S1 Sample details

Table S1. Details on the sampling period, height range and covered area.

Sample	Date	Sampling Time / UTC	Altitude Range / m
F05 - The Fold			
Filter 1	13 June 2024	10:28 - 11:31, 63 min	5744 - 6751
Filter 2	13 June 2024	11:31 - 12:36, 65 min	6699 - 9754
Filter 3	13 June 2024	12:36 - 13:24, 48 min	9675 - 10397
Filter 4	13 June 2024	13:24 - 14:02, 48 min	8353 - 10305
Filter 5	13 June 2024	Blank	
F09 - Convection Hunting			
Filter 1	18 June 2024	13:10 - 13:25, 15 min	9690 - 10058
Filter 2	18 June 2024	13:36 - 14:04, 28 min	995 - 1040
Filter 3	18 June 2024	14:16 - 16:02, 106 min	8234 - 11944
Filter 4	18 June 2024	16:02 - 16:19, 17 min	11858 - 11942
Filter 5	18 June 2024	Blank	

S2 Technical drawings of SOAP

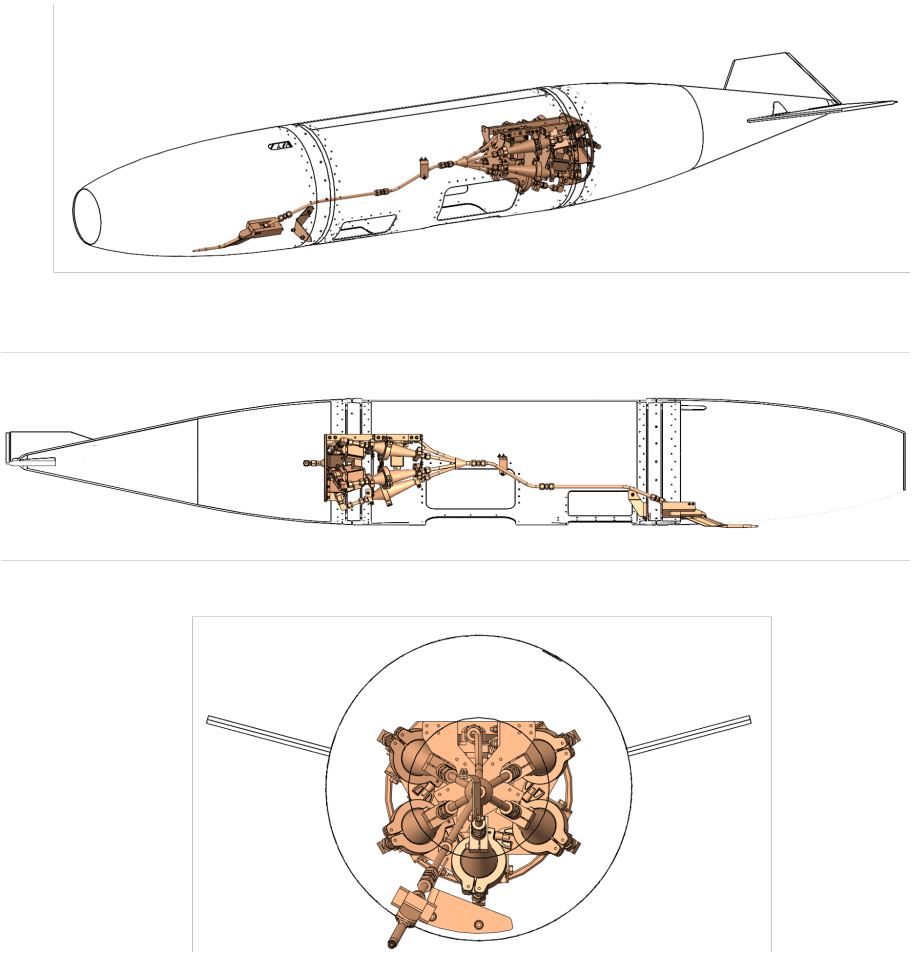

Figure S1. Technical drawings that show the sampler for organic aerosol particles SOAP (orange) in the wingpod KNUFFI. Perspectives are from the side (top and middle) and from the front (bottom).

S3 Estimations on particle loss

S3.1 Particle loss for F05

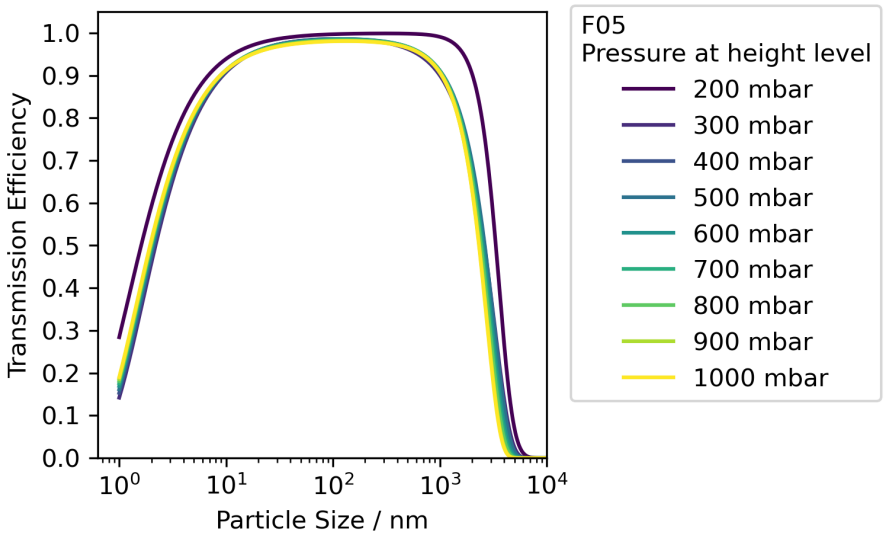

Figure S2. Calculated transmission efficiency for particle sizes from 1 to 10000 nm. The transmission efficiency is calculated for different height levels (200-1000 mbar), covering the whole flight path of F05.

