Organic export from the ocean to the atmosphere - first investigations

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INTRODUCTION

- Oceans cover a substainal part of the earth and there are manifols, to date rarely understood interaction processes between the oceans and the atmosphere
- Among these interactions, organic export from the oceans can significantly influence aerosol composition and therefore affect their behavior towards adsorption and reflection of solar radiation
- The sea surface microlayer (SML) of the oceans – the first 1000 µm of the ocean – plays an important role as it is the direct interface between these two compartments
- First investigations report a different chemical composition of the SML compared to the bulkwater, e.g. an enrichment of organic material [1]
- For a better understanding of the origin and transfer of the organic compounds on marine aerosols a detailed investigation in terms of organic material of the oceanic water and atmospheric phase above the mandatory
- A first step, presented here, is the analysis of organic carbon/nitrogen in different seawater samples from the Baltic sea and the Atlantic regarding bulkwater and SML
- Also analyses of atmospheric relevant single organic compounds (amines, amino acids, carbohydrates) in Baltic seawater was performed

Experimental: *1. Sampling devices*

Principle:

- SML adheres to the surface of the sampler and is then removed by Tefoln lamellas
- Sampling of a film thickness between 100 and 400 µm

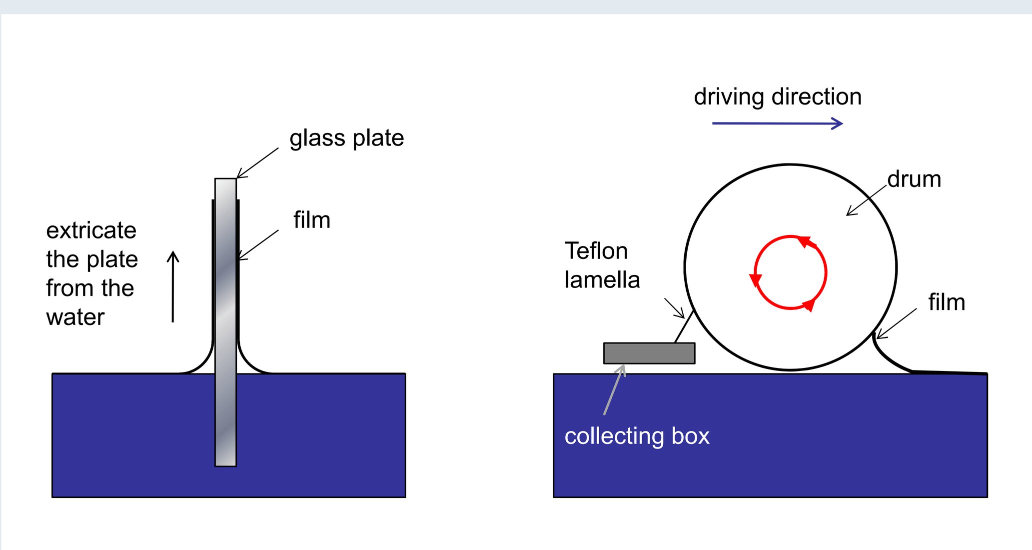

Fig. 1: Sampling of the SML using the glass plate technique (left), and the rotating drum (right)

2. Chemical analysis

Sum parameters:

Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN):

Total organic carbon analyzer (TOC-V_{cph})

- Detection of DOC as CO2 with non-dispersive infrared
- Detection of TDN as NO2 with chemiluminescence

Single organics:

Amines and Amino acids:

- Derivatization with benzenesulfonyl chloride (sulfonamides are formed)
- Enrichment with Solid Phase Extraction using Strata X
- Analysis with HPLC/ESI-ITMS

Carbohydrates:

- Desalting step using a 1:1 mixture of a strong cation exchange and weak anion exchange granulate
- Enrichment due to evaporation on rotary evaporator and re-dissolution in water
- Analysis with anion-exchange chromatography and pulsed amperometric detection

Results and Discussion

1. Sum parameters

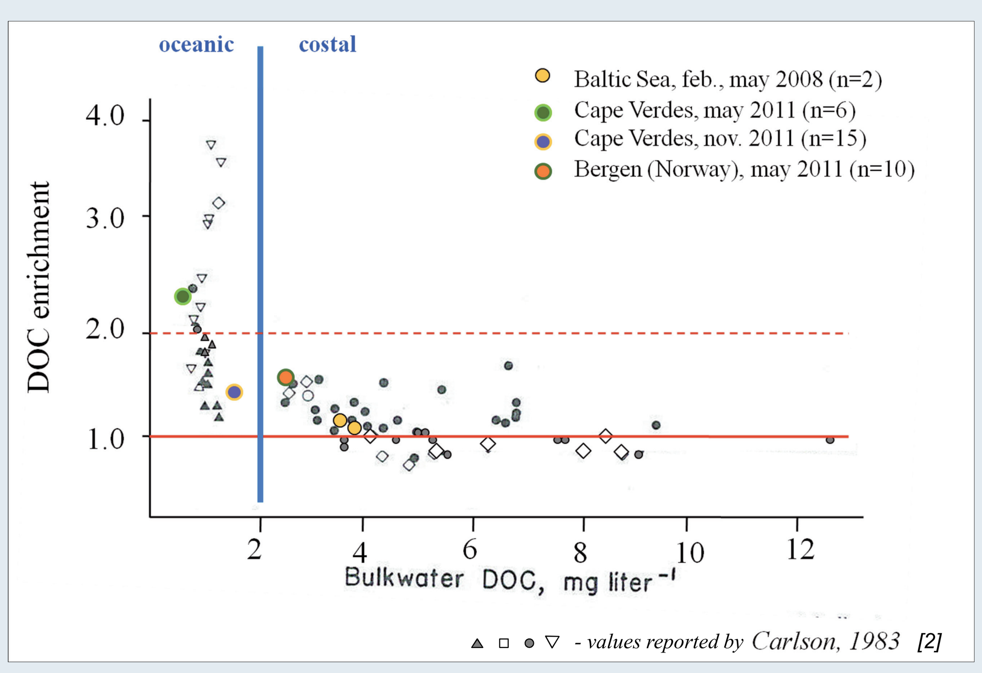

Fig. 2: DOC enrichment vs. DOC bulkwater concentration in different sampling areas (compared with literature values)

