\text{total, Late}} \cdot f_{\text{Late}} \cdot (1 - f_{\text{Late}})}}{N_{\text{total, Late}}}. \quad (6)$$

To account for the total uncertainty when comparing the two periods, the combined uncertainty for P_{Diff} was calculated as the root-sum-square of the individual uncertainties (σ_{Diff}):

$$\sigma_{\text{Diff}} = \sqrt{\sigma_{\text{Early}}^2 + \sigma_{\text{Late}}^2}. \quad (7)$$

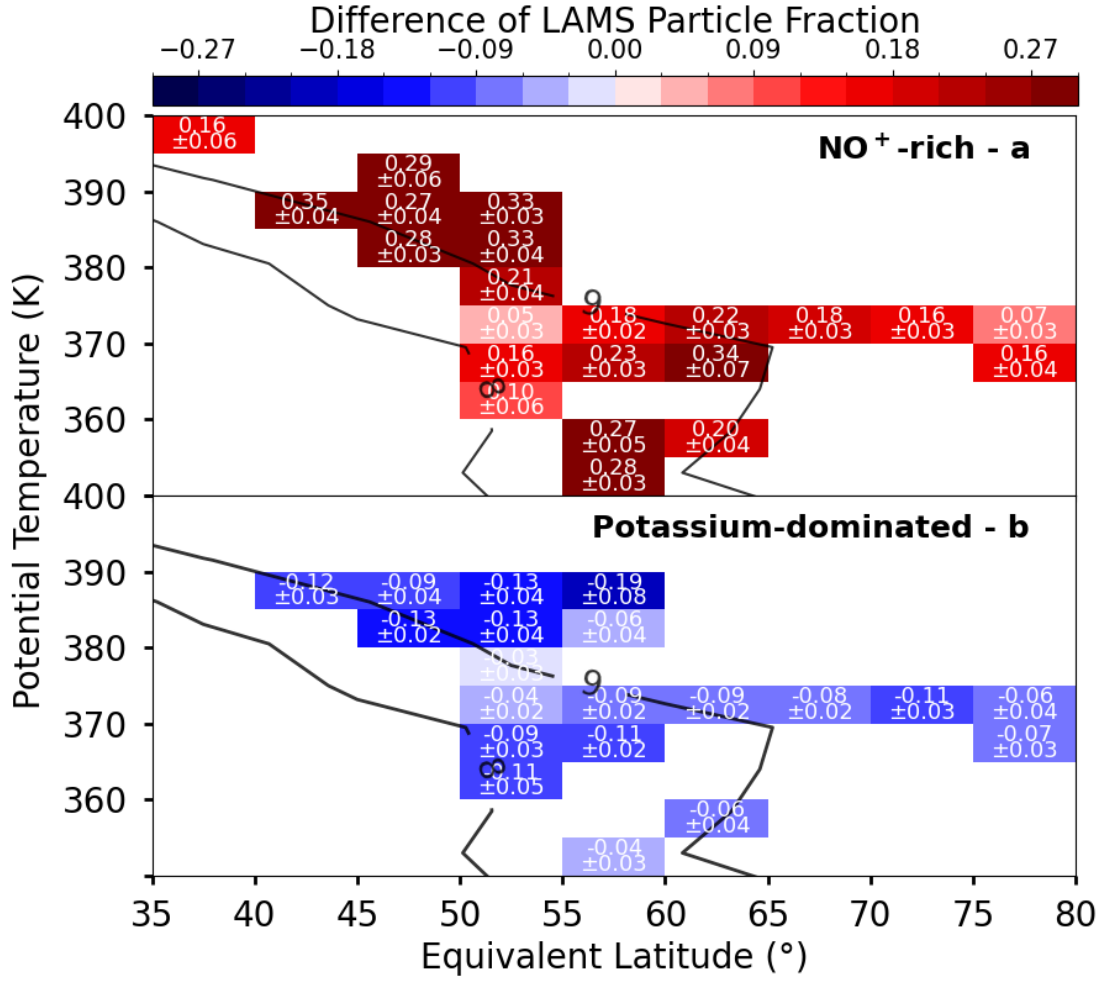


Figure S5. Mean distribution of ERICA-LAMS spectra based on the difference in particle fraction for NO⁺-rich (a), potassium-dominated particles (b) between the Late and Early Phase, as a function of ERA5-derived equivalent latitude and potential temperature. The black solid lines indicate isolines of PV (derived from ERA5) in PVU. The overlaid white numbers in each bin indicate the particle fraction differences (top number) and its associated uncertainty (bottom number), calculated using uncertainty propagation (see Eqs. 2-4). The graph corresponds to Fig. 5 in the main text.

