Phytoplankton communities influence the dissolved organic matter composition of the sea-surface microlayer

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The sea surface microlayer (SML) is the boundary layer at the ocean and atmosphere interface and plays a crucial role in air-sea gas exchange processes and global climate. It is enriched in dissolved organic matter (DOM) compared to the underlying water, but the chemical composition of this material has been insufficiently studied. For improved understanding of the exchange processes it is of utmost importance knowing the molecular composition of the SML. Studying the microlayer is very challenging due to its thinness and strong influence of external forces as wind, UV light and atmospheric deposition on the chemical and microbial composition. The complex and dynamic nature of the microlayer and the enrichment of hydrophobic substances led to the assumption that we find unique chemical composition and distinct compound groups. SML samples of the Indo-Pacific Ocean from R/V Falkor cruise FK161010 (October 2016) were studied with respect to molecular composition of DOM. We analyzed solid-phase extracted DOM with high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). The results were compared to the underlying water (ULW, 1m depth). We found similar molecular DOM composition in the ULW, whereas microlayer extracts were more variable and diverse. This can be related to the influence of changing weather conditions during the cruise on the SML. To reveal molecular changes without interfering external forces, a 5-week indoor mesocosm experiment with induced marine phytoplankton blooms was conducted. A modified solid-phase extraction approach was used to chemically fractionate the microlayer DOM prior to molecular analysis. Our experiment showed that the DOM enrichment in the SML is linked to different phytoplankton communities. In addition, it revealed that depending on the predominant community the DOM concentration can be even depleted in the SML compared to the ULW. Based on the outcome of our field and laboratory studies we conclude that molecular level analysis of surface microlayers is essential to understand the chemical diversity of this highly dynamic boundary layer.