

# Detection of aliphatic amines in seawater and marine aerosol samples

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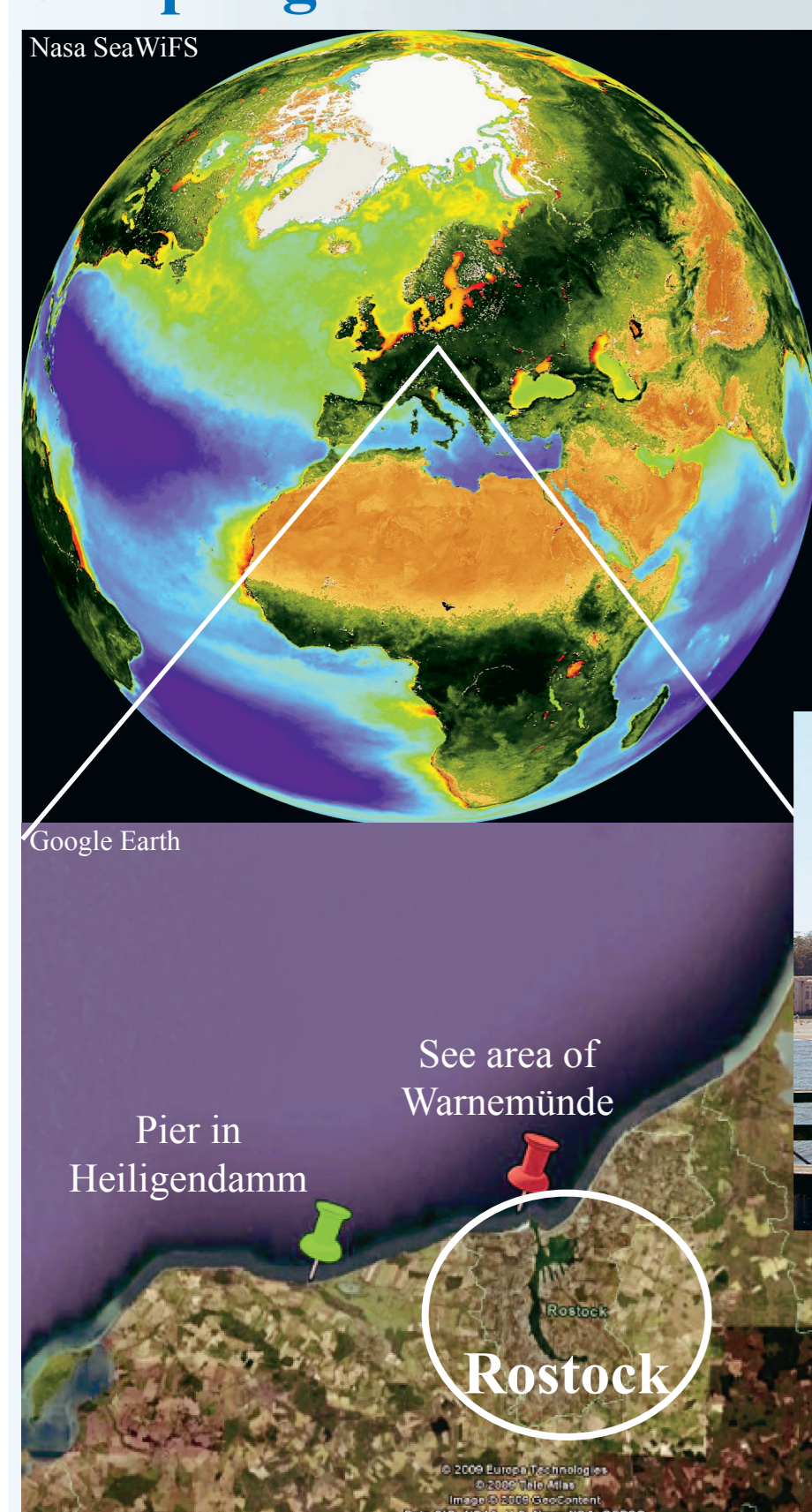
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## Introduction

