

Latitudinal Distribution of Particulate MSA over the Atlantic using a Validated Quantification Method with HR-ToF-AMS

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Motivation

The **marine aerosol** plays an important role in global climate regulation and marine biogenic system.

-**Methanesulfonic acid (MSA)** has been widely used as a tracer for marine biogenic sources, but in the past, it was almost only detected by offline methods offering a time resolution from several hours to days.

-**Online measurements** of MSA were developed in recent decade using new technologies such as chemical ionization mass spectrometry (CIMS), particle-into-liquid sampler - ion chromatography (PILS-IC), quadrupole aerosol mass spectrometer (Q-AMS), and high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), enhancing the time resolution to several minutes.

- However, the **accuracy** of the MSA mass concentration derived from Aerosol Mass Spectrometer (AMS) in field measurement conditions is still questionable because of:

- (1) the previously published quantification methods of MSA using AMS are similar but not identical
- (2) a method validation by direct comparison between AMS and parallel measurements using a chromatographic MSA quantification by offline analysis has rarely been reported

The accurate MSA mass concentration is also helpful for assessing the significance of **DMS contribution to the sulfate** relative to the other sources via MSA to non-sea-salt sulfate (nssSO₄) ratio, as well as for the estimation of the DMS-related secondary organic aerosol (SOA) in the next step.

Measurements

Intensive physical and chemical characterization of the submicrometer marine aerosol over the Atlantic Ocean has been performed on the German RV Polarstern during four cruises (CR) from the Northern Hemisphere to the Southern Hemisphere (Fig. 1), providing a **unique dataset** of marine boundary layer aerosols.

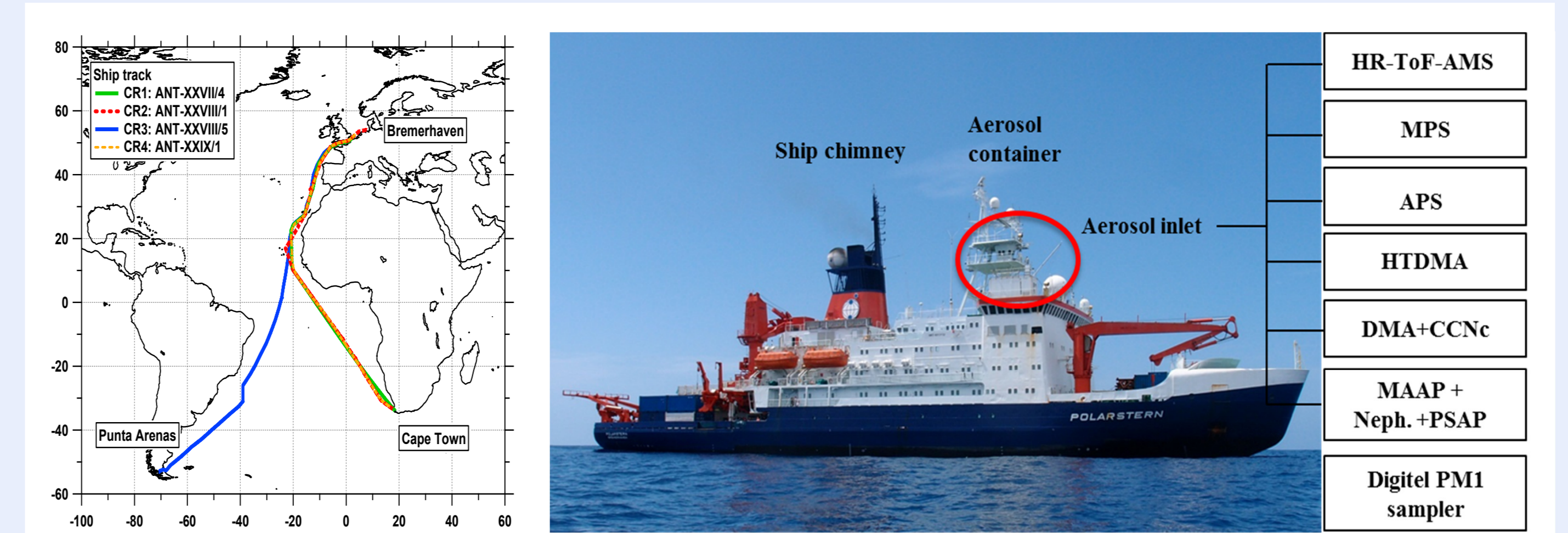


Fig. 1: Ship tracks of 4 cruises (left) and instrumentation (right)

