Seasonal variation of aliphatic amines at the Cape Verde Islands

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Introduction

Over 70 % of the Earth's surface is covered by oceans. For this reason ocean-atmosphere exchange processes are very important for the water cycle, marine and atmospheric chemistry, for marine aerosol production and there physico-chemical properties, CCN activation and hence the global climate. The most important exchange process for the marine non-sea-salt sulfate (nss SO_4^{2-}) aerosol formation is the emission of marine biogenic DMS (dimethyl sulfide). Under ternary nucleation, new particles can be formed in the gas-phase by the combination of sulfuric acid, ammonia and water. Recently, theoretical calculations have shown that aliphatic amines are preferred to form new particles with sulfuric acid instead of ammonia under amine rich conditions (Barsanti et al.; 2009; Kurten et al., 2008). Aliphatic amines are ubiquitous in the atmosphere and it is thought that they are produced by marine organisms such as phytoplankton in the remote marine environment (Gibb et al., 1999; Facchini et al. 2008; Müller et al., 2009). Due to their low effective Henry coefficient they are predominantly in the gas-phase rather than in the particle-phase. Very recently, it has been reported that non-negligible concentrations of amines exist in sub-micrometer marine aerosols, indicating a potential importance of amines in marine secondary organic aerosol (SOA) formation (Facchini et al. 2008; Müller et al., 2009). However, their the exact sources, related biological activities, and the roles in the particle formation and the carbon and nitrogen cycles are still not well understood. Here we present a time series of alkyl amine concentrations and there mass size distributions in marine aerosol collected at the Cape Verde Atmospheric Observatory in the subtropical North Atlantic Ocean. We found a strong connection between the regional bio-productivity and the measured amine concentrations. Moreover, we show that the regional bio-productivity is connected to the winter time Saharan dust deposition and/or ocean upwelling. The observed enhanced biomass production was also reflected in higher amine concentrations (Müller et al. 2009).

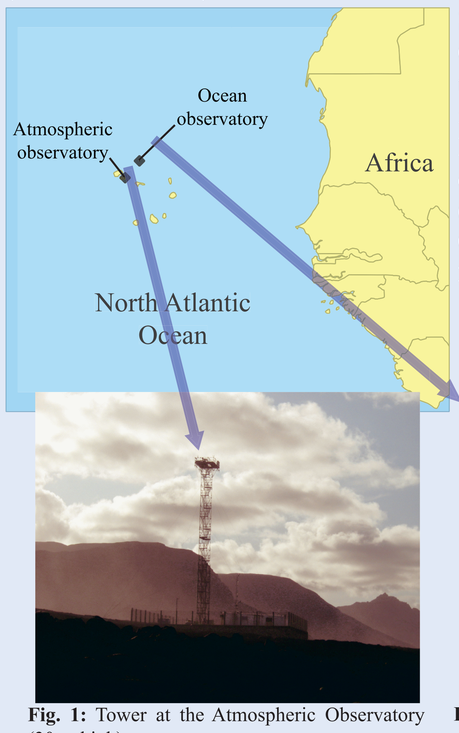


Fig. 1: Tower at the Atmospheric Observatory (30 m high).

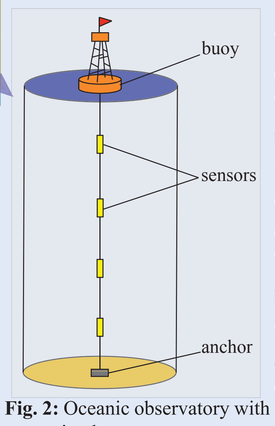


Fig. 2: Oceanic observatory with a mooring buoy.

Sampling site

Cape Verde is an archipelago in the subtropical North Atlantic Ocean at the North-West coast of the African continent. The average annual temperature of the island is 24-25 °C. During the year, the wind direction is dominated by easterly wind and the average precipitation is 55 mm yr^{-1}. At the Cape Verde islands, the highest monthly mineral dust concentration is typically observed between December and January. In the summer time the concentration is about 5 times lower. This observation is opposite to the mineral dust concentration observed at Barbados in the Caribbean where the minimum mineral dust concentration is found between December and January (Fig. 3) (Chiapello et al., 1995). The Cape Verde Observatory consists of an atmospheric (Fig. 1) and an oceanic station (Fig 2). The Atmospheric Observatory (AO) (16°51′49″ N, 24°52′02″ W) is located at São Vicente in the trade wind zone. The Ocean Observatory (OO) (17°35′ N, 24°15′ W) is located in 3600m depth about 60 nautical miles Northeast to the AO in the Mauritanian upwelling region .