(4) Ratio of different ion signal intensities

160 The ion signal intensity ratio between two signals, such as m/z +18 and +30, is calculated using Eq. 8:

$$\text{Ratio}_{x/y} = \frac{\bar{x}}{\bar{y}} \quad (8)$$

Here, $\bar{x}$ and $\bar{y}$ denote the mean ion signal intensities of the respective ion signal intensity ratios, averaged over the different phases (e.g., Early or Late Phase) as presented in this work. The uncertainty of the ion signal intensity ratios (σ_{ratio}) was calculated using the propagation of uncertainty, accounting for the independent variances of the numerator and denominator,

165 as well as their covariance. The formula used for this calculation is:

$$\sigma_{\text{ratio}} = \frac{\sqrt{\left(\frac{\sigma_x}{\bar{y}}\right)^2 + \left(\frac{\sigma_y \cdot \bar{x}}{\bar{y}^2}\right)^2 - 2 \cdot \frac{\bar{x}}{\bar{y}^3} \cdot \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{n-1}}}{\sqrt{n}}, \quad (9)$$

where:

- $\bar{x}$ and $\bar{y}$ are the mean values of the ion signal intensities of the m/z ratio in the numerator and denominator, respectively,
- σ_x and σ_y are the standard deviations of the mean values $\bar{x}$ and $\bar{y}$, respectively,
- 170 – x_i and y_i represent the ion signal intensities of individual points contributing to the mean, and
- n is the total number of observations in the dataset.

The formula considers three components: (1) the contribution of the numerator variability ($\frac{\sigma_x}{\bar{y}}$), (2) the contribution of the denominator's variability ($\frac{\sigma_y \cdot \bar{x}}{\bar{y}^2}$), and (3) the covariance term that accounts for the dependence between x_i and y_i with $\sum (x_i - \bar{x})(y_i - \bar{y})$. Finally, the normalization by $\sqrt{n}$ ensures the uncertainty scales with the sample size.

175 S4 ERICA-AMS: Data Evaluation

S4.1 Data Post-Processing and Data Analysis

A detailed description of the ERICA-AMS data structure is provided in the supplementary material of Appel et al. (2022a). In the ToFWare 2.5.7 software, the settings were customized to meet the specific requirements of the ERICA-AMS data structure. To prevent the software from normalizing each spectrum to m/z 28, a method intended for Aerosol Chemical Speciation Monitor (ACSM) instruments, for which the software was originally developed, the command **'setigorooption poundde-**
180 **fine=tw_ACSM_diffSticks_dontNorm28'** was executed. The software was then recompiled to apply this modification. Additionally, the **Background is blocked beam (adv)** option was enabled. Due to the custom-built shutter unit in our setup, the software was unable to automatically determine the shutter positions. This limitation was addressed by manually defining the positions: 2–12 for total measurements, 14–24 for background measurements, and buffer position 13 for switching. The mass
185 calibration of the AMS species (such as nitrate, ammonium, organics, sulfate, and chloride) were achieved using the ionization efficiency (IE) calibration, the relative ionization efficiency (RIE) factor (Tab. S4) and a reference flow rate of 1.45 cm³/s (see S4.2). Furthermore, an m/z calibration was conducted to accurately identify ion signal peaks. A three-parameter fit, $p_1 \cdot m^{p_3} + p_2$, was applied using the following reference mass-to-charge ratios: CH⁺ ($m/z = 13.0078$), O₂⁺ (31.9898), SO₂⁺ (63.9619), ¹⁸²W⁺ (181.948), ¹⁸⁴W⁺ (183.951), and ¹⁸⁶W⁺ (185.954). ToFWare 2.5.7 was used to generate stick spectra based
190 on these predefined parameters. Baseline correction for all spectra was performed by applying a linear interpolation method with an integration width of 13 and smoothing set to 2. The aerosol signal was calculated as the difference (diff spectrum) between the open-shutter and closed-shutter measurements. During each research flight, two filter measurements were taken and included into the data post-processing. In particular, filter measurements were used to adjust the fragmentation table in