Chemical composition:

- High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS)
- Daily PM₁ Digital filter sampler

Particle Number Size Distribution:

- Aerodynamic Particle Size Spectrometer (APS)
- Mobility Particle Size Spectrometer (MPSS)

Particle Light Scattering and Absorption:

- Integrating Nephelometer (Neph.)
- Multi Angle Absorption Photometer (MAAP)
- Particle Soot Absorption Photometer (PSAP)

Hygroscopic Growth and Mixing State

- Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA)
- Differential Mobility Analyzer - Cloud Condensation Nuclei Counter (DMA-CCNc)

MSA Quantification and Latitudinal distribution

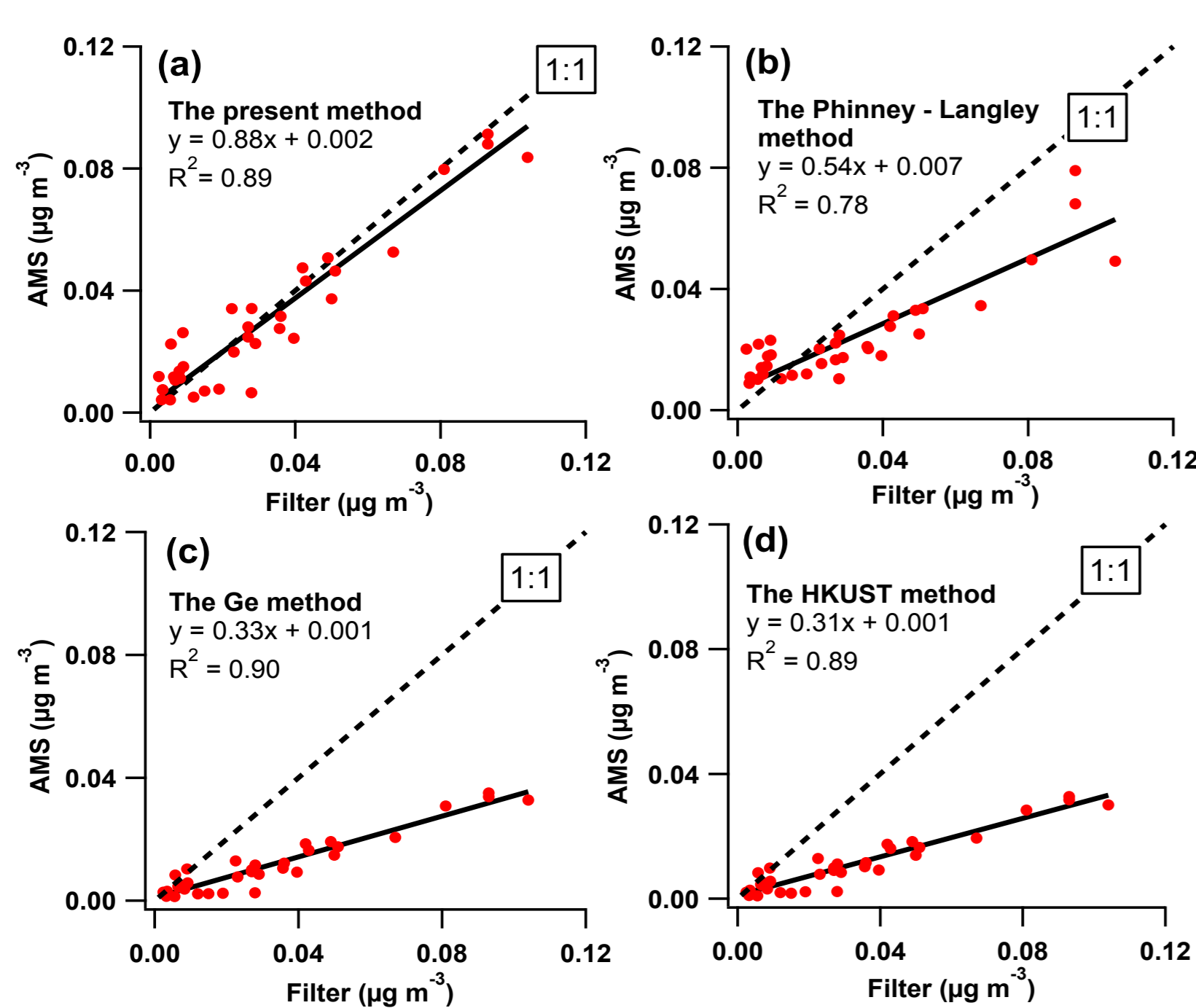


Fig. 2: MSA mass concentrations from AMS using (a) the method developed in this study, the methods from (b) Phinney-Langley, (c) Ge, and (d) HKUST, compared to those from PM₁ filter measurements during the Polarstern cruises.

MSA has been quantified by HR-ToF-AMS using a approach of adjusting fragmentation table based on standard tests.

The method in this study is validated by **excellent agreement (slope = 0.88, R² = 0.89)** between results from HR-ToF-AMS and from filter (PM₁) measurements.

All the three reported methods can properly reproduce the dynamics of the MSA concentrations, but they strongly **underestimated (31% - 54%)** the real concentration of MSA.

MSA shows clear **seasonal variation**, with a higher average mass concentration in spring (0.03 µg m⁻³) than in autumn (0.01 µg m⁻³) in both hemispheres.

Although the seasonality of MSA mass concentrations may be related to seasonally biological activities, a correlation between **MSA and Chl-a** was not found. The comprehensive information of biological activities, long-range transported air masses and meteorological conditions is needed for better understanding of the MSA distribution.