Sampling

The aerosol samples for the time series analysis were collected with a DIGITEL DAH 80 high volume (HV) sampler (PM_{10} inlet) on pre-combusted quartz fiber filter (150 mm, Munktel, 110°C, 24h) with a flow rate of 500 L min^{-1}. The sampling started in May 2007 and finished in June 2008. Additionally, size segregated aerosol samples were taken during two intensive campaigns (17 May – 14 June 2007 and 28 November 2007 – 5 January 2008) using a five stage Berner type impactor (0.14µm, 0.42µm, 1.2µm, 3.5µm and 10µm). The samples were collected on pre-combusted aluminum foils (300°C, 24h) at a flow rate of 75 L min^{-1}. Sampling duration was 24 h or 48 h depending on the PM loadings during the intensive campaigns. The samples were stored frozen (-20°C) until the analysis.
The oceanic observatory (Fig. 2) consists of a steel wire mooring with autonomous recording instruments. In the time period of July 2006 to February 2008 the temperature was measured (SeaBird) in a depth profile of 27m, 49m, 68m, 90m and 116m with a time resolution of 30 min.
As a proxy for the bio-productivity we use chlorophyll-a (Chl-a) available from MODIS satellite data (NASA Goddard Space Flight Center).

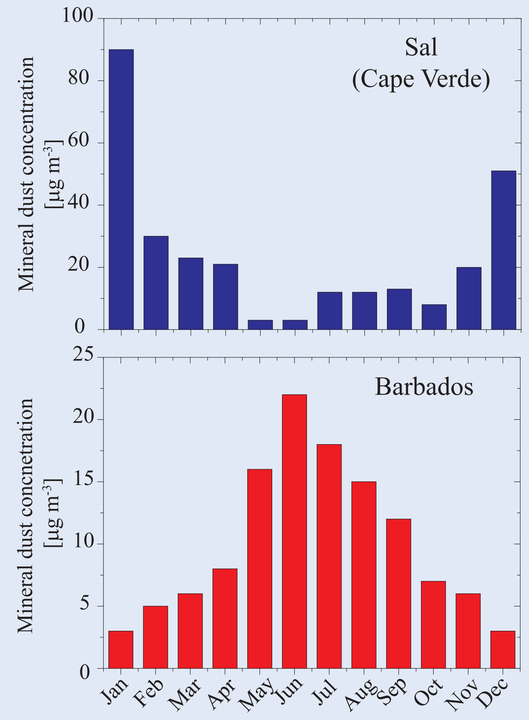


Fig. 3: The seasonal cycle of dust concentration Chiapello et al. (1995).

Results and Discussion

Methylamine (MA), dimethylamine (DMA), diethylamie (DEA) and morpholine (MP) were detected in marine aerosol samples. It is noted that MP was only detect in high volume samples. Additionally, the amine concentrations determined for the quartz fiber filters were ten times higher than for the aluminum foils. The reason for this discrepancy most likely originates from the gas-phase absorption of the basic amines on the acidic quartz fiber filter surface. Nevertheless, the amines measurements from HV filters can be used as an indicator for the seasonal amine variation because both the HV and impactor samples showed similar seasonal trend and amine distribution.

a) Size resolved impactor samples

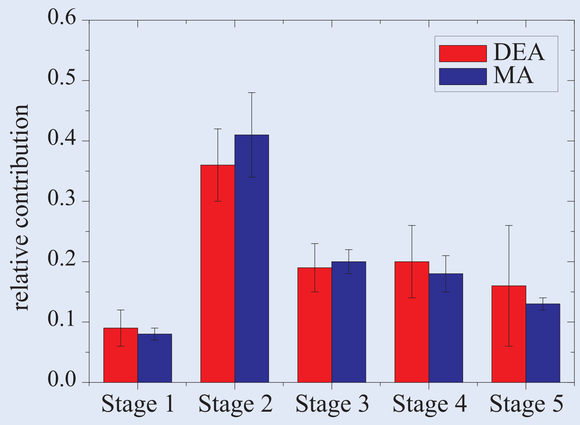


Fig. 4: Relative contribution of methylamine (blue) and diethylamine (red) to the five stages.