Tofware 2.5.7. Finally, all AMS data points during cloud interactions in flights were excluded using cloud flags provided by the BCPD instrument (Lucke et al., 2023).

S4.2 Ionization efficiency (IE) Calibration

A detailed description of the determination of the IE value for the ERICA-AMS dataset is provided in the supplementary material of Appel et al. (2022a). Values of the IE calibration that were conducted during ground-based operation in the hangar are listed in Tab. S4. For the post-processing of the ERICA-AMS dataset with the IE values, it is important to consider the wildfire event during F09 (28.08.2023). During this wildfire event, measurements were taken within a very intense wildfire plume over Canada at altitudes of around 3 km. While correcting the data, we observed that the organic concentration measured by the ERICA-AMS increased significantly after the wildfire event. We assume that our flexible O-ring (as a part of the CPI) was afterwards clogged probably with soot/organic particles for a while. We found indications for this hypothesis in the position settings of the O-ring control unit. As a result, we observed that the following IE value decreased from 2943.99 to 1486.42 $ions\ pg^{-1}$ after this event. Consequently, we processed F09 and all flights before F09 using the IE value of 2943.99 $ions\ pg^{-1}$. The dataset after F09 until F16 was processed using the IE value of 1486.42 $ions\ pg^{-1}$ for the dataset after the event.

For flights F16 and F17, we used the average of the IE calibration values obtained on 14.09.2023 and 18.09.2023. Finally, for all data after F17 we used the IE value of 2301.75 $ions\ pg^{-1}$.

Table S4. Overview of IE Calibrations for PHILEAS.

Date	SIS (mV*ns)	IE ($ions\ pg^{-1}$)	RIE (NH ₄)	RIE (SO ₄)	Valid for Flight
18.07.2023	0.713	4409.12	4.11304	0.838158	F02
25.08.2023	0.974	2943.99	4.24608	0.879123	F04 - F09
14.09.2023	0.974	1486.42	4.19520	0.594948	F09 - F15
14.09.2023	0.812	2040.79	4.72384	0.574809	–
18.09.2023	0.812	2456.42	4.41489	0.684701	–
Average of 14.09.–18.09.2023	0.812	2248.61	4.56937	0.629755	F16 - F17
18.09.2023	0.828	2301.75	4.36447	0.720949	F18 - F20

S4.3 Detection Limits

The determination of the detection limits (DLs) for nitrate, sulfate, ammonium and organic matter is analogous to the evaluation described in Appel et al. (2022a). The DLs for PHILEAS were calculated point-by-point. The average DLs for the Late and Early Phases are presented in Tab. 2 in the main text. It should be noted that the average DLs became slightly higher over the course of the campaign (from the Early to the Late Phase). We assume that the same factor that influenced the IE also influenced the detection limit at the same time.

215 Furthermore, we determined the DLs for each bin in order to assess whether ambient concentrations are above the DLs with Eq. 10 (see Fig. S6).

$$DL_{\text{bin}} = \text{mean}(DL_i) \quad (10)$$

To account for statistical uncertainty in bins with fewer data points, we further adjusted the DLs using the standard error of the mean (SEM) principle:

220 $DL_{\text{bin, adjusted}} = \frac{DL_{\text{bin}}}{\sqrt{n}}$ (11)

where n is the number of data points in the respective bin. Bins containing fewer than 10 data points were excluded from the analysis to ensure statistical reliability. Additionally, we determined vertically resolved profiles of aerosol concentration as a function of potential temperature, including error bars that reflect the SEM, calculated from the bin-wise standard deviation:

$$SEM_{\theta} = \frac{s}{\sqrt{n}} \quad (12)$$

225 where s denotes the sample standard deviation of the concentration values in a given θ -bin. These profiles were plotted separately for Early and Late Phases, providing further context for phase related aerosol differences across the ExLS background.