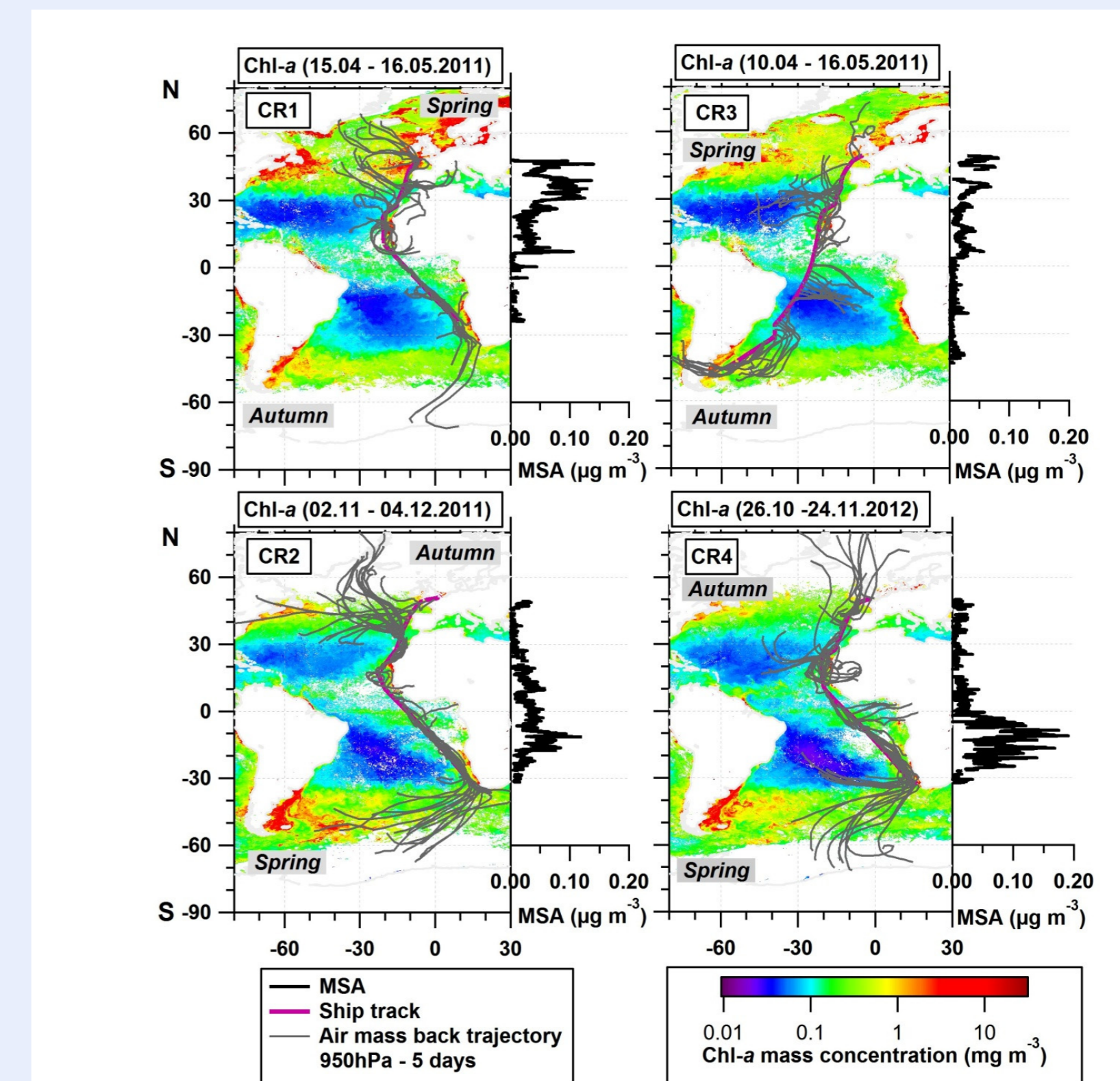