S3.2 Particle loss for F09

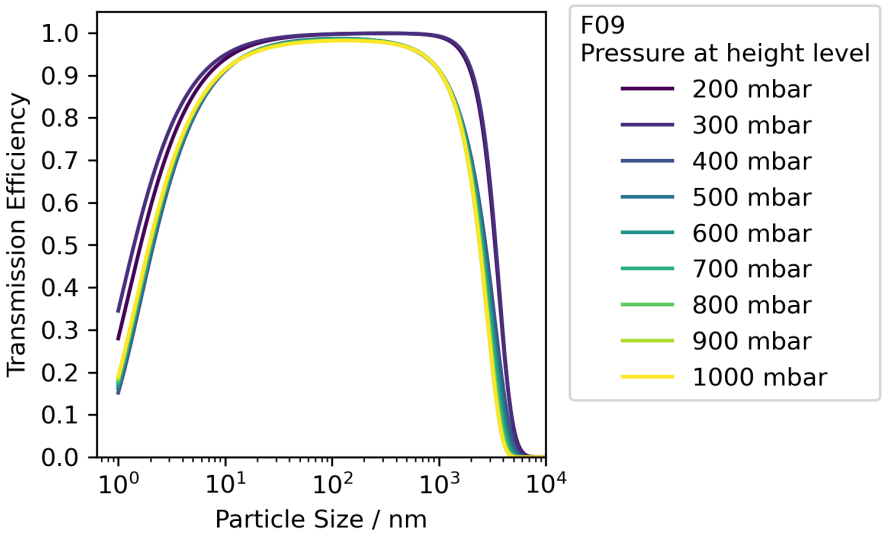

Figure S3. Calculated transmission efficiency for particle sizes from 1 to 10000 nm. The transmission efficiency is calculated for different height levels (200-1000 mbar), covering the whole flight path of F09.

S4 Method overview

S4.1 UHPLC-HRMS method

Table S2. Overview of the set parameters of the UHPLC-HRMS method used.

Sampler Modus	
Puncture Offset	2 μm
Wash Speed	20.0 [μL/s]
Injection Wash Mode	Both
Wash Time	5.0 [s]
Dispense Speed	5.000 [μL/s]
Draw Speed	5.000 [μL/s]
Temperature Control	On
Temperature Nominal	15.0 [°C]
Post Column	
Delta Temperature	1.00 [°C]
Temperature Control	On
Temperature Nominal	40.0 [°C]
Equilibration Time	1.0 [min]
Column	
Mode	
Delta Temperature	0.50 [°C]
Temperature Control	On
Temperature Nominal	40.00 [°C]
Equilibration Time	1.0 [min]
Pump	
Pressure lower limit	0 [bar]
Pressure upper limit	737 [bar]
Maximum Flow Ramp Up	6.00 [mL/min^2]
Maximum Flow Ramp Down	6.00 [mL/min^2]
Method	
Pump Flow Nominal	0.400 [mL/min]
0.000 min	1.0 [%] B1
1.000 min	1.0 [%] B1
19.000 min	99.0 [%] B1
21.000 min	99.0 [%] B1
22.000 min	1.0 [%] B1
25.000 min	Stop Run

Overall method settings	
Method duration	25.00 min
Chrom. Peak width	6 s
Experiment	
Full MS	
Polarity	negative and positive
dd-MS2	Discovery
Resolution	70,000
#Scan ranges	1
Scan Range	50 to 750 m/z
AGC Target	1e6
Maximum IT	auto
Microscans	1
Spectrum data type	Profile
dd-MS2 Discovery	
Resolution	17,500
Isolation window	3.0 m/z
(N)CE / Stepped (N)CE	
Default charge state	ce: 15,30,45
AGC Target	1e5
Maximum IT	auto
Loop count	1
Minimum AGC Target	5e4
Intensity Threshold	auto
Apex trigger	0.5 to 3 s
Dynamic exclusion	auto
Exclude isotopes	on
Spectrum data type	Profile
Setup	
Lock Masses	
112.98562 (Formic Acid dimer w Na)	negative
100.07569 (N-Methyl-2pyrrolidone, floor stripper)	positive

S4.2 Compound Discoverer workfolw - negative mode or positive mode

Created with Discoverer version: 3.3.2.31

Input Files (0)
–>Select Spectra (2)

Select Spectra (2)
–>Align Retention Times (ChromAlign) (23)

Align Retention Times (ChromAlign) (23)
–>Detect Compounds (21)

Detect Compounds (21)
–>Group Compounds (4)

Group Compounds (4)
–>Fill Gaps (17)
–>Assign Compound Annotations (11)
–>Compound Class Scoring (35)
–>Calculate Mass Defect (37)
–>Search mzCloud (31)
–>Search mzVault (32)
–>Predict Compositions (5)

Fill Gaps (17)
–>Mark Background Compounds (18)
Mark Background Compounds (18)
Assign Compound Annotations (11)
Compound Class Scoring (35)
Calculate Mass Defect (37)
Search mzCloud (31)
Search mzVault (32)

Predict Compositions (5)
Descriptive Statistics (24)
Differential Analysis (25)

Processing node 0: Input Files

Processing node 2: Select Spectra
1. Spectrum Properties Filter:
- Lower RT Limit: 1.7
- Upper RT Limit: 22
- First Scan: 0
- Last Scan: 0
- Ignore Specified Scans: (not specified)
- Lowest Charge State: 0
- Highest Charge State: 0
- Min. Precursor Mass: 50 Da
- Max. Precursor Mass: 5000 Da
- Total Intensity Threshold: 1000
- Minimum Peak Count: 1

2. Scan Event Filters:
- Mass Analyzer: Is FTMS
- MS Order: Any
- Activation Type: Is HCD
- Min. Collision Energy: 0
- Max. Collision Energy: 1000
- Scan Type: Any
- Polarity Mode: Is - (or +)
- MS1 Mass Range: (not specified)
- FAIMS CV: (not specified)

3. Peak Filters:
- S/N Threshold (FT-only): 5

4. Replacements for Unrecognized Properties:
- Unrecognized Charge Replacements: 1
- Unrecognized Mass Analyzer Replacements: ITMS
- Unrecognized MS Order Replacements: MS2
- Unrecognized Activation Type Replacements: HCD
- Unrecognized Polarity Replacements: -
- Unrecognized MS Resolution@200 Replacements: 60000
- Unrecognized MSn Resolution@200 Replacements: 30000

5. General Settings:
- Precursor Selection: Use MS1 Precursor
- Use Isotope Pattern in Precursor Reevaluation: True
- Provide Profile Spectra: Automatic
- Store Chromatograms: False

Processing node 23: Align Retention Times (ChromAlign)

Processing node 21: Detect Compounds
1. General Settings:
- Mass Tolerance (ppm): 5 ppm
- Min. Peak Intensity: 100000
- Min. # Scans per Peak: 5
- Use Most Intense Isotope Only: True

2. Trace Detection:
- Max. Number of Gaps to Correct: 2
- Min. Number of Adjacent Non-Zeros: 2

3. Peak Detection:
- Chromatographic S/N Threshold: 5
- Remove Baseline: False
- Gap Ratio Threshold: 0.35
- Max. Peak Width (min): 0.2
- Min. Relative Valley Depth: 0.2

4. Isotope Pattern Detection:
- Group Isotopes for: Br; Cl
- Use Peak Quality for Isotope Grouping: True
- Filter out Features with Bad Peaks Only: True
- Zig-Zag Index Threshold: 0.2
- Jaggedness Threshold: 0.4
- Modality Threshold: 0.9
- Remove Potentially False Positive Isotopes: True

