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Behaviour of VHOCs in a coastal sea surface during a short term mesocosm experiment

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The volatile halogenated organic compounds (VHOCs) are a strong source of highly reactive halogen oxide radicals catalysing the destruction of ozone in the atmosphere. The industrial activity over the last decades caused a significant increase of these climate-relevant trace gases in the environment. Additional biological sources, like marine algae, are also known to produce high quantities of these compounds. The final release of the marine derived organohalogens to the atmosphere depends on the equilibrium between algal production, microbial decomposition and various physicochemical parameters.

Due to the fact that aquatic systems and their interactions with the atmosphere affect the earth climate and conversely, marine ecosystems are sensitive to these climate and environmental changes, an enhanced knowledge about the relations on a smaller scale is essential before predictions can be made about the future global environment.

Therefore, to improve the understanding of VHOCs behavior in the sea surface, a short term surface mesocosm experiment was conducted in the coastal Baltic Sea in September 2010. The main aim was to understand dynamics of halogenated hydrocarbons in the sea/air interface with special attention to autotrophic production under the influence of light, particularly the UV-fraction of it. The floating mesocosm with a gas tight hood enclosed the surface water and the atmosphere above, acted as a headspace collector for gases produced in the water phase beneath. The optical properties of the transparent mesocosm material allowed studying the role of different light quality on biota and gases. The visible light intensity inside the mesocosm was similar to the outside, however UV-radiation was blocked. Three time points with different light conditions were chosen for sampling. The water samples were taken simultaneously, both inside and outside the mesocosm, at the immediate water surface and 20 cm below.

High autotrophic biomass was found in all samples (Chla > 10 mg m^{-3}) with the highest values measured in the surface at the beginning of the experiment. The chlorophyll a concentrations inside the mesocosm were fairly stable over the whole period while the concentrations in the outside samples were decreasing, especially in these from the upper layer. The phytoplankton biomass of all samples was dominated by Litostomataceae ($\sim$60%) and Euglenophyceae ($\sim$30%), followed by Diatomophyceae and Cryptophyceae. For the brown algae inside the mesocosm the photosynthetic yield was stable over the whole period. The lowest yield was observed in the outside surface sample during the highest radiation. The microbial productivity, determined by thymidine- and leucine-incorporation, was relatively constant in all samples. Ten from fourteen analysed brominated, iodinated and chlorinated compounds were detected. The measured concentrations of VHOCs ranged from 0.3 to almost 200 ng L^{-1}. The increase with time, both inside and outside the mesocosm, was seen for brominated and most of the iodinated compounds. Diiodomethane was found only inside the mesocosm at the beginning of the experiment. Slightly higher concentrations were observed in the outside samples. In case of bromoform, which generally had the highest concentrations, the increase in the surface sample during the midday was significantly higher outside than inside the mesocosm. Despite the large differences in bromoform concentration over the time, the δ^{13}C values were stable (-21 - -23 ‰). A different situation was noticed for chloroform. A significant increase in the surface concentrations was observed inside the mesocosm, followed by large changes in the delta values.

The differences in VHOCs behaviour between samples inside and outside of the mesocosm are most likely due to the differences in the radiation exposure. Whether this is caused by direct (e.g. photolysis) or indirect effects (radiation exposure to biota) needs further investigations, which will be carried out during a spring phytoplankton bloom in the coastal Baltic Sea. Nevertheless, these preliminary results show that the experimental set-up can be successfully employed to study VHOCs dynamics at the sea surface.