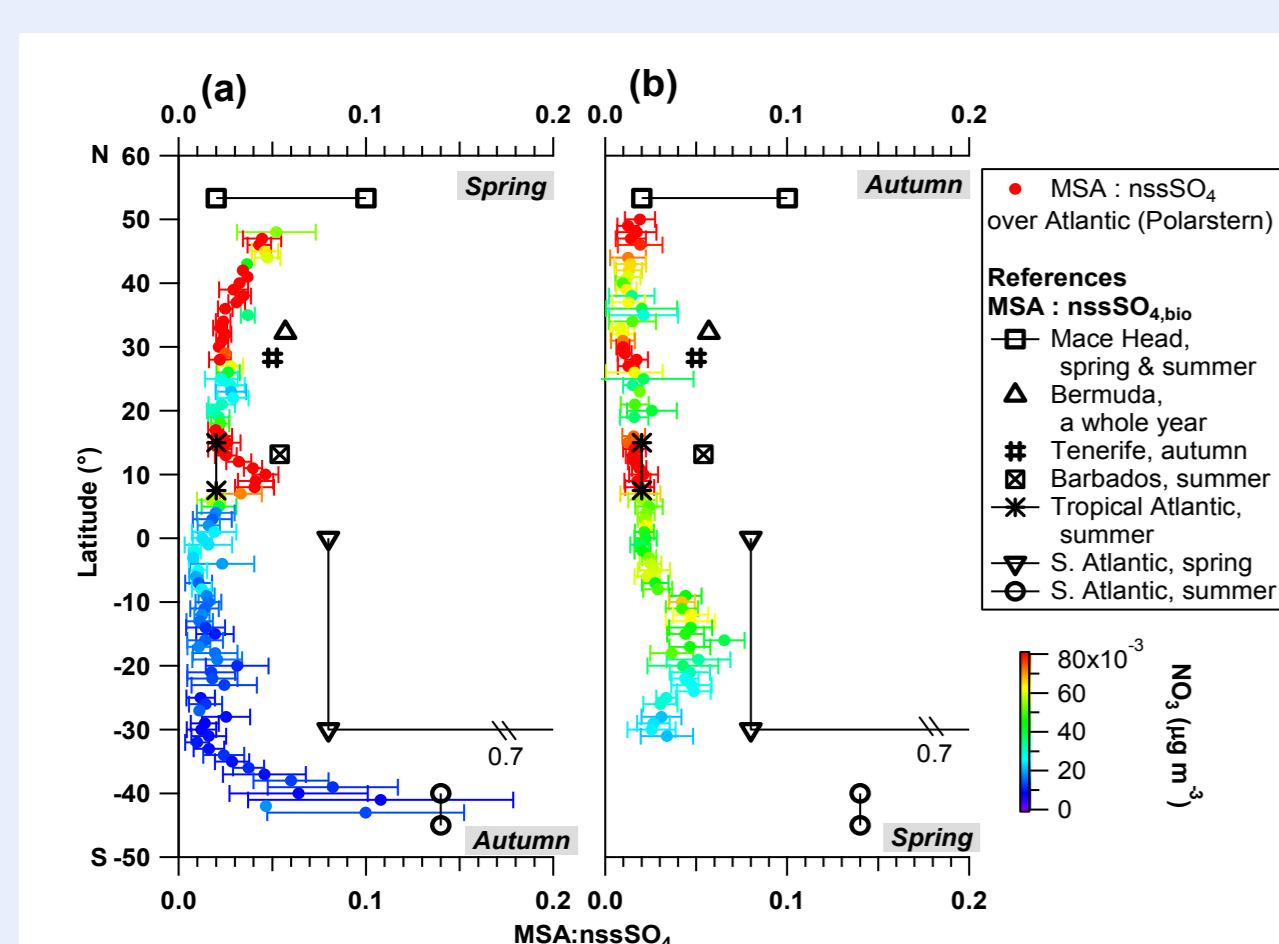