Aliphatic amines are ubiquitous in the environment. They originate from both biogenic and anthropogenic sources such as marine algae or livestock farming. It is well established that ammonia is important for the stabilization and the growth of  $\text{H}_2\text{SO}_4$  clusters in the gas phase. Recently, it is suggested that the organic ammonium sulfate formation is preferred over inorganic ammonium sulfate in the particle formation processes (Kurtén et al., 2008) and aliphatic amines may play an important role in the nucleation process (Smith et al., 2010), especially in the clean marine environment even the gas phase amine concentrations are a factor 10 to 30 lower compared to ammonia (Gibb et al., 1999). Furthermore, it is known that the amines are important for the marine C and N cycle because they can contribute as much as 11% to the water soluble organic carbon content in smaller particles (Facchini et al., 2008). However the exact source, the gas to particle conversion processes and their role in the carbon and nitrogen cycle are still not well understood. Here we present the results from marine aliphatic amine analysis performed in two field studies conducted at the Cape Verde Atmospheric Observatory in the subtropical North Atlantic Ocean (CVAO) and the Baltic Sea coast.

## Sampling



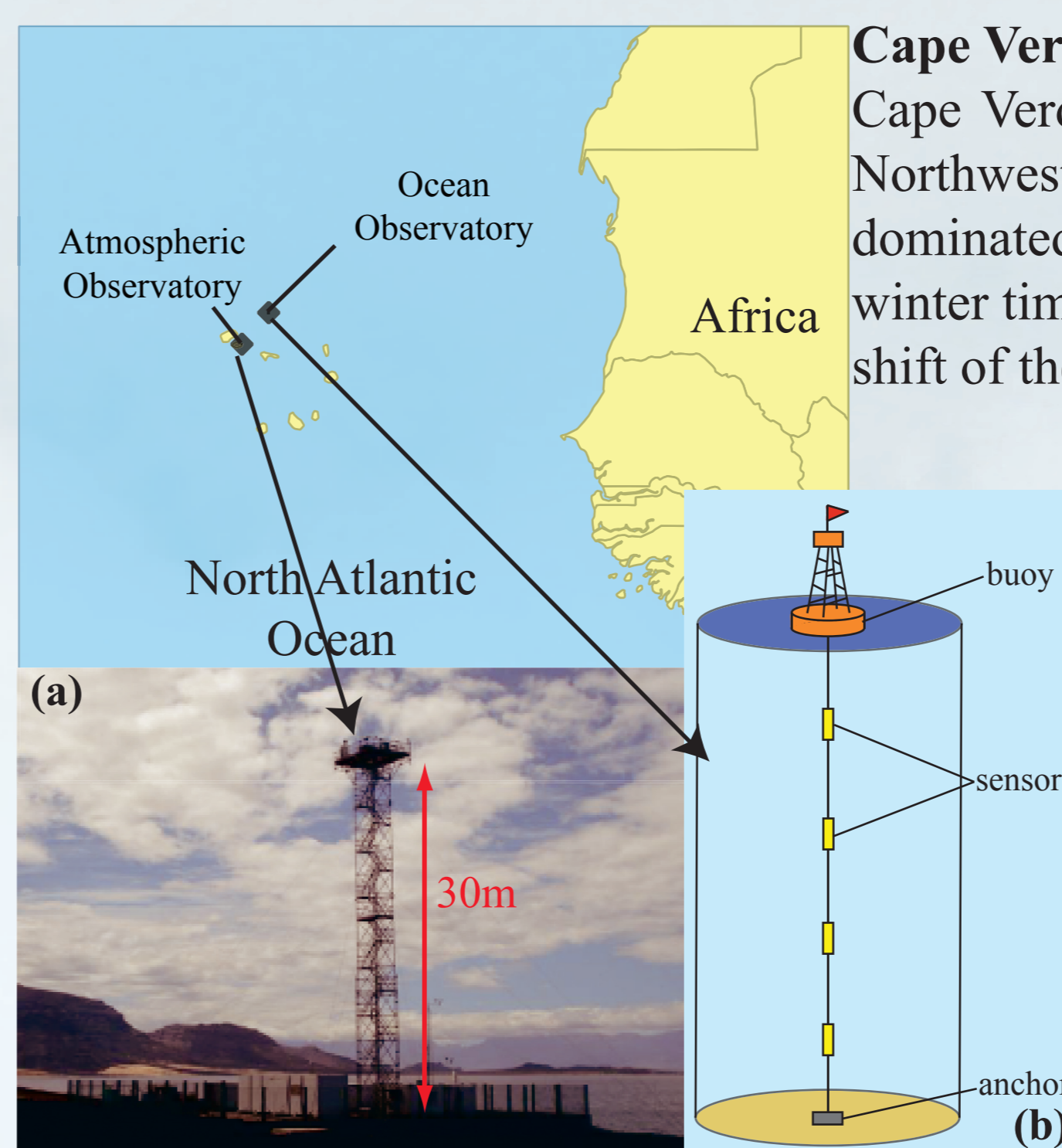
### Baltic Sea - Surface seawater

The Baltic Sea is the second largest inland sea in the world. Due to the limited fresh water exchange and the discharged lakes of the bordering states the salinity is lower (17 PSS, Practical Salinity Scale) than the majority of seawater (>35 PSS). Furthermore, the Baltic sea is separated from ocean currents and this causes large annual temperature fluctuations in the water body.