5. Compound Detection:
- Ions: [2M-H]-1; [M-CO2-H]-1; [M-H]-1; [M-H-H2O]-1 or [M+H]+1; [M+K]+1; [M+Na]+1; [M+NH4]+1
- Base Ions: [M-H]-1 or [M+H]+1
- Remove Singlets: True

6. AcquireX Settings:
- Detect Persistent Background Ions: False

Processing node 4: Group Compounds
1. General Settings:
- Mass Tolerance: 2 ppm
- RT Tolerance [min]: 0.2
- Align Peaks: False
- Preferred Ions: [M-H]-1 or [M+H]+1
- Area Integration: Most Common Ion

2. Peak Rating Contributions:
- Area Contribution: 3
- CV Contribution: 0
- FWHM to Base Contribution: 5
- Jaggedness Contribution: 5
- Modality Contribution: 5
- Zig-Zag Index Contribution: 5

3. Peak Rating Filter:
- Peak Rating Threshold: 5
- Number of Files: 2

Processing node 17: Fill Gaps
1. General Settings:
- Mass Tolerance: 2 ppm
- S/N Threshold: 5
- Use Real Peak Detection: True
- Apply Restrictive Gap Filling: True

Processing node 18: Mark Background Compounds
1. General Settings:
- Max. Sample/Blank: 5
- Max. Blank/Sample: 0
- Hide Background: True

Processing node 11: Assign Compound Annotations
1. General Settings:
- Mass Tolerance: 2 ppm

2. Data Sources: - Data Source #1: Predicted Compositions
- Data Source #2: mzVault Search
- Data Source #3: mzCloud Search (Compound Class)

3. Scoring Rules:
- Use mzLogic: True
- Use Spectral Distance: True
- SFit Threshold: 20

- SFit Range: 20

4. Reprocessing:
- Clear Names: True

Processing node 35: Compound Class Scoring
1. General Settings:
- Compound Classes: R-OSO3, R-SO3.cLib|R-NO3.cLib
- S/N Threshold: 50
- High Acc. Mass Tolerance: 15 ppm
- Low Acc. Mass Tolerance: 0.5 Da
- Use Full MS Tree: True
- Allow DIA Scoring: True

Processing node 37: Calculate Mass Defect
1. Mass Defect:
- Fractional Mass: False
- Standard Mass Defect: True
- Relative Mass Defect: False
- Kendrick Mass Defect: True
- Nominal Mass Rounding: Round
2. Kendrick Formula:
- Formula 1: C H2

Processing node 31: Search mzCloud
1. General Settings:
- Compound Classes: All
- Precursor Mass Tolerance: 10 ppm
- FT Fragment Mass Tolerance: 10 ppm
- IT Fragment Mass Tolerance: 0.4 Da
- Library: Autoprocessed; Reference
- Post Processing: Recalibrated
- Max. # Results: 10
- Annotate Matching Fragments: True
- Search MSn Tree: False

2. DDA Search:
- Identity Search: HighChem HighRes
- Match Activation Type: True
- Match Activation Energy: Match with Tolerance
- Activation Energy Tolerance: 20
- Apply Intensity Threshold: True
- Similarity Search: None
- Match Factor Threshold: 60

3. DIA Search:
- Use DIA Scans for Search: False
- Max. Isolation Width [Da]: 500
- Match Activation Type: False
- Match Activation Energy: Any

- Activation Energy Tolerance: 100
- Apply Intensity Threshold: False
- Match Factor Threshold: 20

Processing node 32: Search mzVault
1. Search Settings:
- mzVault Library: AP_O3_rA_MW_neg.db| AP_O3_UV_rA_MW_neg.db| BCY_O3_rA_MW_neg.db| BCY_O3_UV_rA_MW_neg.db| BP_O3_rA_MW_neg.db| BP_O3_UV_rA_MW_neg.db| D3C_O3_rA_MW_neg.db| D3C_O3_UV_rA_MW_neg.db| LIM_O3_rA_MW_neg.db| LIM_O3_UV_rA_MW_neg.db| NAP_O3_UV_rA_MW_neg.db| TMB_O3_UV_rA_MW_neg.db| TOL_O3_UV_rA_MW_neg.db| XYL_O3_UV_rA_MW_neg.db
- Max. # Results: 10
- Match Factor Threshold: 80
- Search Algorithm: HighChem HighRes
- Match Analyzer Type: True
- IT Fragment Mass Tolerance: 0.4 Da
- FT Fragment Mass Tolerance: 10 ppm
- Use Retention Time: True
- Precursor Mass Tolerance: 10 ppm
- Apply Intensity Threshold: True
- Match Ionization Method: True
- Ion Activation Energy Tolerance: 20
- Match Ion Activation Energy: Match with Tolerance
- Match Ion Activation Type: True
- Compound Classes: All
- Remove Precursor Ion: True
- RT Tolerance [min]: 1

Processing node 5: Predict Compositions
1. Prediction Settings:
- Mass Tolerance: 2 ppm
- Min. Element Counts: C H
- Max. Element Counts: C90 H190 Br4 Cl4 N6 O20 P S6
- Min. RDBE: 0
- Max. RDBE: 40
- Min. H/C: 0.1
- Max. H/C: 3.5
- Max. # Candidates: 10
- Max. # Internal Candidates: 200

2. Pattern Matching:
- Intensity Tolerance [%]: 30
- Intensity Threshold [%]: 0.1
- S/N Threshold: 5
- Min. Spectral Fit [%]: 30
- Min. Pattern Cov. [%]: 90
- Use Dynamic Recalibration: True

3. Fragments Matching:
- Use Fragments Matching: True
- Mass Tolerance: 2 ppm
- S/N Threshold: 5

Processing node 24: Descriptive Statistics
No parameters

Processing node 25: Differential Analysis
1. General Settings:
- Log10 Transform Values: True

2. Peak Rating Contributions:
- Update Peak Rating: True
- Area Contribution: 3
- CV Contribution: 0
- FWHM to Base Contribution: 5
- Jaggedness Contribution: 5
- Modality Contribution: 5
- Zig-Zag Index Contribution: 5

