

Introduction to special issue on natural halocarbons in the atmosphere

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Natural halocarbons are becoming increasingly accepted as important contributors to key atmospheric processes. While CH_3Cl , mainly from natural sources, has long been recognised as providing a significant part (~ 13%) of the chlorine which causes stratospheric O_3 depletion, natural bromine and iodine containing compounds have been more recently acknowledged to also have an important role in destroying tropospheric O_3 and contributing to stratospheric O_3 loss. The increasing role of very short-lived (VSLs) chlorinated compounds, such as CH_2Cl_2 and CHCl_3 , in the stratosphere has been another recent example of the contribution of halocarbons to chemical budgets and reactions in the atmosphere. It has been suggested that a combination of increased halocarbon emissions and projected increases of vertical transport into the tropical stratosphere could lead to increased contributions of such compounds to halogen background levels and thus to ozone depletion (Dessens et al. 2009; Hossaini et al. 2012, 2015; Tegtmeier et al. 2012). However, the evidence base for such predictions is currently limited, with a lack of knowledge of the environmental controls of natural halogen emissions and of the contribution of natural and anthropogenic sources to halogen background levels.

In this issue, eight studies provide new information on source processes and chemistry of atmospheric halogens.

More than 60% of the global CH_3Cl budget is thought to be accounted for by tropical terrestrial sources. Anthropogenic emission strengths are a large uncertainty in the global CH_3Cl budget. Li et al. present a regional estimation of industry-derived CH_3Cl emissions in China and find that global anthropogenic emissions of CH_3Cl , which have not been regulated under the Montreal Protocol (MP) or its successor amendments, have been substantially underestimated. The oceans are a small natural source of CH_3Cl , arising from chemical production, macroalgal emissions, and phytoplankton. Abe et al. find that production rates

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of CH_3Cl from the diatom *P. tricornutum* were dependent on water temperature, and increased as incubation temperature increased from 10 to 25 °C. Berberich et al. measured CH_3Cl , CHCl_3 , and CHBr_3 emissions from red wood ants and suggest a new route to CHCl_3 via this pathway, supplementing other known terrestrial biogenic routes to formation such as termites (Khalil et al. 1990, 1999). A new photochemical route to gaseous Cl is proposed by Wittmar et al. which occurs when HCl converts to Cl on iron-containing aerosol particles at low pH. These experiments indicate that iron-induced Cl formation may be important for highly soluble combustion-aerosol particles in marine environments in the presence of gaseous HCl.

In a study of volatile organic iodine compounds (VOIs) in a Japanese bay, Shimizu et al. find that seasonal peaks in seawater concentrations of CH_3I , $\text{C}_2\text{H}_5\text{I}$, CH_2I_2 , and CH_2ClI have little contribution from macro algal production but are associated with the decay of the diatom spring bloom. The authors show that $\text{C}_2\text{H}_5\text{I}$ production is associated with bacterial degradation of organic matter produced by the bloom, and that CH_2I_2 and CH_2ClI seawater concentrations may be associated, somewhat later in the season, with decay of the diatom spring bloom possibly via reaction of seawater DOM with I_2 . CH_2I_2 and CH_2ClI can be important contributors to tropospheric iodine. Carpenter et al. show that these compounds have strong diurnal cycles both in air and in surface seawater, due predominantly to their fast photolytic destruction in air and seawater. However, the data reveal an additional night-time loss of CH_2I_2 , not currently accounted for in models, and speculate that a reaction with nitrate radical may be an important sink for CH_2I_2 .

In contrast to VOIs, macro algae are a very important source of VSLS bromocarbons. Yokouchi et al. remarkably find that the relative concentrations of CH_2Br_2 and CHBr_3 in clean marine air on a global scale could be characterised by a single chemical decay line. This supports previous suggestions that CH_2Br_2 and CHBr_3 derive from a common process, and that the emission ratios of these compounds vary systematically across the oceans (Carpenter and Liss 2000). Yokouchi et al. also identified widespread bromocarbon sources in Southeast Asia, likely from multiple coastal sources (the region comprises more than ten thousand islands) from warm waters.

Ziska et al. calculate historical and future trends in sea-to-air fluxes of the VSLS CH_2Br_2 , CHBr_3 and CH_3I from 1979 to 2100, using three CMIP5 models. Assuming constant concentration fields in the ocean and atmosphere, i.e. changes induced only via the gas transfer coefficient k_w , increases of 6–8% are predicted to have occurred during 1979–2013, due almost entirely to increases in wind speed. For the time period 2006–2100, the multi-model mean increases for RCP 8.5 were 29%, 23% and 6% for CHBr_3 , CH_2Br_2 , and CH_3I , respectively, due mainly to increases in SST which are predicted to range from 2 to 4 K in all latitudinal bands across all models. The actual influence of future ocean productivity changes on the oceanic halocarbon production rates and concentrations are currently unclear and need to be assessed in follow-up studies.

References

- Carpenter, L.J., Liss, P.S.: On temperate sources of bromoform and other reactive organic bromine gases. *J. Geophys. Res.* **105**, 20539–20547 (2000). doi:[10.1029/2000JD900242](https://doi.org/10.1029/2000JD900242)
- Dessens, O., Zeng, G., Warwick, N., Pyle, J.: Short-lived bromine compounds in the lower stratosphere; impact of climate change on ozone. *Atmos. Sci. Lett.* **10**, 201–206 (2009). doi:[10.1002/asl.236](https://doi.org/10.1002/asl.236)
- Hossaini, R., Chipperfield, M.P., Dhomse, S., Ordonez, C., Saiz-Lopez, A., Abraham, N.L., Archibald, A., Braesicke, P., Telford, P., Warwick, N., Yang, X., Pyle, J.: Modelling future changes to the stratospheric

- source gas injection of biogenic bromocarbons. *Geophys. Res. Lett.* **39**, L20813 (2012). doi:[10.1029/2012GL053401](https://doi.org/10.1029/2012GL053401)
- Hossaini, R., Chipperfield, M.P., Montzka, S.A., Rap, A., Dhomse, S., Feng, W.: Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone. *Nat. Geosci.* **8**, 186–190 (2015). doi:[10.1038/ngeo2363](https://doi.org/10.1038/ngeo2363)
- Khalil, M.A.K., Rasmussen, R.A., French, J.R.J., Holt, J.A.: The influence of termites on atmospheric trace gases: CH₄, CO₂, CHCl₃, N₂O, CO, H₂, and light hydrocarbons. *J. Geophys. Res. Atmos.* **95**, 3619–3634 (1990)
- Khalil, M.A.K., Moore, R.M., Harper, D.B., Lobert, J.M., Erickson, D.J., Koropalov, V., Sturges, W.T., Keene, W.C.: Natural emissions of chlorine-containing gases: reactive chlorine emissions inventory. *J. Geophys. Res.-Atmos.* **104**, 8333–8346 (1999)
- Tegtmeier, S., Krüger, K., Quack, B., Atlas, E.L., Pisso, I., Stohl, A., Yang, X.: Emission and transport of bromocarbons: from the West Pacific ocean into the stratosphere. *Atmos. Chem. Phys.* **12**, 10633–10648 (2012). doi:[10.5194/acp-12-10633-2012](https://doi.org/10.5194/acp-12-10633-2012)