Fig. 1: Sampling site at the German Baltic Sea coast to collect the surface seawater samples from 2 m depth.

Surface seawater samples were collected over six months from the German Baltic Sea coast. The water samples were taken every Thursday at the pier in Heiligendamm (54°08'46"N, 11°50'36"O) from end of January to the end of July 2008. A clean glass bottle mounted on a telescopic rod was used to collect the surface seawater from 2 m depth. Immediately after the sampling, the water was filtrated with Whatman GF/F filters and stored frozen at -20°C until the analysis.



### Cape Verde Island - Marine aerosol

Cape Verde is an archipelago in the subtropical North Atlantic Ocean at the Northwest coast of the African continent. During the year, the wind direction is dominated by easterly wind and the average precipitation is 55 mm yr<sup>-1</sup>. In the winter time the Island is strongly influenced by dust deposition due to seasonal shift of the intertropical convergence zone (ITCZ).

The aerosol samples were collected at the CVAO (Fig. 2) which is located at São Vicente (16°51'49" N, 24°52'02" W). About 60 nautical miles northeast to the CVAO, the Ocean Observatory (CVOO) (17°35' N, 24°15' W) was located in the Mauritanian upwelling region at 3600 m depth.

The aerosol particles for the time series were collected with a high volume sampler (PM<sub>10</sub> inlet) on pre-combusted quartz fiber filters with a flow rate of 500 L min<sup>-1</sup>. The sampling started in May 2007 and finished in June 2008. Additionally, size segregated aerosol samples were taken in three intensive campaigns (17.05.-14.06.2007, 28.11.2007-05.01.2008 and 29.12.2008-06.01.2009) using a five stage Berner type impactor. The samples were collected on aluminum foils at a flow rate of 75 L min<sup>-1</sup>. Sampling duration was 48 h and 24 h during the intensive campaigns. The samples were stored frozen (-20°C) until the analysis.

Fig. 2: The Cape Verde Observatory consists of an atmospheric (CVAO) and an ocean observatory (CVOO). (a) Aerosol sampling at the top of the 30 m high tower. (b) Temperature measurements in different depth.

## Results and Discussions

MA, DMA and DEA were the dominant detected amine species in both the surface seawater and aerosol samples. Moreover, MP, which was first identified as a positive sampling artifact in aerosols, was also found in the surface seawater. EOHA present in the surface water wasn't found in the aerosol phase.