S5 AMS and UHSAS measurements

S5.1 AMS measurements for F09

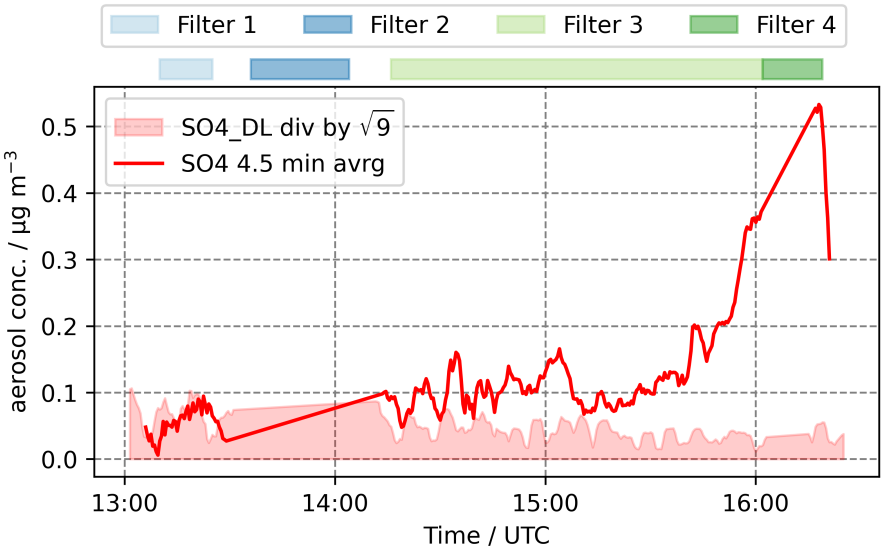

Figure S4. Displayed in red is the aerosol concentration of SO_4^{2-} in μg m^{-3} for the flight F09. The data points are averaged to 4.5 min (9 data points, one data point each 30 sec) and thus the detection limit is devided by $\sqrt{9}$. Additionally, the filter sampling periods are displayed in the respective colors light blue: filter 1, blue: filter 2, light green: filter 3 and green: filter 4.

S5.2 AMS measurements for F05

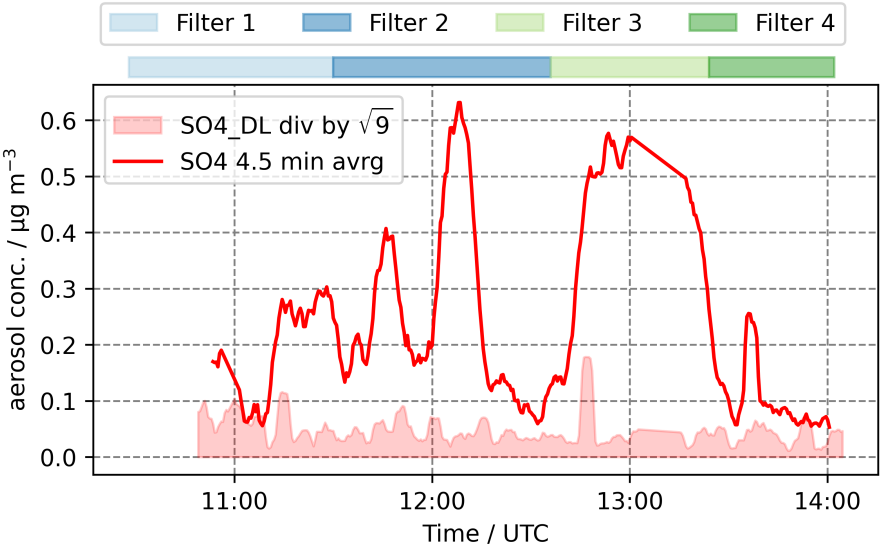

Figure S5. Displayed in red is the aerosol concentration of SO_4^{2-} in μg m^{-3} for the flight F05. The data points are averaged to 4.5 min (9 data points, one data point each 30 sec) and thus the detection limit is devided by $\sqrt{9}$. Additionally, the filter sampling periods are displayed in the respective colors light blue: filter 1, blue: filter 2, light green: filter 3 and green: filter 4.

S5.3 UHSAS measurements for F09

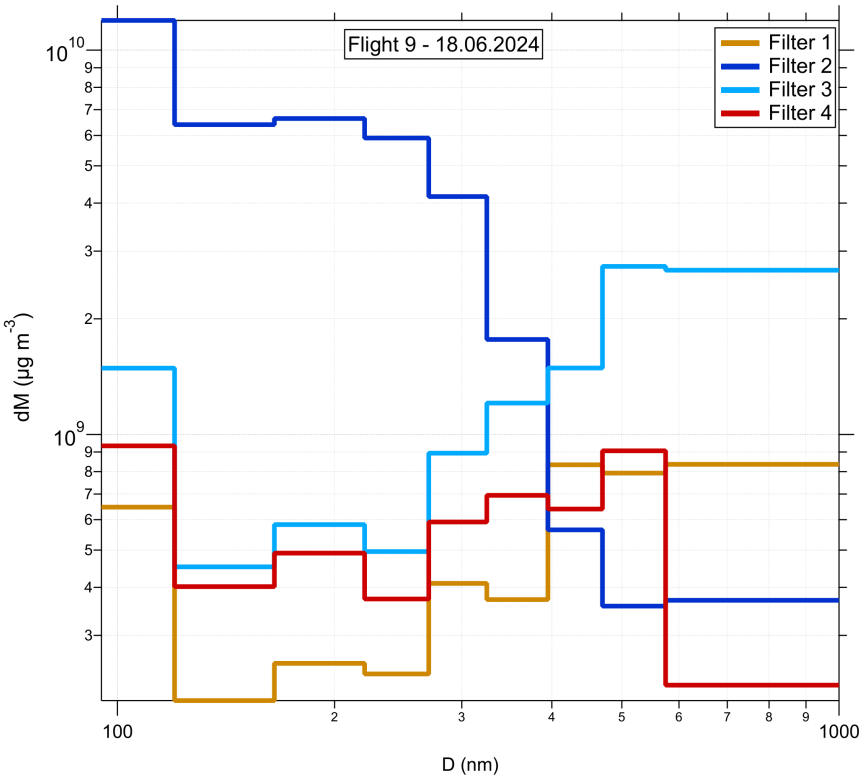

Figure S6. Size distribution from 100 to 1000 nm for filter 1 to 4 of flight F09 - 18 June 2024, averaged based on the filter collection time.