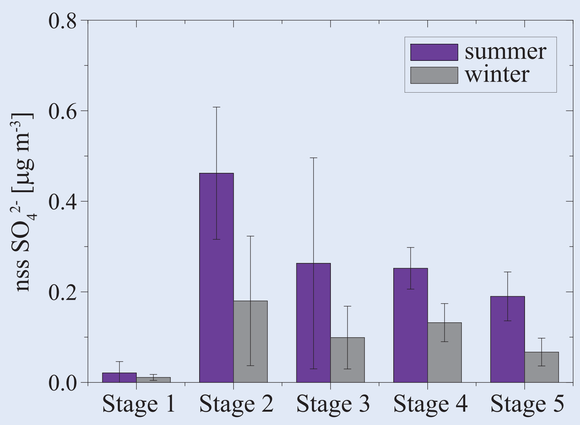


Fig. 5: The non sea salt sulfate (nss SO_4^{2-}) concentration detected in five stage impactor samples. Only samples with air masses originating from the open North Atlantic Ocean are considered.The summer months (May and June) are in purple and the winter months (December and January) are in gray.

The chemical analysis for the Berner impactor samples from the two intensive campaigns shows the highest amine concentration on stage 2 (0.14 – 0.42 µm) samples (Fig. 4). The most abundant amine was DMA, followed by DEA and MA (Fig. 6). Beyond that DMA and DEA show a good correlation (Fig. 7), indicating a simila origin of these two amines. Monomethylamine (MA) shows no correlation with DMA and DEA though similar seasonal variation can be seen (Fig. 8).

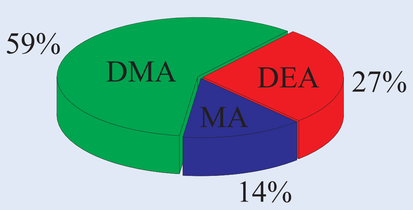


Fig. 6: The percentages of the detected amine concentrations in stage 2 Berner samples. Most abundant amine was dimethylamine (DMA), followed by diethylamine (DEA) and monomethylamine (MA).

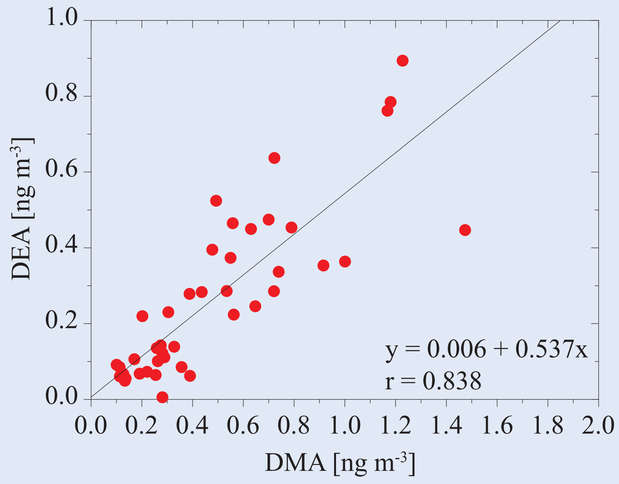


Fig. 7: Correlation bewteen dimethylamine (DMA) and diethylamine (DEA) detected in stage 2 Berner impactor samples.

