

Foreword to the research front on ‘Fluxes and Chemistry of Marine Biogenic Volatile Organic Compounds’

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Volatile organic compounds (VOCs) emitted from both natural and anthropogenic sources play a significant role in the global carbon budget and the regional ozone formation or destruction in both the troposphere and stratosphere (Carpenter *et al.* 2012; Yu and Li 2021). In addition, they can also serve as an important source of secondary aerosols, further impacting the radiation budget, precipitation and climate. Knowledge of emissions of terrestrial VOCs, and their transformation to aerosols, has advanced considerably over the past few decades, while the role that the ocean plays in the global VOC budget and their controlling processes remain unclear. Seawater contains an extremely complex, diverse and largely unrecognised mix of VOCs, which are directly or indirectly produced by bacteria, phytoplankton and seaweeds, as well as by reactions involving dissolved organic matter (DOM). The most widely known marine biogenic VOCs include dimethyl sulfide (DMS), halocarbons, methane (CH₄), nitrogen-containing gases and non-methane hydrocarbons (NMHCs). These VOCs in the ocean are generally oversaturated relative to the atmosphere; thus the ocean is considered to be a significant net source of atmospheric VOCs.

As the most abundant natural sulfur-containing gas in the atmosphere, research on oceanic DMS had been conducted extensively since the ‘CLAW’ hypothesis was proposed (Charlson *et al.* 1987). Dimethyl sulfide can be oxidised in the atmosphere and form sulfate aerosols, which play the largest role in mitigation of global warming by both scattering solar radiation and altering cloud condensation nuclei (CCN) and albedo (Hoffmann *et al.* 2016). Recent studies have proven that CCN over remote oceans and polar regions are primarily composed of non-sea-salt sulfate (nss-SO₄²⁻) (Quinn *et al.* 2017; Park *et al.* 2021), although the identification of a new reservoir of marine sulfur in the atmosphere may reduce the DMS contribution to aerosol generation (Veres *et al.* 2020). Certain volatile halocarbons (e.g. iodinated halocarbons and several bromoalkanes) released primarily from the ocean may cause ozone depletion by producing atmospheric iodine and bromine radicals (Hossaini *et al.* 2015). Some NMHCs with highly reactive groups (e.g. carbon-carbon double bonds) readily participate in atmospheric chemistry, thus contributing to the formation or destruction of tropospheric ozone and the formation of secondary organic aerosol (SOA, Griffin *et al.* 1999; Claeys *et al.* 2004).

Global measurements show a large range in seawater VOC concentrations, which may be correlated with chlorophyll-*a* in

some cases, and are also affected by various environmental parameters, such as temperature, light intensity and biological activity (Yu and Li 2021). Accordingly, SOAs, formed by oxidation of marine VOCs, exhibit clear spatial and seasonal variations, and dominate aerosol chemical composition in the submicron size range during high biological activity periods. Coral reefs as a source of marine biogenic aerosols is an emerging topic, and DMS can play a significant role in coral ecophysiology (e.g. alleviation of oxidative stress and contribution to ‘thermostat’; Jackson *et al.* 2020). In addition, the impact of ocean acidification on production of marine trace gases may cause potentially large modifications of DMS and nitrous oxide (N₂O) fluxes (Hopkins *et al.* 2020). Quantifying the emissions of CH₄ and N₂O from coastal wetlands is critical in the assessment of natural ‘blue carbon’ sinks (Rosentreter *et al.* 2021).

This research front was proposed to address the limited availability of survey data and knowledge gaps about marine biogenic VOCs, and contains nine original research papers focusing on the production, distribution and emissions of various VOCs in marine environments and their contributions to aerosols and correlations with marine biota. Zhang *et al.* (2021) estimated the DMS sea-to-air flux across the Southern Ocean, south-east Indian Ocean, and north-west Pacific Ocean, and analysed the influence of DMS fluxes on sulfate aerosols. Wu *et al.* (2021) conducted a comprehensive survey of DMS distribution, production and transformation in the East China Sea (ECS) during summer, including the measurements of DMS and dimethylsulfoniopropionate (DMSP) in surface seawater, DMSP in sediment pore water, and nss-SO₄²⁻ and methanesulfonate (MSA) in atmospheric aerosols. The production and microbial consumption rates of DMS are also investigated through incubation experiments. Han *et al.* (2021) conducted laboratory incubation experiments of *Ulva prolifera* to examine the effects of temperature and nutrients on its biogenic sulfur emissions during the decline period. These survey and experimental results provide useful information and improve our understanding of oceanic DMS biogeochemistry and its impact on aerosol properties.

He *et al.* (2021) investigated the concentrations and fluxes of five methyl halides in the Yellow Sea and the ECS. The influence of marine environmental factors on the sources of these volatile halocarbons was also examined. These results help to reasonably assess the ocean contribution of halocarbons and

understand their roles in ozone depletion and global climate change. Liu et al. (2021a) investigated the photochemical generation of bromophenols in the presence of DOM and demonstrated that DOM enhances the photobromination reaction. The result indicates that the bromination process induced by sunlit DOM contributes to the natural sources of organobromine compounds in marine environment.

Li et al. (2021) investigated the horizontal and vertical profiles of 10 NMHCs along with phytoplankton biomass and species in the ECS and examined the roles of phytoplankton assemblages in the occurrence and emissions of NMHCs. This study provides a better understanding of the biogeochemical cycling of NMHCs in marine systems. Liu et al. (2021b) investigated dissolved CH₄, N₂O and other hydrological parameters over tidal cycles in Golden Bay mangrove ecosystem from 2019 to 2021. The survey data has improved our understanding of fluxes of greenhouse gases in mangroves and assessment of 'blue carbon' sinks.

Xu et al. (2021) characterised the concentrations, size distributions and chemical pathways of aerosol aminiums over a coastal city and marginal seas, and estimated the contribution of marine biogenic sources. This study can facilitate our understanding about the interactions between human activities, biogenic emissions and the atmospheric environment. Wang et al. (2021) conducted a time-resolved observational study on the mass concentrations of gaseous and particulate ions to help explore the formation pathways and forms of secondary aerosols in Southern Ocean in summer. The study enriches the background data and illuminates the formation mechanism of secondary aerosols in the Southern Ocean, and provides the theoretical support for understanding global climate change.

Conflicts of interest

The authors declare no conflicts of interest.

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