S6 Five-day backward trajectories for F05 and F09

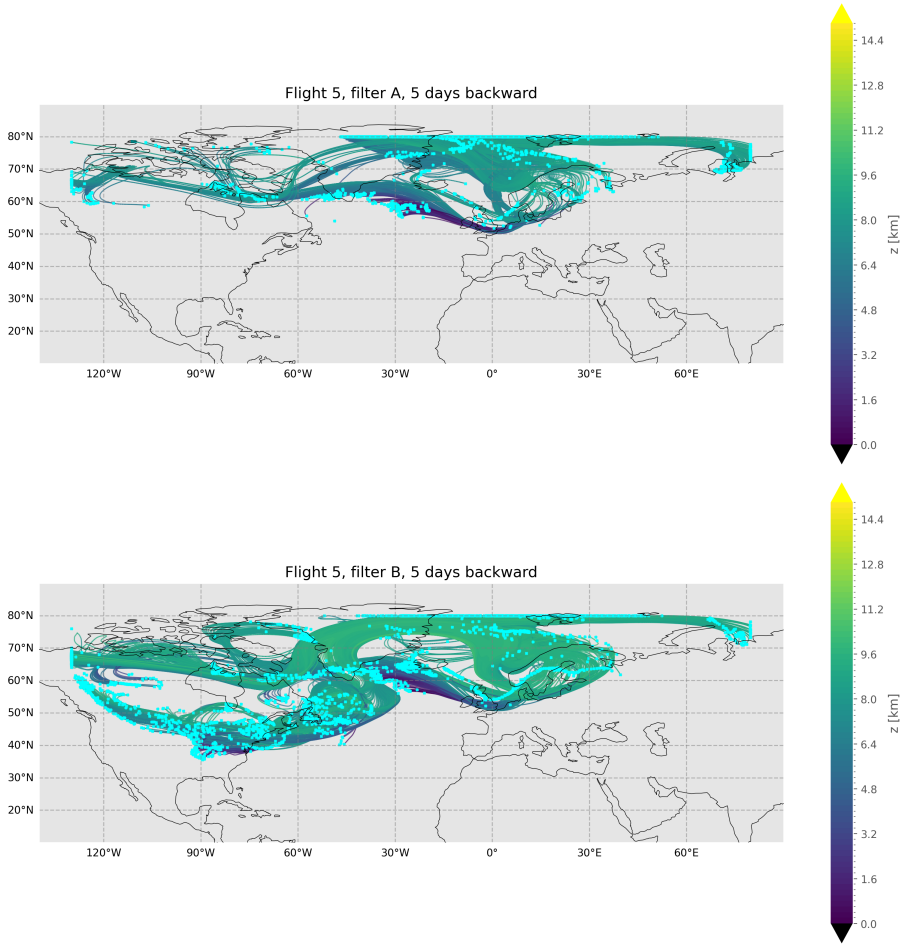

Figure S7. Five-day backward trajectories of the sampled period for F05: filter 1 (A, top) and 2 (B, bottom). The altitude of the air mass is displayed by the color in km. The origin of the respective air mass is marked by a blue dot.

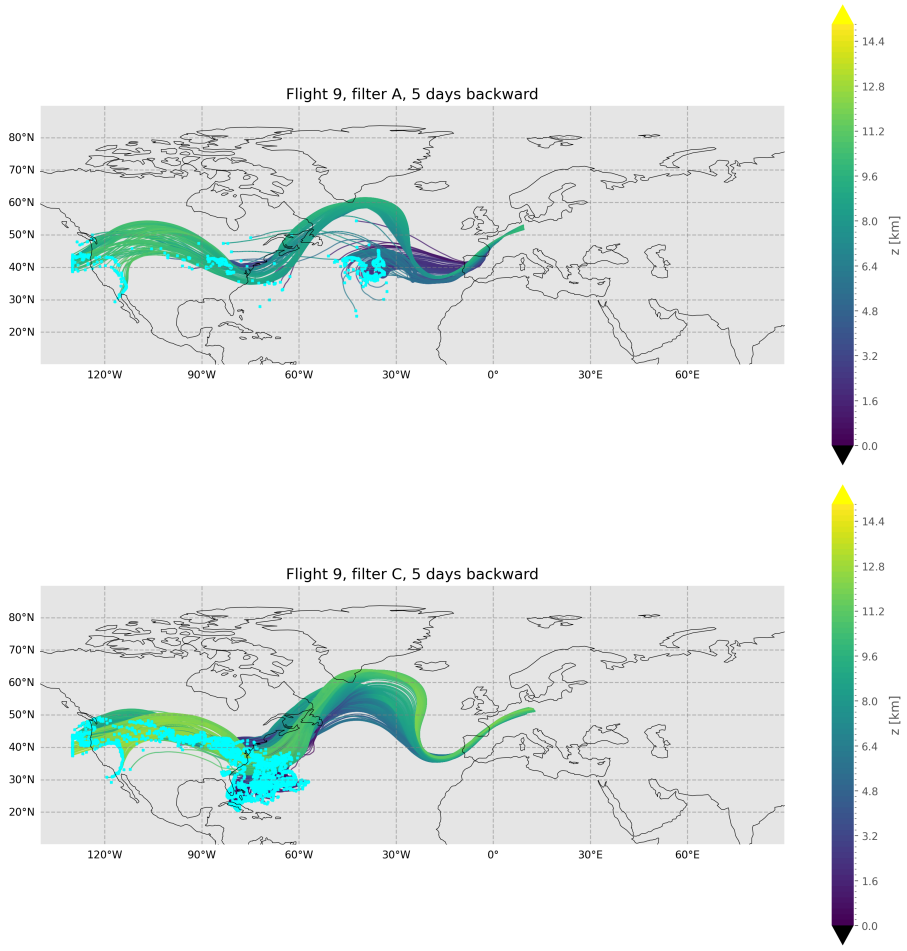

Figure S8. Five-day backward trajectories of the sampled period for F09: filter 1 (A, top) and 3 (C, bottom). The altitude of the air mass is displayed by the color in km. The origin of the respective air mass is marked by a blue dot.

S7 Additional information from trajectories on vertical lifting prior to observations

S7.1 Trajectories for F05

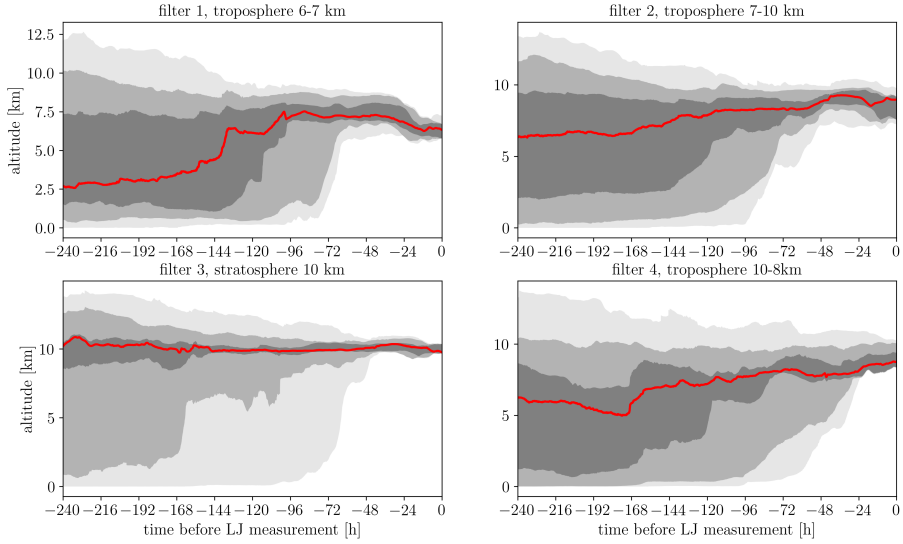

Figure S9. Evolution of parcel altitude in the 240 h prior to the Learjet observations of F05. The median altitude is shown by the red line, the interquartile range by the dark grey shading, the 5th–95th percentile range by the medium grey shading and the the minimum-maximum range by the light grey shading.

