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Halogen cycling and aerosol pH in the Hawaiian marine boundary layer

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Abstract. Halogen species (HCl* (primarily HCl), Cl* (including Cl_2 and HOCl), BrO, total gaseous inorganic Br and size-resolved particulate Cl^- and Br^-) and related chemical and physical parameters were measured in surface air at Oahu, Hawaii during September 1999. Aerosol pH as a function of particle size was inferred from phase partitioning and thermodynamic properties of HCl. Mixing ratios of halogen compounds and aerosol pHs were simulated with a new version of the photochemical box model MOCCA that considers multiple aerosol size bins.

Inferred aerosol pHs ranged from 4.5 to 5.4 (median 5.1, n=22) for super-μm (primarily sea-salt) size fractions and 2.6 to 5.3 (median 4.6) for sub-μm (primarily sulphate) fractions. Inferred daytime pHs tended to be slightly lower than those at night, although daytime median values did not differ statistically from nighttime medians. Simulated pHs for most sea-salt size bins were within the range of inferred values. However, simulated pHs for the largest size fraction in the model were somewhat higher (oscillating around 5.9) due to the rapid turnover rates and relatively larger infusions of sea-salt alkalinity associated with fresh aerosols.

Measured mixing ratios of HCl* ranged from <30 to 250 pmol mol^{-1} and those for Cl* from <6 to 38 pmol mol^{-1}. Simulated HCl and Cl* ($Cl+ClO+HOCl+Cl_2$) mixing ratios ranged between 20 and 70 pmol mol^{-1} and 0.5 and 6 pmol mol^{-1}, respectively. Afternoon HCl* maxima occurred on some days but consistent diel cycles for HCl* and Cl* were not observed. Simulated HCl did vary diurnally, peaking before dusk and reaching a minimum at dawn. While individual components of Cl* varied diurnally in the simulations, their sum did not, consistent with the lack of a diel cycle in observed Cl*.

Mixing ratios of total gaseous inorganic Br varied from <1.5 to 9 pmol mol^{-1} and particulate Br^- deficits varied from 1 to 6 pmol mol^{-1} with values for both tending to be greater during daytime. Simulated Br_t and Br^- mixing ratios and enrichment factors (EFBr) were similar to those observed, with early morning maxima and dusk minima. However, the diel cycles differed in detail among the various simulations. In low-salt simulations, halogen cycling was less intense, Br^- accumulated and Br_t and EFBr increased slowly overnight. In higher-salt simulations with more intense halogen cycling, Br^- and EFBr decreased and Br_t increased rapidly after dusk. Cloud processing, which is not considered in this version of MOCCA, may also affect these diel cycles (von Glasow et al., 2003). Measured BrO was never above detection limit (~2 pmol mol^{-1}) during the experiment, however relative changes in the BrO signal during the 3-hour period ending at 11:00 local time were mostly negative, averaging -0.3 pmol mol^{-1}. Both of these results are consistent with MOCCA simulations of BrO mixing ratios.

Increasing the sea-salt mixing ratio in MOCCA by ~25% (within observed range) led to a decrease in O_3 of ~16%. The chemistry leading to this decrease is complex and is tied to NO_x removal by heterogeneous reactions of $BrNO_3$ and $ClNO_3$. The sink of O_3 due to the catalytic Cl-ClO and Br-BrO cycles was estimated at -1.0 to -1.5 nmol mol^{-1} day^{-1}, a range similar to that due to O_3 photolysis in the MOCCA simulations.

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