

## Foreword to the Special Issue on ‘Naturally Produced Organohalogen – Atmosphere and Soil’

The co-evolution of biota and the geochemical environment has resulted in a multitude of complex feedbacks in the Earth's system. The interface between land and marine surfaces and the atmosphere is of utmost importance for the exchange of energy as well as inorganic and organic substances. Climate variability and atmospheric processes, such as transport and deposition of chemicals, are major constraints on both natural and anthropogenic biogeochemical cycles. The deposition of gases and aerosols from the atmosphere can strongly influence the functioning of terrestrial ecosystems. Sometimes gases and aerosols induce productivity, sometimes they act as toxic substances.

Organic compounds containing halogen atoms – especially chlorine – have been considered for a long time to be of industrial origin only, and it was assumed that the production and emission of these compounds could easily be controlled by humans in case they would pose a threat for life on Earth. Recent environmental problems such as stratospheric ozone destruction and the increasing pollution of the biosphere through semi-volatile organohalogen are considered to have a large impact on the well-being of mankind.

Since the mid-1970s it became clear that some reactive organohalogen identified by chemists are purposefully but also unintentionally produced by nature, e.g. in soils and sediments of hyper saline salt lakes. To date almost 5000 different organohalogen are known to be naturally produced by biogeochemical and biochemical processes. In addition to volatile alkyl halides and polar organohalogen such as haloacetates, there is evidence that even semi-volatile organohalogen and halogenated humic substances are naturally formed by abiotic geochemical processes. For instance nature's production of chloromethane (5–6 Mt) exceeds the anthropogenic production (50 Kt) by a factor of 100.

While anthropogenic organohalogen pollution is certainly an important issue and the emissions of some compounds as stipulated in international treaties have to be carefully controlled, it is high time to commence with a comprehensive study of the natural release of organohalogen species, in particular to the lower atmosphere and the terrestrial environment. The importance of very short-lived halogenated substances (VSLs) for the budget for stratospheric bromine was stressed in 2007 by the World Meteorology Organization.<sup>[1]</sup> Many of these VSLs are of natural origin and are comprised in this project.

Increasing greenhouse gas concentrations are expected to enhance the inter-annual variability of summer climate in Europe and other mid-latitude regions such as Central Asia, causing more frequent heat waves. Climate models consistently predict an increase in the variability of summer temperature.<sup>[2]</sup> In some regions climate change will lead in consequence of higher temperature, lower rainfall and higher evaporation to an increase in quantity and scale of hyper saline salt lakes, salty soils and salt/dust storms especially in Central Asia, the Middle East, Northern and Southern Africa and Australia. Climate change in these regions will affect the formation of naturally produced organohalogen tremendously and elevated fluxes to

the atmosphere are conceivable in the 21st century, resulting in additional climate feedbacks and phytotoxic effects.

This Special Issue presents 11 contributions dealing with various aspects of halogenation processes from soil–water–atmosphere interfaces and comprises mainly results from a concerted effort of a research consortium funded by the German Research Foundation (DFG) from 2008 to 2015.

Two review papers will overarch the issue: Comba et al.<sup>[3]</sup> address the formation mechanisms of natural organohalogen with particular attention to recent advances in biomimetic chemistry as well as in radical-based Fenton chemistry. Iron-catalysed oxidation in biotic and abiotic systems converts organic matter in nature to organohalogen. In his review Gribble<sup>[4]</sup> presents the naturally occurring organohalogen compounds discovered in 2014 raising the total number of more than 5000 halogen-containing compounds mainly attributed to a multitude of marine and terrestrial plant and animal sources. Many of these compounds possess extraordinary biological activity, including anticancer, antiviral and antibacterial activity of potential human benefit.

The order of the following papers is inferred from the three environmental compartments involved: soil, atmosphere, and ocean.