$$EF = \frac{c(SML)}{c(bulkwater)}$$

- DOC enrichment diminished with increasing bulk water concentrations (in agreement with Carlson, 1983 [2])
- Lower enrichment of DOC can be caused by biological, physical and chemical DOC removal from the SML
- Such effects might be more effective in areas with higher DOC (mostly costal)

2. Single Organics (in Baltic Seawater)

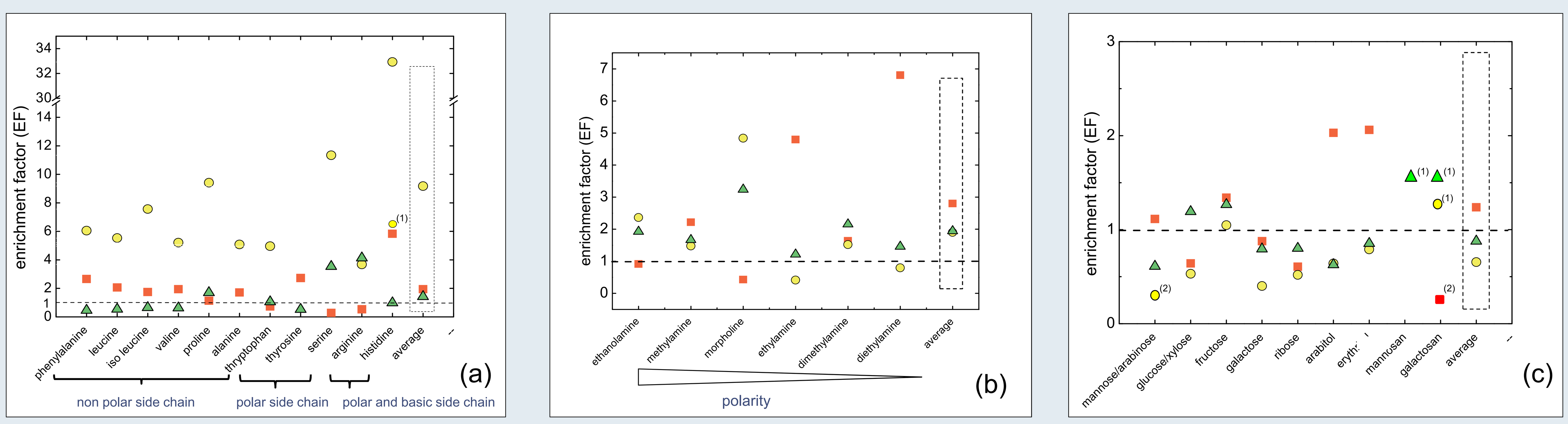

Fig. 3: EF of free dissolved compounds for the three investigated samples, RSD < 12%, n=2, (1) compounds were detected in the SML but not in the bulk water, (2) compounds were detected in the bulk water but not in the SML, legend: ○ - 13.07.2006 (summer sample), ▲ - 20.02.2008 (winter sample), ■ - 09.05.2008 (spring sample).

Amino Acids:

- Majority of the proteinogenious amino acids (11 out of 18) were found in the samples with average concentrations between 50 ng L^{-1} and 1600 ng L^{-1}.
- Most abundant amino acids were serine, proline, valine and iso-leucine.
- Enrichment factors (EF) between 1.4 and 9.2
- Highest enrichment in winter sample when bacterial activity was low implies enrichment due decreased bacterial uptake [3]

Amines:

- All aliphatic amines were detected in the samples in concentrations between 170 and 900 ng/L
- Average EFs between 2-3
- Summer: enhanced enrichment for amines with longer chain length (decreased polarity) was observed
- Winter: lower enrichment or even depletion of the volatile amines probably due to higher wind speed and therefore enhanced transfer to the atmosphere

Carbohydrates:

- Sugar alcohols, monosaccharides and monosaccharide anhydrates were found in concentrations between 1900 - 4400 ng L^{-1}
- Mono. anhydrates were observed nearly exclusively in the SML samples, with high concentrations in winter and spring
- Sugar alcohols (biological markers) showed a high variability of the EF (enrichment in summer, depletion in winter)
- Average EFs between 0.7 and 1.2; trend towards depletion, but high variability in concentration and enrichment

References and Funding

[1] van Pinxteren et al. Environ. Sci. Technol., *DOI: *10.1021/es204492b Publication Date (Web): April 4, 2012
[2] Carlson, D. J. *Limnol. Oceanogr.* **1983,** *28*, (3), 415
[3] Stolle, C., Nagel, K., Labrenz, M., and Juergens, K. (2010), *Biogeosci.*, *7*(9), 2975.

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Summary and Outlook

- DOC enrichment in SML compared to bulkwater DOC concentration was found for Atlantic and Baltic seawater
- Baltic seawater:
  - Amino acids, amines and carbohydrates were detected in SML and bulkwater
  - Significant enrichment of amines and amino acids in the Baltic seawater SML
  - Less enrichment/depletion for carbohydrates
  - Dependencies on meteorological and biological parameters
- **Next steps:**
  - Analyses of single organics in Atlantic seawater
  - Investigations of the atmospheric layer above the oceans (chem. analyses of aerosol and gas phase)