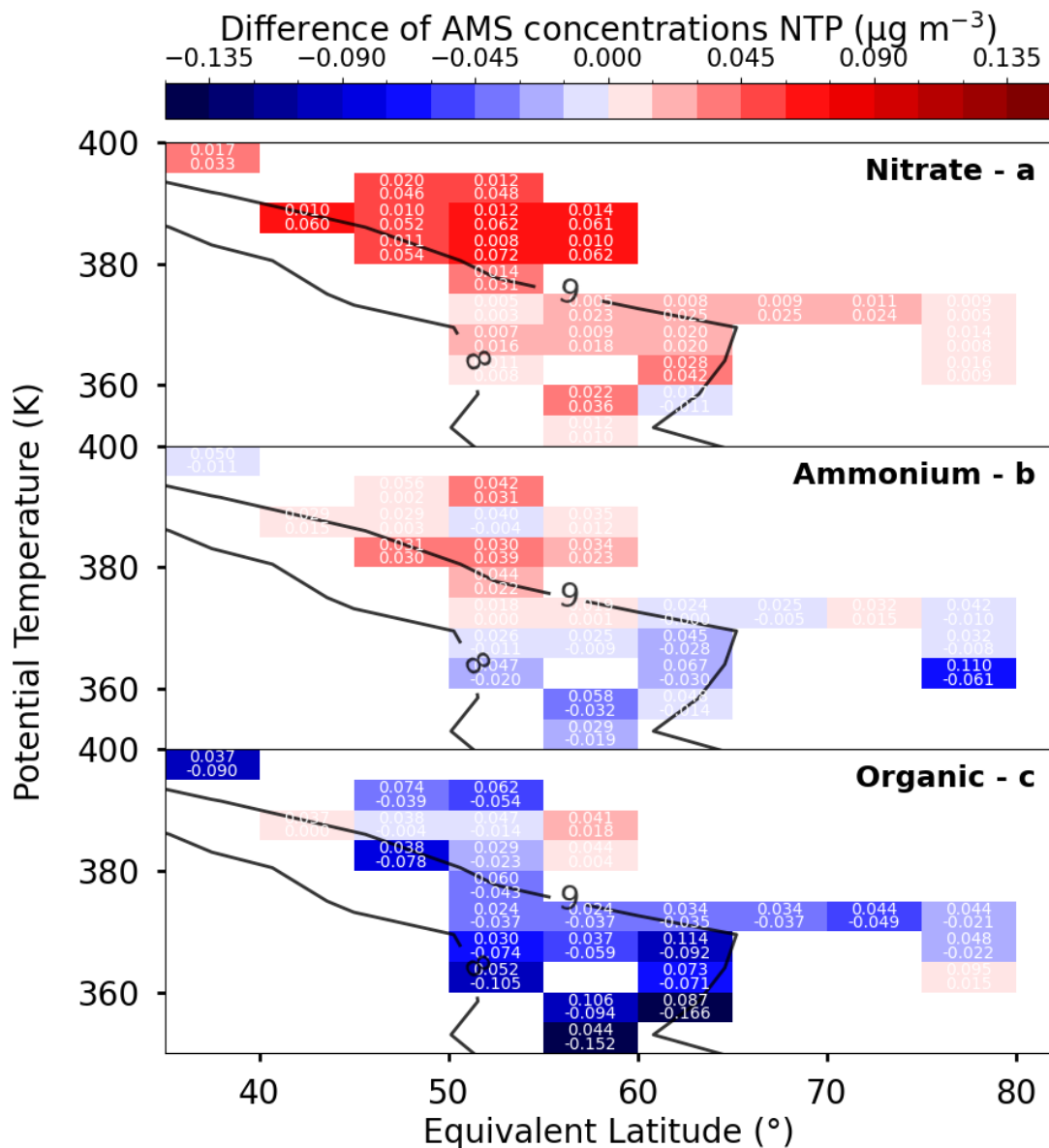


Figure S6. Mean distribution of ERICA-AMS nitrate (a), ammonium (b), and organic matter (c) mass concentrations, shown as the difference between the Late and Early Phases, as a function of ERA5-derived equivalent latitude and potential temperature. Black contours indicate isolines of potential vorticity (ERA5-derived) in PVU. The white numbers inside each bin represent the concentration difference (bottom number) and the detection limit (top number) in $\mu\text{g m}^{-3}$ at NTP conditions. Bins with fewer than 10 data points were excluded. The graph corresponds to Fig. 4a-c in the main publication.

A possible explanation for the variability in the ERICA-AMS detection limits (Tab. 2 in the main text) between individual flights is related to instrumental conditions during the campaign. Prior to flight F08, the ERICA-AMS chamber was unintention-

tionally re-pressurized with ambient air during ground-based operation. In addition, during flight F09 the instrument sampled
230 an intense BB plume with exceptionally high aerosol concentrations, which may have caused minor residual contamination effects despite subsequent pumping procedures. However, the instrument was extensively pumped after both events and returned close to normal operating conditions. The resulting detection limits remained within a reasonable range for UTLS aerosol measurements and did not affect the interpretation of the presented results.

S5 Identification of Stratospheric Background Air Masses