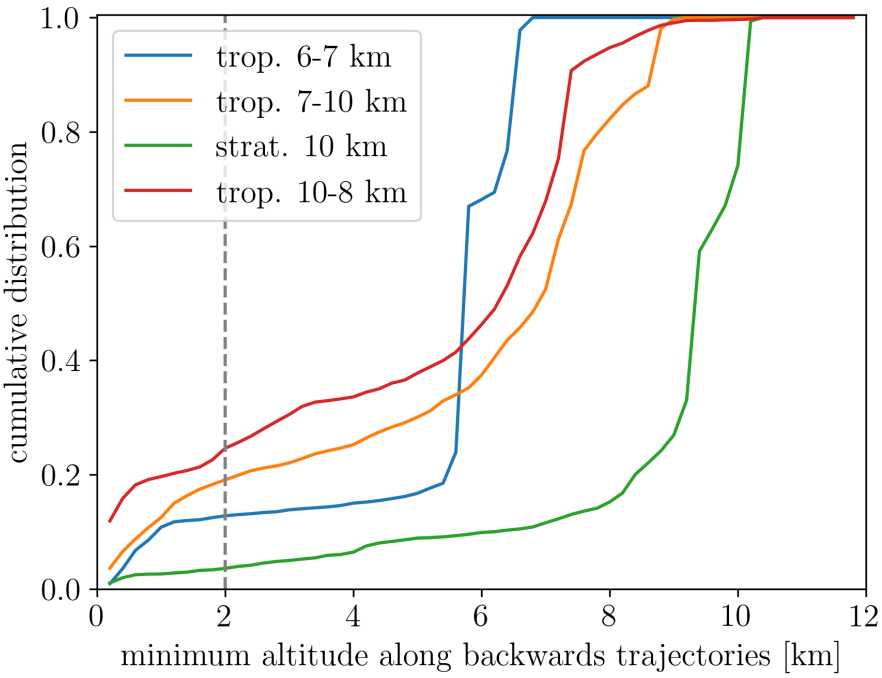

Figure S10. Fraction of trajectory that descend below a given altitude in the 240 h prior to the Learjet observations of F05. The different colors represent the different time ranges along the flight path sampled by the different filters as indicated in the legend.

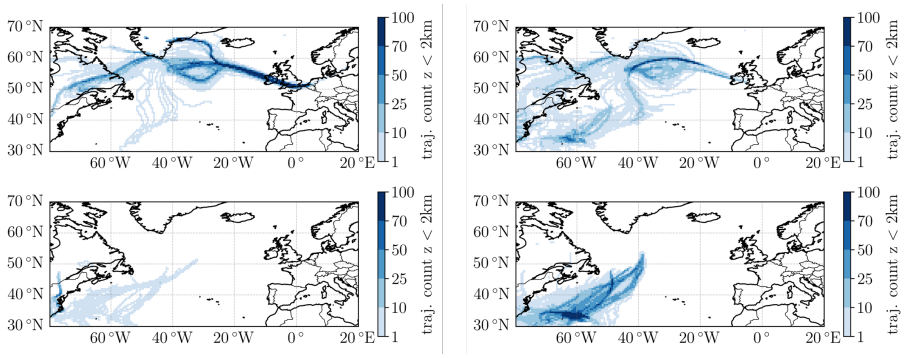

Figure S11. Spatial distribution of trajectory position below 2 km altitude for the airmasses sampled by the different filters of F05: a) filter 1, b) filter 2, c) filter 3, and d) filter 4.

S7.2 Trajectories for F09

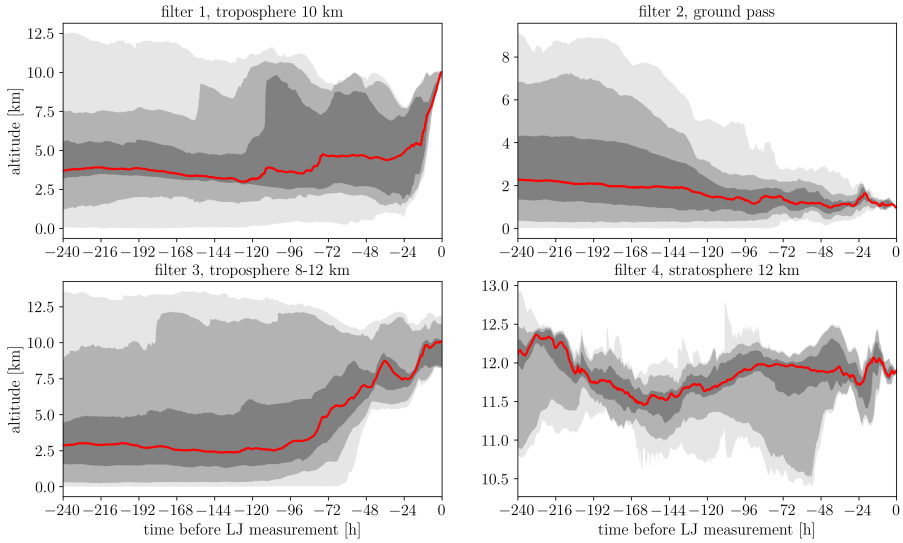

Figure S12. Evolution of parcel altitude in the 240 h prior to the Learjet observations of F09. The median altitude is shown by the red line, the interquartile range by the dark grey shading, the 5th–95th percentile range by the medium grey shading and the the minimum-maximum range by the light grey shading.