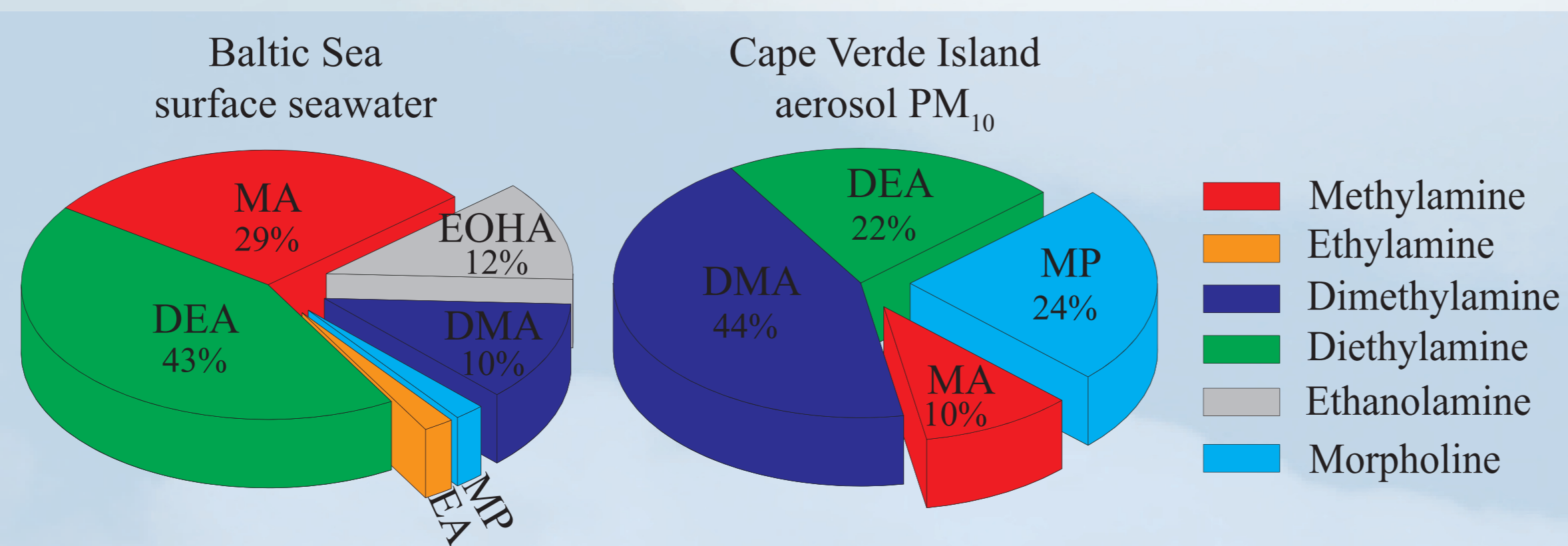
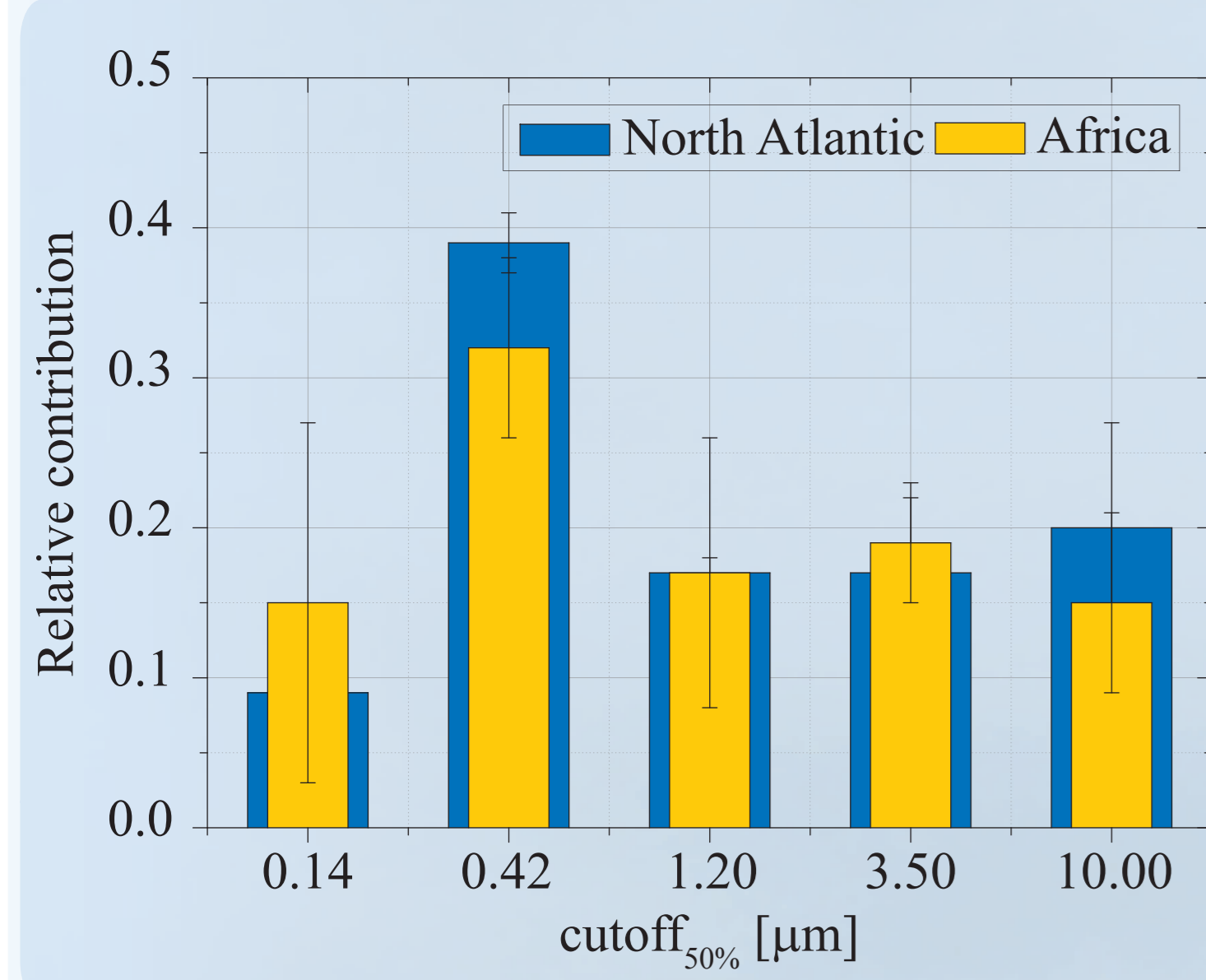


