

Fig S1: Timeseries of main ions measured at the SMEARIII station with ToF-ACSM during the spring 2014 campaign.



Figure S2:Sensitivity analysis for NO2+ using mass calibration perturbations of +/- 20 ppm.



Figure S3: Sensitivity analysis for SO+ using mass calibration perturbations of +/- 20 ppm.



Figure S4: Sensitivity analysis for SO2+ using mass calibration perturbations of +/- 50 ppm.



Figure S5: Sensitivity analysis for SO3+ using mass calibration perturbations of +/- 50 ppm.



Figure S6: Sensitivity analysis for HSO3+ using mass calibration perturbations of +/- 50 ppm.



Figure S7: Sensitivity analysis for H2SO4+ using mass calibration perturbations of +/- 50 ppm.



Figure S8: Time-series of ACSM species during episode 1 derived from integrated peak intensities observed with the ToF-ACSM at the Neumayer station at the beginning of December 2014.



Figure S9; Airmass backtrajectory during episode 1. shows that air mass had transported in low altitude above sea area during last days before arriving to Neumayer station.



Figure S10: Time-series of ACSM species during episode 2 derived from integrated peak intensities observed with the ToF-ACSM at the Neumayer station in January 2015.



FigureS11: Sensitivity of CH3SO2+ to mass cal @ 100 ppm: 5% -> clear that this peak is nearly all MSA.





Figure S12: Correlation between MSA main fragments a) HSO2+ vs CH4SO3+, b)CH3SO2+ vs HSO2+, c) CH3SO2+ vs CH4SO3+.

b)

	CH3S+	CHS+	CH2SO2+	СНЗЅО2+	HSO2+	CH4SO3+
CH3S+	1					
CHS+	0.061827	1				
CH2SO2+	0.135439	0.294476	1			
CH3SO2+	0.237239	0.446346	0.696882	1		
HSO2+	0.265439	0.36614	0.598735	0.892511	1	
CH4SO3+	0.232336	0.333807	0.534572	0.742081	0.719259	1

Table S1: Correlation (Pearson correlation r) between all fragments associated with the MSA



Figure S13: Example MS showing the trichloroethylene peaks with assumed overlapping interferences from organic background ions. The mass defect at 130 and 132 Th is visibly more negative than at the surrounding peaks.



Fig S14: Compensating for the mass positions of calibrant peaks by assuming interferences are present of equal magnitude and mass defect to the surrounding isobaric peaks.



Figure S15: Example mass spectrum showing the HR fits for As_2^+ and the organic background peaks at 150 Th.



Figure S16: Scatter plot of the fitted peak intensities for As⁺ and As₂⁺



Figure S17: Sensitivity analysis of peak-fitting at 66 Th showing a non-zero contribution from the ion ⁶⁶Zn⁺.



Figure S18: Sensitivity analysis of peak-fitting at 115 Th showing a weak but non-zero contribution from the ion In+.



Figure S19: Sensitivity analysis of peak-fitting at 63 Th showing high sensitivity of the fitted intensity of the Cu+ ion to mass calibration.



Figure S20: Scatter plot of the difference signal for the fitted intensities of the $C_3H_5O^+$ and CO_2^+ ions.

Parameterisation of Stark et al. (2015) for the calculation of carbon oxidation state from mass excess (ME):

OSc = A*ME + B*m/Q + C*[ME / (m/Q)] + D

where A = 2.796, B = -1.304e-3, C = -4.05e3, D = 1.295