235 Measurements of trace gases like N_2O and CO are essential for characterizing stratospheric background air masses and air masses influenced by pollution events, such as from the ASM region (e.g., Müller, 2015; Müller et al., 2016). In this case, the UMAQS dataset was used to categorize all ERICA-AMS and ERICA-LAMS measurements according to stratospheric background criteria. First, all flight data were combined and measurements with N_2O mixing ratios below 336 ppbv were classified as stratospheric air masses (Riese et al., 2025). Second, within this subset, CO measurements were used to further
240 differentiate between stratospheric background and recently polluted stratospheric air masses. To accomplish this, a relative frequency distribution of all CO data points in the stratosphere ($\text{N}_2\text{O} < 336$ ppbv) were constructed using 1 ppbv bin widths. The resulting distribution is shown in Fig. S7a. Based on the observed bimodality, a threshold of 40 ppbv CO was defined to separate background stratospheric air from polluted events such as from ASM air masses. To evaluate the reliability of this threshold-based approach, ERA5-derived PV values were used as an independent diagnostic for stratospheric air masses. Figure S7b
245 presents the relative frequency distribution of PV values for all data classified with $\text{N}_2\text{O} < 336$ ppbv and $\text{CO} < 40$ ppbv. The vast majority of these classified air masses exhibit high PV values (greater than 8 PVU), which is indicative of stratospheric origin. This comparison confirms that the chosen in-situ thresholds (N_2O and CO) reliably identify stratospheric background air. Consequently, for this study, $\text{N}_2\text{O} < 336$ ppbv and $\text{CO} < 40$ ppbv were used as the primary criteria for filtering both in-situ measurement data and CLaMS modeling results.