The terrestrial compartment section commences with Rücker et al.<sup>[5]</sup> who present results from Western Australian salt lakes. They quantified VOX emissions from an acidic salt lake in biotic and abiotic microcosm experiments under controlled laboratory conditions and revealed that biota is the main driver of halogenation processes. Mulder et al.<sup>[6]</sup> investigated the thermolytic degradation of methylmethionine and its role in DMS and MeCl formation in hypersaline environments. Methyl methionine has been hypothesised to be a precursor of these two atmospheric gases. Additionally, these gases were also released from fluid inclusions of halite crystals after grinding and from hypersaline soil samples after incubation in headspace vials. McRoberts et al.<sup>[7]</sup> studied chloromethane release from biomass by reaction between chloride ion and methoxyl groups of the biopolymers pectin and lignin. The seasonal changes in the chlorine and methoxyl pools observed in leaves of several deciduous tree species have implications for understanding chlorine volatilisation during biomass burning and estimation of the global chloromethane budget.

The atmospheric section comprises observations of reactive halogen substances above the Dead Sea and simulation experiments in the aerosol smog chamber facility at Bayreuth.

The measurements of vertical profiles of BrO, NO<sub>2</sub> and salt aerosols above the Dead Sea by Holla et al.<sup>[8]</sup> indicate efficient vertical transport barriers in the valley, accumulating the air pollution and the salt aerosol by convective inversion layers and leading to BrO levels above 100 ppt. Simulation experiments by Buxmann et al.<sup>[9]</sup> employing DOAS in a large Teflon chamber, demonstrate a quenching of the BrO release from bromide-containing, artificial salt aerosol in the presence of secondary organic aerosol (SOA) from ozonolysis of  $\alpha$ -pinene, catechol

or guaiacol. Accompanying box-model calculations by the MISTRA model quantify the adverse impact of the SOA by adjusting uptake coefficients for BrO on the three types of SOA to the observations. Simulation experiments of the photochemical halogen activation, induced by Fe<sup>III</sup>-doped, artificial salt-aerosol droplets in the same Teflon chamber, were performed by Wittmer et al.<sup>[10]</sup> employing the radical-clock technique for the simultaneous detection of OH radicals and Cl and Br atoms. Photo-Fenton like mechanisms of Fe<sup>III</sup>-Cl complexes are found to induce a noticeable source of atomic Cl, that is catalyzed by the presence of NO<sub>2</sub> and O<sub>3</sub> but slightly inhibited by the presence of SO<sub>2</sub>. Photochemical formation of new particles, observed above salt lakes in Western Australia and related to changes in regional precipitation pattern, has been studied by Kamilli et al.<sup>[11]</sup> in an aerosol simulation chamber with traces of ozonised 1,3-cineol and limonene as particle precursor above a typical salt-lake solution of NaCl, NaBr and Na<sub>2</sub>SO<sub>4</sub> and various traces of FeCl<sub>3</sub> and FeSO<sub>4</sub>. Irradiation, organic precursors and Fenton-like mechanisms turned out to be essential for the formation of ultra-fine particles, which contained organohalogen and organosulphur compounds.

Polyhalomethane formation is the focus of two publications from the marine environment. Bahlmann et al.<sup>[12]</sup> reported  $\delta^{13}\text{C}$ -values of polyhalomethanes released from three brown algae species (*Laminaria digitata*, *Fucus vesiculosus*, *F. serratus*) and one seagrass species (*Zostera noltii*).  $\delta^{13}\text{C}$  values for CHCl<sub>3</sub> and CHI<sub>2</sub>Br from laboratory incubations under variable light and water level conditions showed a systematic effect of the halogen substituents that could empirically be described in terms of linear free energy relationships (LFER) and may be used in future to discriminate between different marine sources. Orlikowska et al.<sup>[13]</sup> investigated the effect of natural levels of UV light on the dynamics of volatile halogenated organic compound formation in mesocosm experiments with ocean water. The experiments showed that natural levels of UV radiation had no significant influence on organohalogen formation. The variable  $\delta^{13}\text{C}$  values of bromoform also indicate that different autotrophic organisms were responsible for its formation in the two investigated coastal environments.

To understand the formation and distribution of natural organohalogens in the environment a broad approach is mandatory. This Special Issue addresses sources, fluxes and transformations of organohalogens in different environmental compartments, mechanisms of halogenation and dehalogenation by abiotic and biotic processes, and assessing the natural contribution to the global halogen burden of the atmosphere.

It has been a great pleasure to edit this Special Issue on the occurrence and significance of naturally produced organohalogens in the environment and we thank all the authors for their excellent contributions to this momentous realm of environmental concern.

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