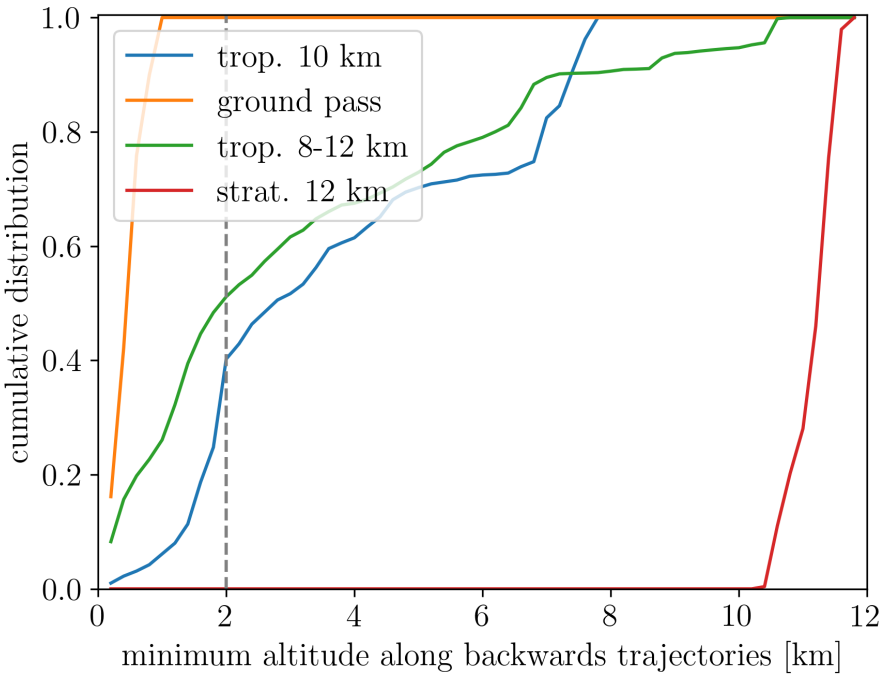

Figure S13. Fraction of trajectory that descend below a given altitude in the 240 h prior to the Learjet observations of F09. The different colors represent the different time ranges along the flight path sampled by the different filters as indicated in the legend.

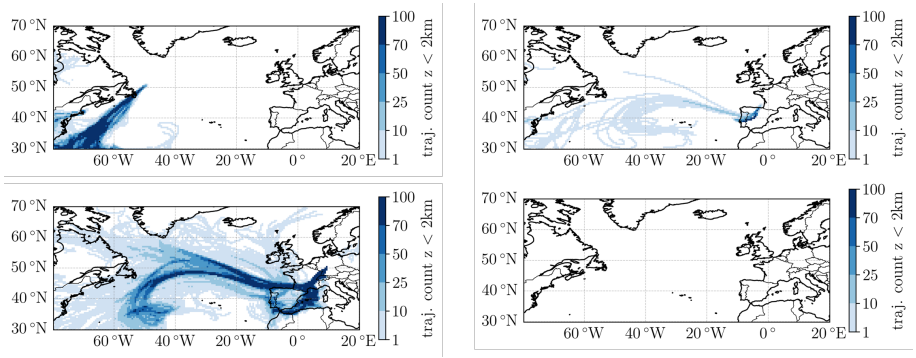

Figure S14. Spatial distribution of trajectory position below 2 km altitude for the airmasses sampled by the different filters of F09: a) filter 1, b) filter 2, c) filter 3, and d) filter 4.

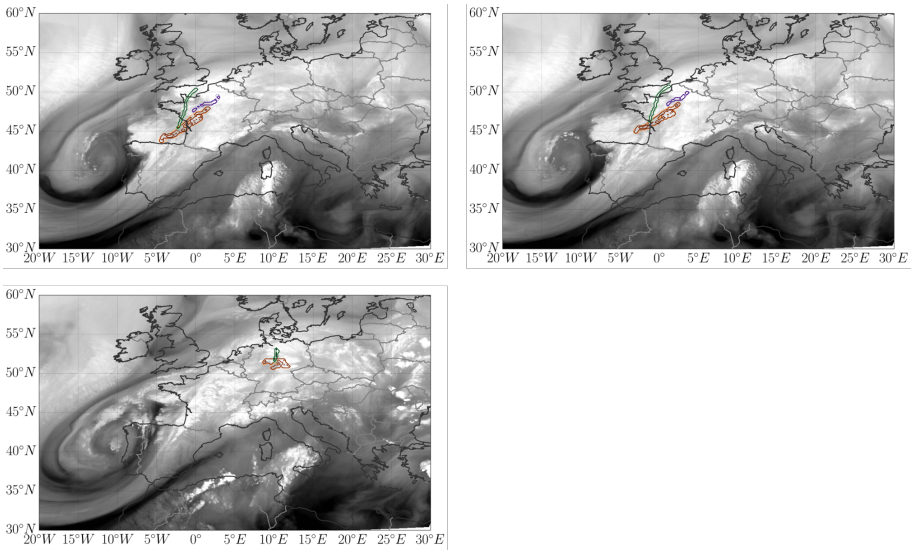

Figure S15. Co-location of trajectories of F09 with altitudes larger than 7 km and MSG WV 6.2 μm channel Images. The positions of trajectories sampled by filter 1, 2, 3, and 4 are shown in purple, blue, orange, and green, respectively. Snapshots are shown at a) 6:57 UTC, b) 7:57 UTC and c) 14:57 UTC.