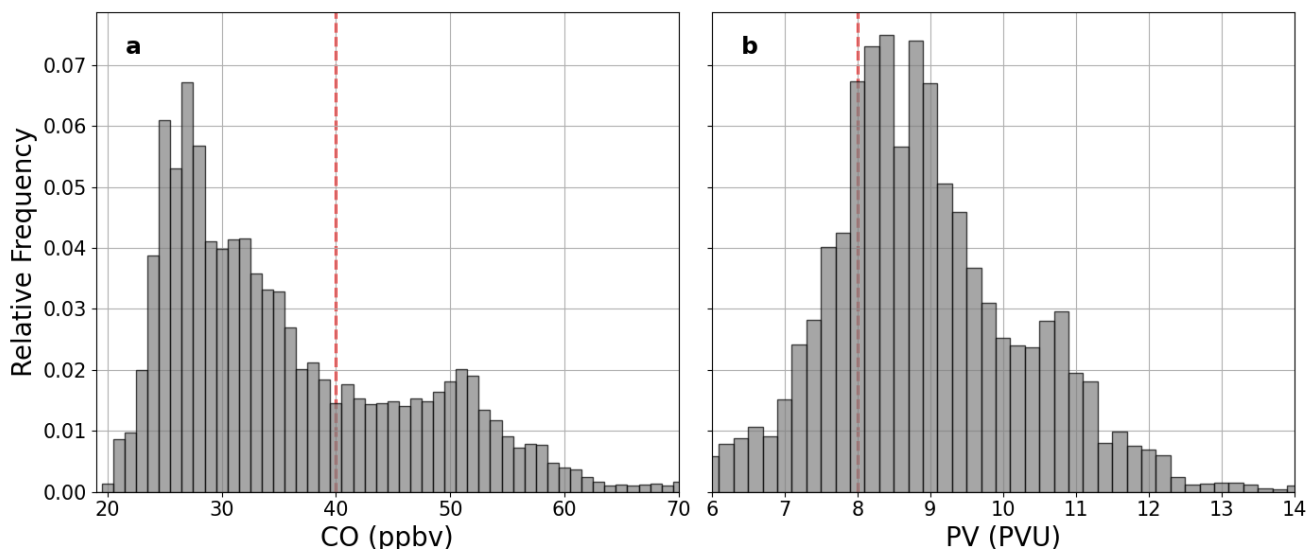


Figure S7. Relative frequency distributions of (a) CO for all data with $\text{N}_2\text{O} < 336$ ppbv and (b) ERA5-derived PV for data with both $\text{N}_2\text{O} < 336$ ppbv and $\text{CO} < 40$ ppbv. Red dashed lines indicate the applied thresholds for stratospheric background air ($\text{CO} < 40$ ppbv, $\text{PV} > 8$ PVU). The bimodal distribution in (a) illustrates the separation between stratospheric background air and recently polluted stratospheric air masses. The distribution in (b) demonstrates that data selected using the N_2O and CO thresholds also show high PV values (> 7 PVU), thus independently confirming that these criteria reliably identify stratospheric air masses.

250 S6 CLaMS Backwards Trajectories for Early and Late Phase

The CLaMS backward trajectories were initialized along the flight track of each PHILEAS flight. All back trajectories are separated into two groups according to the PHILEAS Early and Late Phases, as described in detail in the main text. The trajectories shown in Fig. S8 were selected based on the potential temperature range of 350 to 380 K, and the trajectory counts were not normalized by the physical grid box area. The maps therefore show the number points of trajectory positions in regular
255 $1^\circ \times 1^\circ$ longitude and latitude grid boxes, rather than an area weighted density. This choice was made because the analysis focuses on identifying preferred transport pathways and regions of enhanced trajectory occurrence. Since the main trajectory locations discussed here are located mainly in tropical and subtropical regions, the variation in physical grid box area due to the convergence of longitudes with latitude is comparatively small and does not affect the qualitative interpretation of the transport patterns. The trajectories shown in Fig. S8 are restricted to the potential temperature range from 350 to 380 K. This
260 range represents the lower stratospheric transport regime in which quasi horizontal transport from the AMA into the ExLS is expected to occur.