Fig. 3: Percentage contribution of the single amines to the total detected aliphatic amine concentration.



Independent from the incoming air masses (blue from North Atlantic and yellow from the African continent) the highest amine concentrations were detected in the sub-micrometer particles (< 0.42 μm) (Fig. 4). Additionally, the aliphatic amines showed no adsorption on sea salt or dust particles.

Fig. 4: The relative contribution of the amines detected in the single stages of the Berner Impactor samples to the total measured amines in the marine aerosol PM<sub>10</sub>. Represented are the sum of MA, DMA and DEA. The data are separated by the incoming air masses (blue - North Atlantic and yellow - African continent).

DMA and DEA were dominantly present in the seawater as well as the aerosol samples. In addition, the secondary aliphatic amines shows a good correlation (Fig. 5) which indicates a similar source for these two amines.

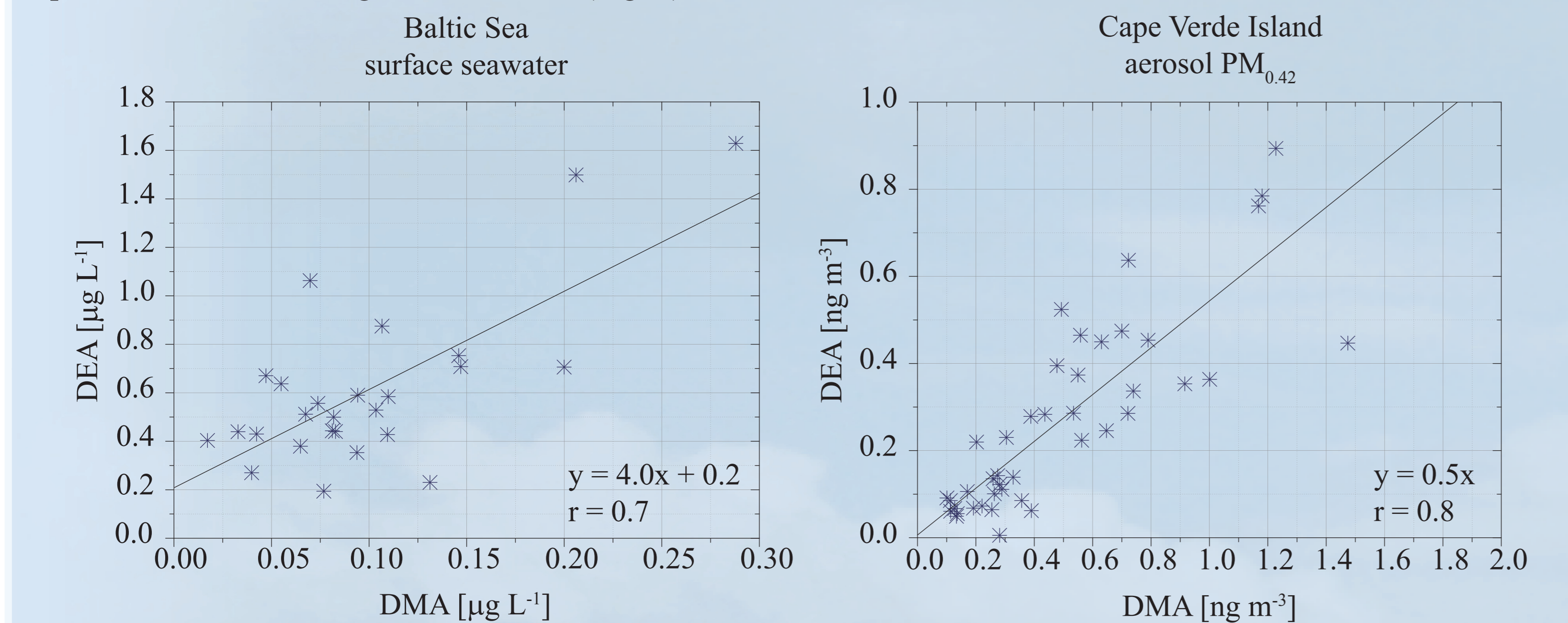


Fig. 5: Correlations between DMA and DEA in surface seawater (left) and aerosol (right) samples.