Fig.3: Spatial distribution of the MSA mass concentration in the four cruises. Background plots provide simultaneous Chlorophyll-a (Chl-a) mass concentration (rolling 32-day average), obtained from MODIS aboard the satellite Aqua. Air mass back trajectories are for the past 5 days at 950 hPa.

MSA:nssSO₄



The ratio MSA:nssSO₄ suggests a ubiquitous and significant influence of **anthropogenic sources** on aerosols in the marine boundary layer.

Fig. 4: Latitudinal distribution of the measured MSA:nssSO₄ ratio in (a) spring (in NH) and (b) autumn (in NH) (filled points) colored by the anthropogenic tracer nitrate; reference values mainly (or solely) influenced by biogenic sources (MSA:nssSO_{4,bio}) are also plotted (all in black).

References and Acknowledgement

For more details: Huang, S., Poulain, L., van Pinxteren, D., van Pinxteren, M., Wu, Z. J., Herrmann, H., and Wiedensohler, A.: Latitudinal and Seasonal Distribution of Particulate MSA over the Atlantic using a Validated Quantification Method with HR-ToF-AMS, Environ. Sci. Technol., 51, 418-426, 2017.

References: Phinney, L.; Richard Leaitch, W.; Lohmann, U.; Boudries, H.; Worsnop, D. R.; Jayne, J. T.; Toom-Saunty, D.; Wadleigh, M.; Sharma, S.; Shantz, N.. Deep Sea Res., Part II 2006, 53 (20-22), 2410-2433; Ge, X.; Zhang, Q.; Sun, Y.; Ruehl, C. R.; Setyan, Environ. Chem. 2012, 9 (3), 221-235; Huang, D. D.; Li, Y. J.; Lee, B. P.; Chan, C. K. Environ. Sci. Technol. 2015, 49 (6), 3672-3679.

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