b) Seasonal amine variation

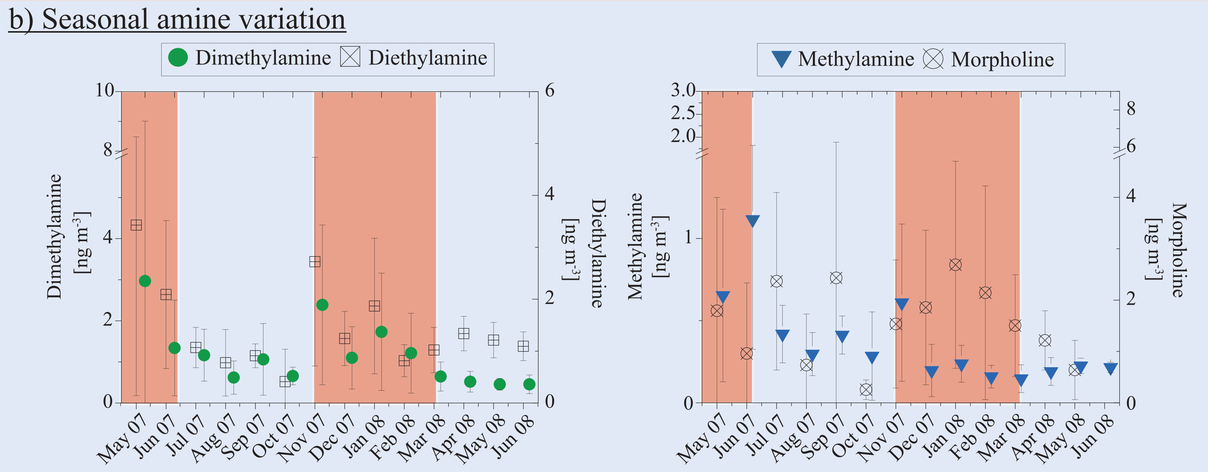
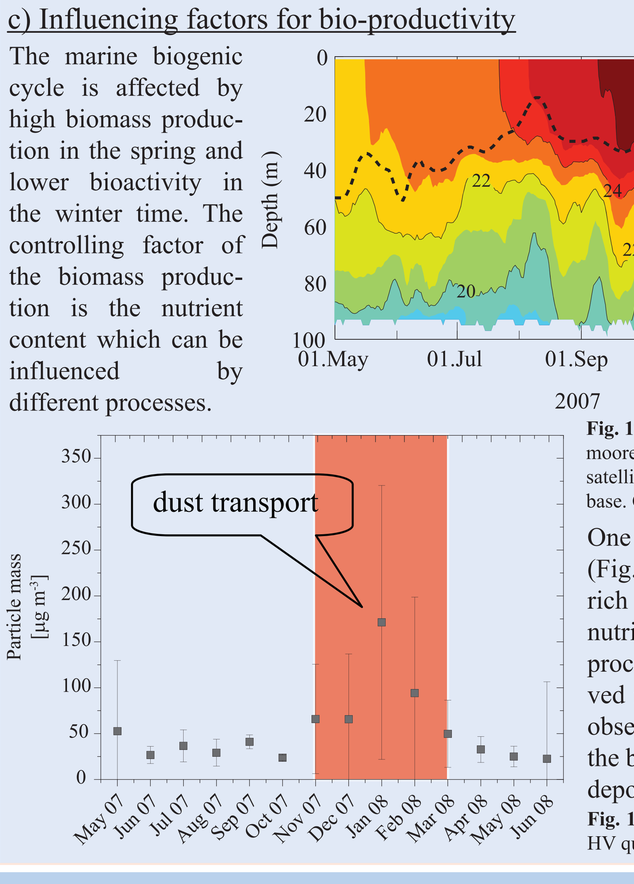


Fig. 8: Monthly averages with standard diviation of dimethylamine (DMA, filled green circle), diethylamine (DEA, crossed quarter), monomethylamine (MA, filled blue triangle) and morpholine (MP, crossed circle) detected in quartz fiber filter from high volume (HV) sampler [ng m^{-3}].



In a one year field campaign (May 2007 – June 2008) aerosol samples were taken with a HV sampler which was equipped with a PM_{10} inlet. The measured seasonal aliphatic amine concentrations show high values in spring 2007. Additionally, a second period with high amine values can be seen in the winter season 2007/2008 (Fig. 8). The comparison with satellite measured chlorophyll-a concentration shows a good agreement between the high amine values and the enhanced bio-proactivity (Fig. 9).

Fig. 9: Monthly modeled MODIS ocean color based time series of chlorophyll-a (12.5 – 20.5°N / 20.5 – 28.5°W) (green filled squares).

c) Influencing factors for bio-productivity

The marine biogenic cycle is affected by high biomass production in the spring and lower bioactivity in the winter time. The controlling factor of the biomass production is the nutrient content which can be influenced by different processes.

Fig. 10: Temporal evolution of the upper ocean temperature structure based on moored instruments from the Ocean Observatory and merged with AMSR-E satellite sea surface data. The broken line indicates the depth of the mixed layer base. Contours are given for every 2°C, color coding is every 1°C.

One process to increase the nutrients is the upwelling (Fig. 10). The upwelling is the transport of cooler nutrient rich deep sea water to the surface water. Another form of nutrient input is the dust deposition process (Fig. 11). Both processes the upwelling and the dust deposition were observed in the winter 2007/2008 and are possible to induce the observed winter algal bloom. It is not clear at the moment if the bloom had more influence from the upwelling or the dust deposition.

Fig. 11: Monthly averaged and variability of the particle mass in µg m^{-3} from HV quartz fiber filters.

References

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