The exact amine source in the marine environment is still unknown but the field studies indicate that the aliphatic amines are probably produced by algae in the surface water. The detected DMA concentrations were higher when the algal productivity in the Baltic Sea was enhanced (Fig. 6).

A similar observation was made for the Cape Verde Island. The detected amine concentrations in the aerosol samples were higher when the marine biomass production was enhanced in the surface seawater (Fig. 7).

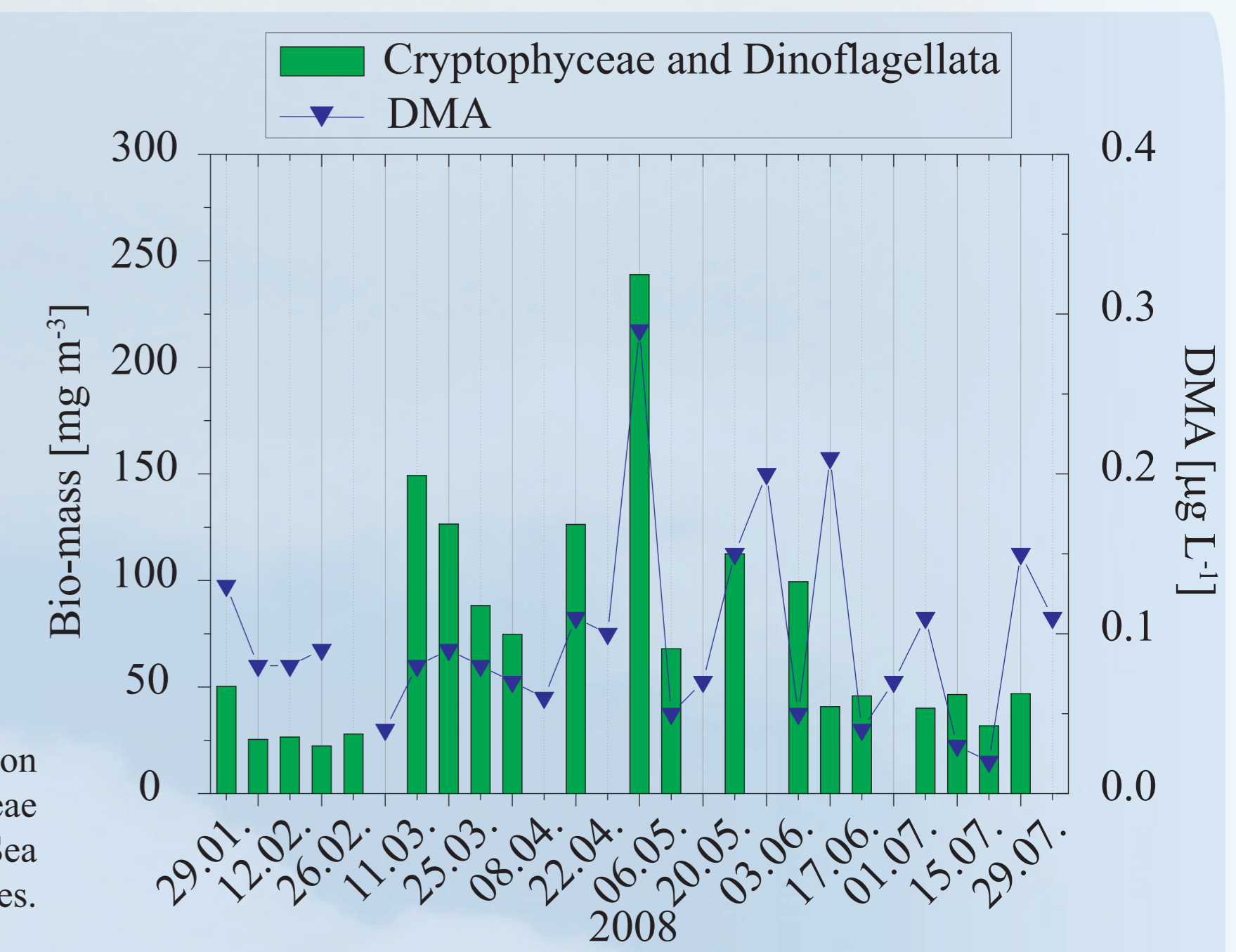


Fig. 6: The temporal variations of the DMA concentration (green bars) and the bio-mass of the algae Cryptophyceae and Dinoflagellata (blue triangles) measured in Baltic Sea seawater samples.