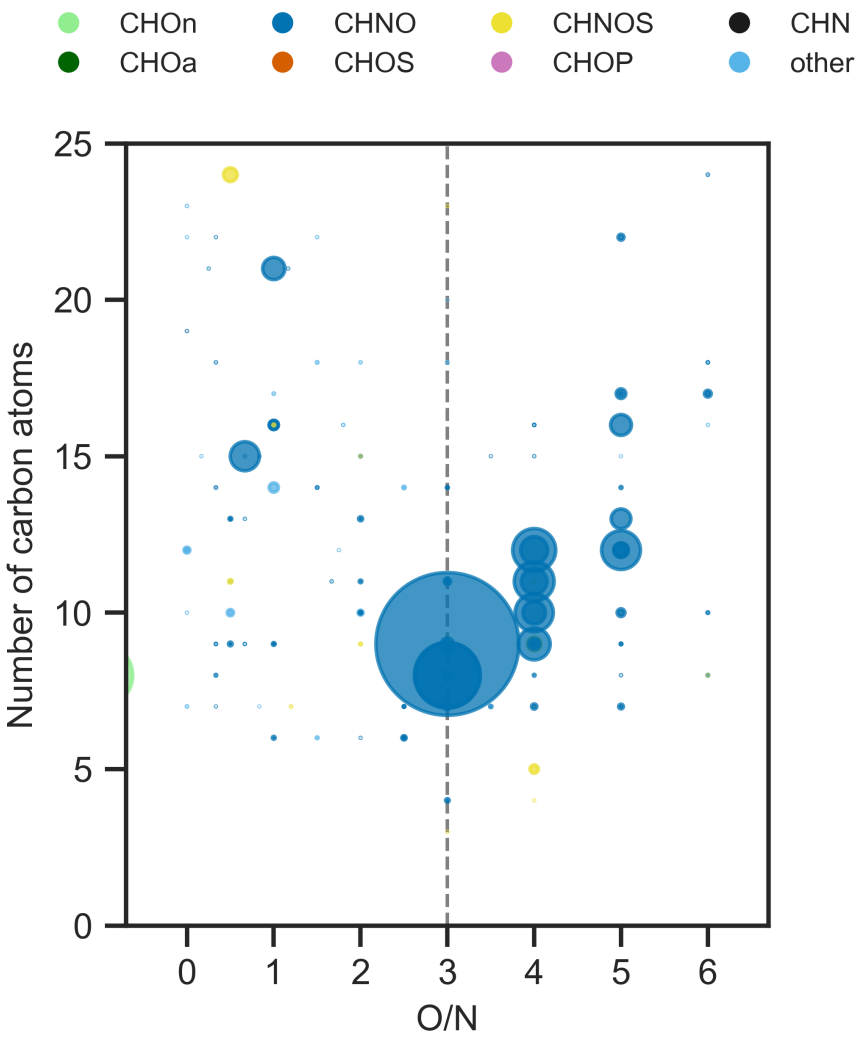

Figure S16. O/N ratio (x-axis) against the number of carbon atoms on the y-axis, for the stratospheric filter of F05. The circle diameter of each compound represents the relative intensity, and the circle colour the group that is assigned (CHOn, CHOa, CHNO, CHOS, CHNOS, CHOP, CHN and *other*). All compounds displayed were measured in HESI negative ionization mode.

S9 Target analysis

S9.1 Ratio for estimating the anthropogenic influence

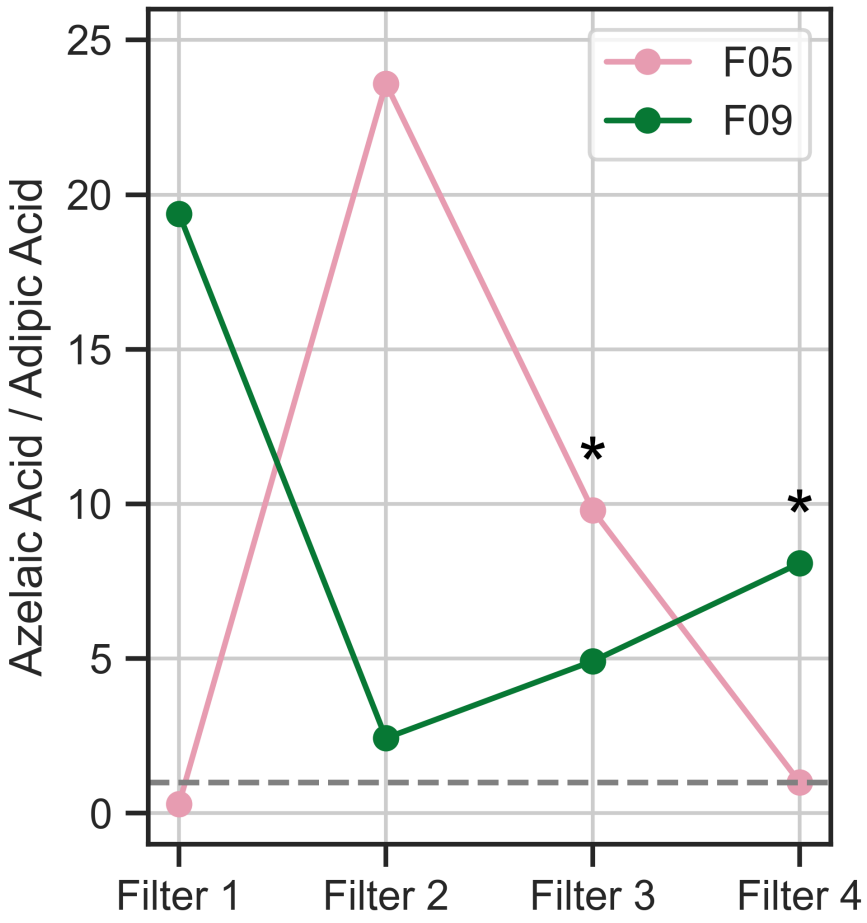

Figure S17. Displayed is the ratio of azelaic acid (C9) to adipic acid (C6) for each filter of F05 (rose) and F09 (green). The stratospheric filters are marked with a star (*) and the horizontal dashed line marks an equal ratio between C9 to C6.

S9.2 Isotopic fine structure and identification of TCPP

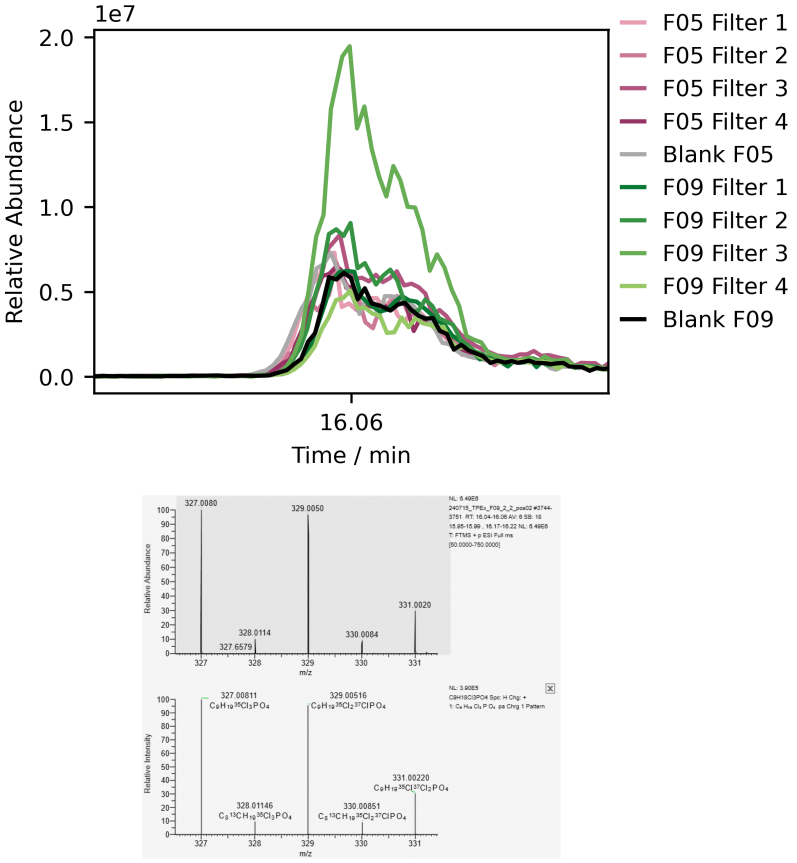

Figure S18. The upper plot shows the chromatograms for the mass trace of TCPP (m/z = 327.0081) of the respective filters. The lower plot displays the ions measured at the respective retention time 16.06 min (upper one) and the isotopic simulation for $C_9H_{18}Cl_3PO_4$ (lower one).