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Interactions and implications of halogens and VOCs on tropospheric oxidant cycles in the remote atmosphere

Eric C. Apel
National Center for Atmospheric Research, Atmospheric Chemistry Division, Boulder, United States of America (apel@ucar.edu)

Reactive halogens have wide-ranging consequences on tropospheric chemistry including ozone destruction, HOx and NOx partitioning, oxidization of volatile organic compounds (VOCs) and initiation of new particle formation. Of particular note and importance, the tropospheric Ox loss due to halogens is estimated to be between 10-20% globally, and up to 50% in some local marine environments. In this work, we include a state-of-the-art coupled halogen and VOCs chemical mechanism into the CAM-Chem global model. Complementing the model development and providing the opportunity to test the model are recent results from the NASA Atmospheric Tomography (ATom) experiment. ATom was conducted with a heavily instrumented NASA DC-8 aircraft over the course of two and a half years, transecting the lengths of the Pacific and Atlantic Oceans during four seasons, constantly profiling from the surface (200 m) to the upper troposphere/lower stratosphere (12000 m). The ATom payload included instruments that measured both inorganic halogens and organic halogen-containing very short-lived substances (VSLS), as well as those that measured additional volatile organic compounds (VOCs), including hydrocarbons and oxygenated VOCs (OVOCs), both of which react with halogens. Modeled BrO is sensitive to the inclusion of reactions between Br and OVOCs, particularly the aldehydes, which rapidly convert Br to HBr, a far less reactive form of Br_y. These reactions can have large implications in the remote troposphere where the ATom measurements have revealed significant emissions and chemical production of low molecular weight aldehydes over the remote marine environment. A version of CAM-chem, updated to include aldehyde emissions from the ocean to close the gap between models and measurements, is used in these analyses. Comparisons between measured and modeled halogen containing species, both organic and inorganic, is presented along with a summary of the implications of our findings on the overall budgets of tropospheric halogens and ozone.