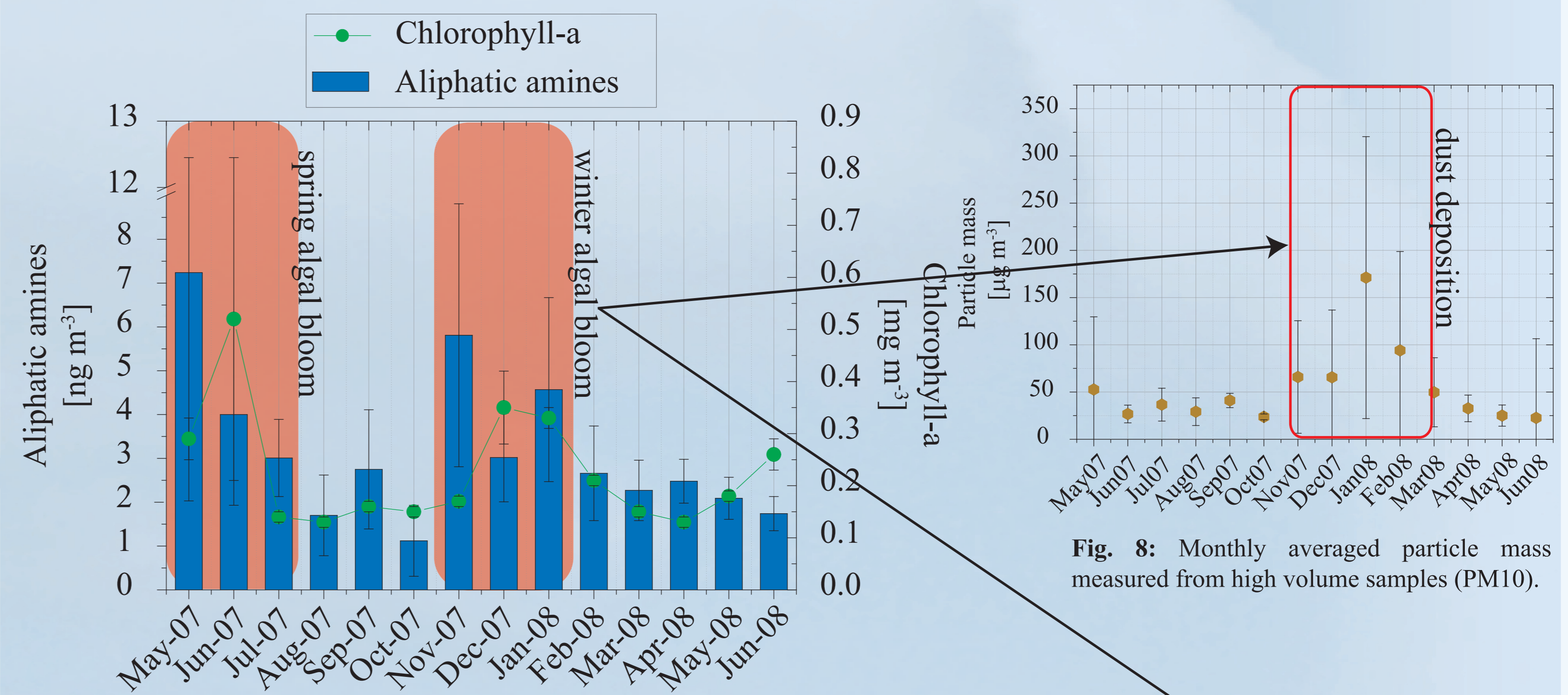


Fig. 7: Monthly averages of the aliphatic amines (sum MA, DMA and DEA) (blue bars) detected from the marine aerosols collected with a high volume sampler (PM<sub>10</sub>). The monthly averaged chlorophyll-a (green circles) concentrations calculated from MODIS satellite data are shown. Periods with higher concentrations are highlighted.

The observed winter algal bloom (Fig. 7) was supported by regional influences such as dust deposition (Fig. 8) or local upwelling (Fig. 9).

