



Aliphatic amines in the tropical marine environment: abundance, possible origins and air-sea fluxes

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Aliphatic amines are dynamic constituents of the nitrogen cycle and widely distributed in the marine environment. However, their roles in atmospheric chemistry, biogenic origins and the formation process are still not well known. In this work, we present information of their abundance and possible origins by combining bulk ocean water, sea surface microlayer (SML), gas and particle phase amine measurements obtained from field campaigns at the Cape Verde island Sao Vicente.

The qualitative and quantitative analysis of the amines in seawater was performed with Solid Phase Microextraction combined with Gas Chromatography - Nitrogen Phosphorous Detection which enabled a robust determination of the amines in high saline complex matrices such as water samples from the Atlantic Ocean. The analysis of SML and bulk water samples showed that concentrations of the amines were in the nmol/L range and they seemed to be enriched in the SML. Amines in the particulate and gaseous phase were measured with ion chromatography. The combination of the particulate amine measurements with biogeochemical tracers from a two-years data set revealed that no clear correlation pattern was found when combining the amine concentrations with several tracers, such as calcium (dust tracer) and sulphate (particle acidity tracer). In addition, a correlation to sodium (sea salt tracer) and wind speed was absent implying that wind-mediated processes such as bubble bursting do not essentially drive the transfer of amines. Although the amines are suggested to be of marine sources, a direct link of the amines to chlorophyll-a (chl-a) was missing. The amine concentration coincidences with high chl-a concentrations in winter, however, in other times lower amine concentrations are observed at high chl-a peaks. This ambivalent behaviour might be explained with varying sources of the amines. Another reason could be a potential time lag between the high productive period (as expressed by chl-a peaks) and the particulate amine abundance, e.g. there could be a “delay” between the production of biological material and the transfer to the particulate phase. Furthermore, there might be other biological processes to be taken into account for amine production. As a qualitative tool to distinguish between different sources of the amines, a statistical source apportionment approach (principal component analysis, PCA) was applied to the data set. Three factors could be extracted from the statistical analysis: sea spray, photochemical production and a third factor that seemed to be correlated to calm, sunny weather and warm temperatures, but could not be clearly attributed to one distinct source or formation mechanism. Especially this third factor will be elucidated in more detail in future studies.

Finally, from the concentrations of dimethylamine in seawater and in the gas phase, mass fluxes between sea and air were calculated and varied between $1.6\text{E-}12$ and $-3.2\text{E-}12$ mol m^{-2} s^{-1} . This suggests that the ocean can act as sink (negative flux) or source (positive flux) for amines. It is likely that the source/sink capabilities of the ocean vary due to different ambient conditions e.g. a diurnal oxidation capacity of the atmosphere.