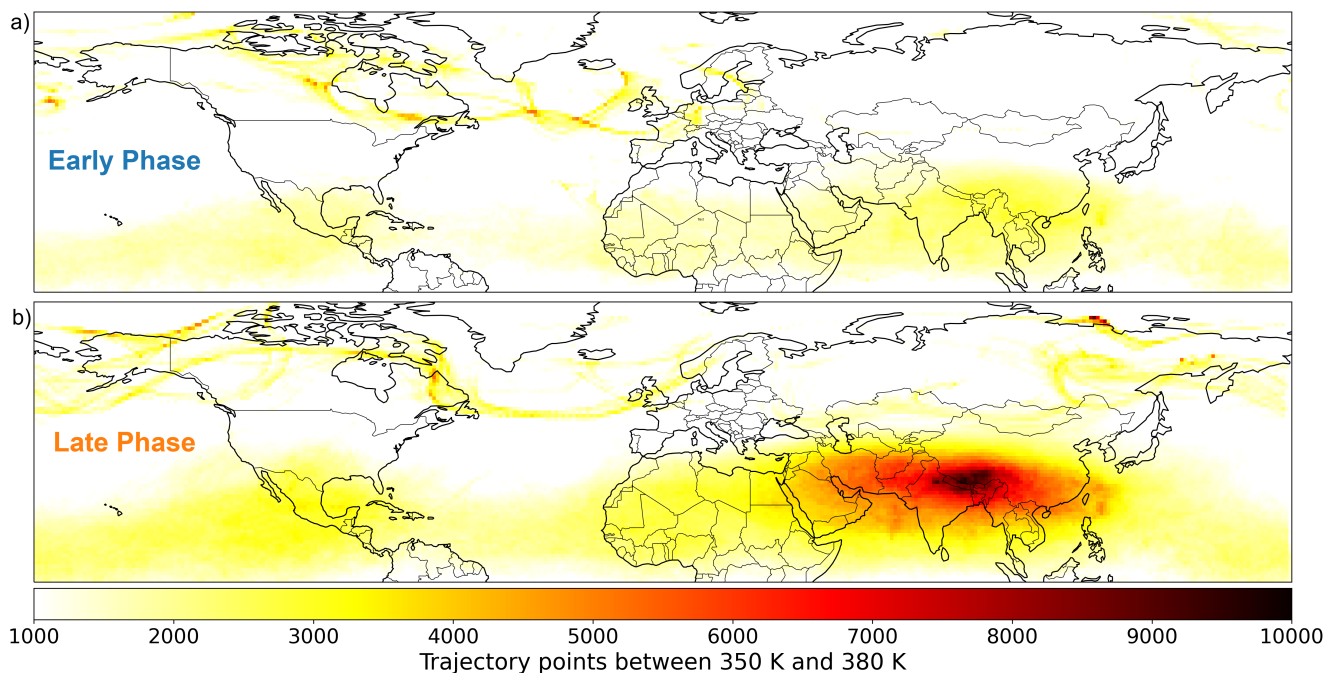


Figure S8. CLaMS backward trajectories located between 350 K and 380 K potential temperature during the Early (a) and Late Phases (b) of the PHILEAS campaign. The value in each grid box represents the number of selected trajectory positions in that grid box. The values are not normalized by grid cell area. Thus, the figure shows the horizontal occurrence of trajectory positions within this potential temperature range and does not indicate the fraction of trajectories reaching the surface or the lowest model level.

S7 Chemical Composition Changes of NO^+ -rich Particles from the ATAL to the ExLS

The NO^+ -rich particles measured within the AMA during the StratoClim 2017 mission were analyzed to provide a compositional reference for this particle type closer to its source region. In particular, we selected particles measured below 370 K potential temperature, corresponding to the lower ATAL region in the upper troposphere (UT) as defined by Appel et al. (2022b). This selection was used to characterize NO^+ -rich particles in the upper tropospheric part of the ATAL, where the influence of aged stratospheric background air is expected to be negligible.

Figure S9 summarizes the selected ion signal ratios for NO^+ -rich particles in the lower ATAL from StratoClim and compares them with the PHILEAS phases discussed in the main text. The comparison among the AMA filament, the Late Phase, and the Early Phase is described in detail in Sect. 3.2. Here, the StratoClim lower ATAL data are used as an additional reference to place the PHILEAS observations into a broader chemical context. Compared with the lower ATAL reference, the AMA filament observed during PHILEAS shows a much lower nitrate-to-sulfate ratio and a lower ratio of less-to-more oxidized organic fragments. This indicates that NO^+ -rich particles in the AMA filament air masses sampled in the ExLS were already chemically processed relative to particles observed within the lower ATAL. In contrast, the ammonium-to-nitrate ratio remains

275 similar between the lower ATAL and the AMA filament, suggesting that the most pronounced differences are associated with the relative sulfate contribution and the oxidation state of the organic component. The Early Phase shows the strongest deviation from the lower ATAL reference. In particular, the ratio of less-to-more oxidized organic fragments is substantially lower, indicating a stronger contribution of more oxidized organic fragments. This supports the interpretation that NO⁺-rich particles in the aged ExLS background (Early Phase) had undergone additional chemical processing during prolonged residence
280 in the stratosphere. The very low nitrate-to-sulfate ratio in the Early Phase further suggests a stronger relative sulfate signature compared with both the lower ATAL and the more recently transported PHILEAS air masses.

