Determination of organic matter in oceanic water samples and the corresponding marine aerosol

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Introduction

Marine aerosols contain, besides sea salt, a significant amount of organic material. Recent investigations suggest that the organic content of marine aerosols, especially of particles in the sub-micron range, is strongly connected to the biological activities of the ocean. It was reported that at times of high biological activity the organic fraction on the particles is dominant (comprising more than 50% of the particle mass) where at times of low biological activity the organic fraction decreases to about 15% [1]. To study the interaction processes a detailed chemical investigation in terms of organic material of the oceanic water and atmospheric phase above the mandatory. In this context, the sea surface microlayer (SML) formed due to different physicochemical properties of the water and the air plays an important role. The SML is operationally defined as the first 1000 micrometers of the ocean surface and therefore the direct interface for all gaseous, liquid and particulate mass transfer between the ocean and the atmosphere. Being often enriched with organic and inorganic matter, the SML may play a key role in the export of organic material from the ocean to the atmosphere mediated by processes such as bubble bursting and gas transfer (Fig. 1).
In the present work, first investigations of seawater and aerosol samples taken at the Cape Verde island Sao Vicente (16°51'49"N, 24°52'02"W) are shown.

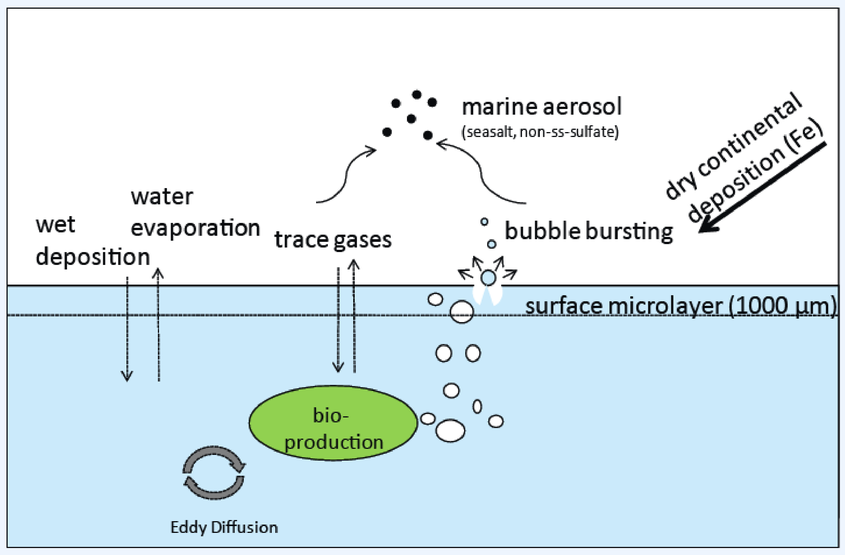

Fig. 1: Scheme of interaction processes between the oceans and the atmosphere.

Sampling devices

In former years high biological activity was observed in late spring/early summer in the Cape Verde region due to local upwelling leading to the transfer of nutrients from the deeper ocean to the surface [2]. Therefore, a field campaign was performed in may 2011. Marine aerosols smaller than 1 µm (PM_1) were collected on top of a 30 m tower at the CVAO station at São Vicente using a high-volume sampler. Oceanic water was collected near the CVAO station. Besides bulk water (BW) in a depth of 2 meters, the sea surface microlayer (SML) was sampled with a glass plate that is vertically immersed in the water and slowly removed (Fig. 2). The film adheres to the surface of the glass and is removed by framed Teflon wipers. This sampling technique requires low instrumental equipment and allows the sampling of a film thickness of several hundred micrometers. After sampling the samples were filtered (whatman GF/F filters, pore size: 0.7 µm, Whatman International Ltd., Maidstone, UK) and cooled to -20°C. Samples were transported to the laboratories of the IfT Leipzig in a cooling container at -20 °C.

Fig. 2: Sampling of the SML using the glass plate technique,(left), Collection of the SML using Teflon Wipers (right).

Chemical analyses of DOC and TDN

Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN -as the sum of dissolved inorganic ammonium, nitrite and nitrate and dissolved organic nitrogen-containing compounds) were determined using a total organic carbon analyzer (TOC-V_{cph}) which was equipped with a TNM-1 device (Shimadzu, Kyoto, Japan). The oxidation of the carbon and nitrogen within the sample was performed at pH 2 by adding 300 µL of the solutions to a catalyst (aluminum oxide/platinum) held at a temperature of 720 °C. The formed carbon dioxide was detected by NDIR (non-dispersive infrared), while the formed nitrogen monoxide was further oxidized to nitrogen dioxide by ozone and subsequently detected by chemiluminescence. DOC and TDN contents were determined by using an external calibration with potassium hydrogen phthalate and potassium nitrate, respectively.

Results and Discussion

Backwards trajectories

In order to obtain information about the origin of the air masses, backward trajectories were calculated in heights of 250, 200 and 700 m showing the pathway of the air masses in the last 96 hours. All presented aerosol data are of marine origin, as for example shown in Fig. 3.