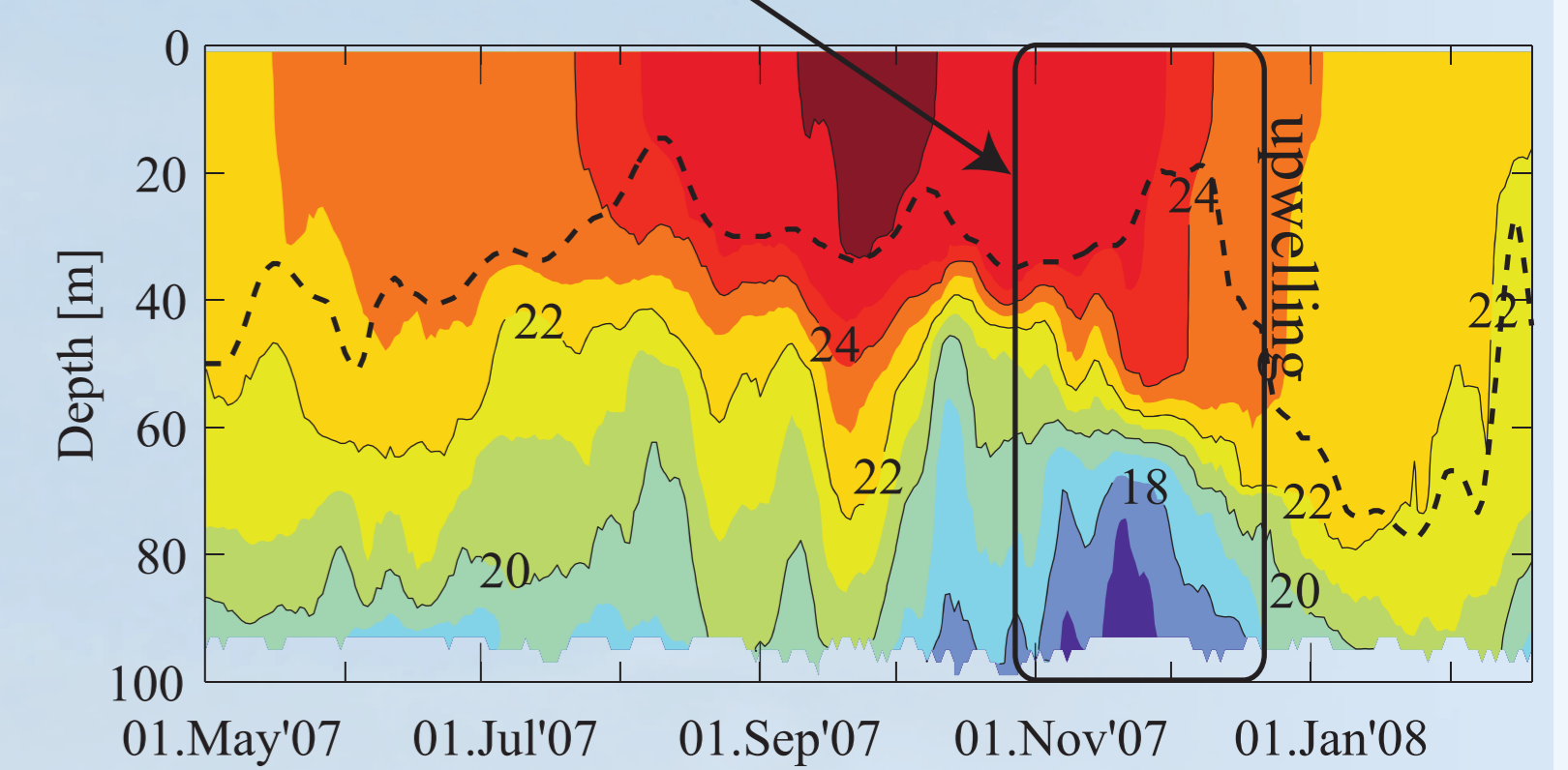


Fig. 9: Temporal evolution of the upper ocean temperature structure based on moored instruments from the CVOO and merged with AMSR-E satellite sea surface data.

## Summary and Outlook

- Similar amines were found in the surface seawater and marine aerosol samples
- Aliphatic amines were detected in highest concentrations in smaller particles
- Temporal variation showed some correlations to phytoplankton productivity in the surface water for both regions

Detailed information on the aliphatic amines measurement in the marine particles collected at the CVAO can be found at Müller et al. (2009).

## References

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