However, this comparison has to be interpreted with caution. The StratoClim and PHILEAS measurements were performed in different years and during different ASM seasons. Therefore, the lower ATAL particles measured in 2017 cannot be treated as a direct precursor of the AMA influenced particles observed during PHILEAS in 2023. Interannual variability in the strength,
285 transport pathways, emission patterns, and chemical processing within the ASM may affect the comparability of both data sets. Consequently, the StratoClim data are used here only as a qualitative reference for NO⁺-rich particles closer to the ATAL source region. Within this limitation, the observed differences support the interpretation that transport from the AMA into the ExLS and subsequent stratospheric residence are associated with increasing chemical aging, especially with respect to organic oxidation and the relative sulfate contribution.

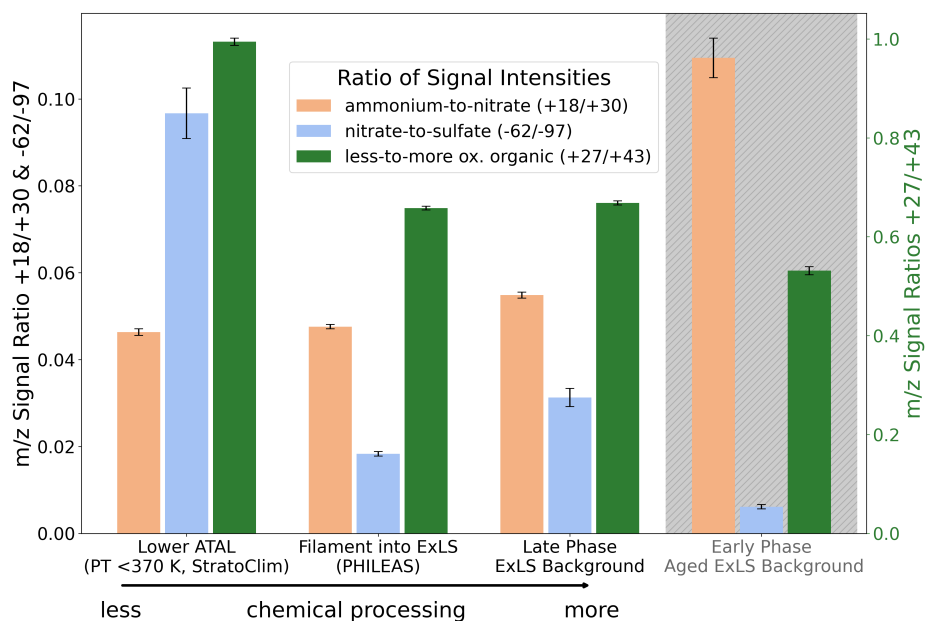


Figure S9. Ratios of key ion peaks in NO^+ -rich particles across different PHILEAS phases. The green bar represents the ratio of less oxidized to more oxidized organic components, highlighting changes in organic composition over time. The orange bar represents the ammonium-to-nitrate signal intensity ratio. And the blue bar represents the nitrate-to-sulfate signal intensity ratio. The arrow at the bottom indicates the temporal evolution and chemical processing from NO^+ -rich particles within the lower ATAL (StratoClim), AMA filaments into the ExLS, and Late Phase to the Early Phase, emphasizing how long term stratospheric residence alters particle composition. The gray dashed area in the Early Phase is a visual marker to illustrate that the Early Phase differs from the other phases in terms of its long-term residence time in the stratosphere and the associated impact on the particle composition. More information about the uncertainty in Supplement Information Sect. S3.5

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