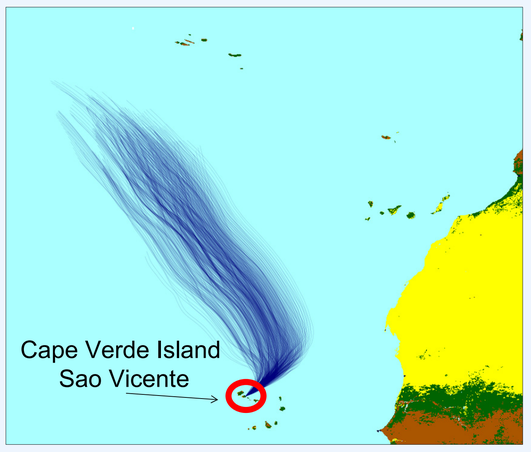

Fig. 3: Backward trajectories for the air masses arriving to Sao Vicente on 02.05.2011.

DOC / TDN concentration and SML enrichment

The concentrations of DOC and TDN for marine aerosol and SML are presented in Figure 4. The average concentration of DOC in marine aerosols was 0.2 µg m^{-3} and therefore close to the average DOC concentration of this region (0.18 µg m^{-3}). Average TDN concentration was 0.04 µg m^{-3}. DOC and TDN together accounted for 4% of the particle mass. Concentrations of DOC and TDN in the SML were on average 1.5 mg L^{-1} (DOC) and 0.3 mg L^{-1} (TDN) being mildly correlated (R^2= 0.5). By calculation the enrichment factor (EF = C (SML) / C (BW)) a 2-3 fold enrichment of DOC and TDN in the SML was found.(Fig. 5), indicating that the organic composition of the surface differs to the corresponding bulk water.

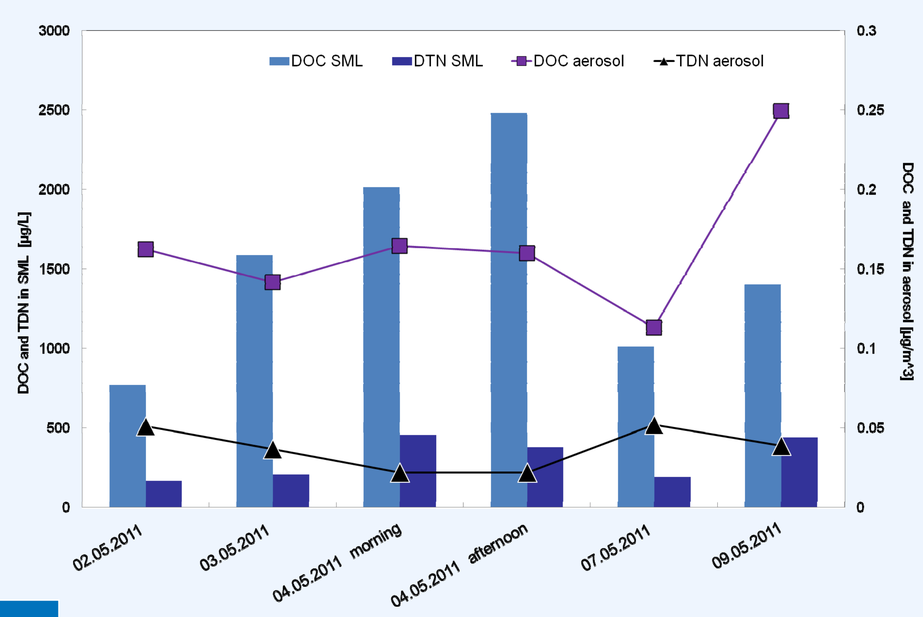

Fig. 4: Concentrations of DOC / TDN in marine aerosol particles and SML.

Summary and Outlook

- *First results of organic sum parameters in marine aerosol and seawater were obtained.*
- *Significant enrichment of DOC and TDN in the SML was found.*
- *Further combination of organic composition in the ocean and the atmosphere will follow.*
- *Determination of single organic species in both compartments will further reveal connection between oceans and atmosphere.*

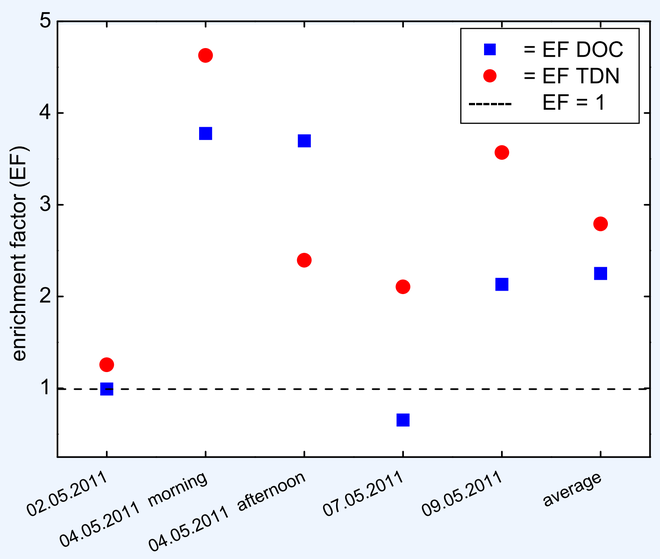

Fig. 5: Enrichment factors (EF) of DOC and TDN.

References

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