HOCl and Cl_2 in the Remote Marine Atmosphere

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The chlorine (Cl) atom may be an important sink for methane, ozone, and non-methane hydrocarbons in the marine atmosphere. However, the processes giving rise to Cl remain poorly understood, and estimates of Cl concentration vary widely. Cl atom concentrations have been inferred using the hydrocarbon clock technique, methane and methane isotope budgets, and gas/aerosol photochemical models. To date, there have been very few measurements of Cl atom precursors in marine air. We measured HOCl and Cl_2 at the Cape Verde Atmospheric Observatory (CVAO) in the remote tropical Atlantic (17 °N, 25 °W) during May-June 2010. HOCl ranged from <10-103 ppt and was primarily present during the daytime. Cl_2 ranged from <1-35 ppt and was primarily present at night. The levels of these Cl atom precursors were elevated in air masses originating over southwestern Europe, and lower in air masses originating over the remote Atlantic. The photolysis rates of HOCl and Cl_2 provide a lower bound on Cl atom production. Based on this estimate for Cl production alone, Cl accounted for up to ~8% of local daily methane destruction during the campaign. However, multiphase photochemical box model simulations show that the total Cl production rate was significantly larger than this estimate. Observed HOCl levels during the campaign were higher than predicted by the model, suggesting the existence of an unidentified mechanism for the production of reactive chlorine in marine air.

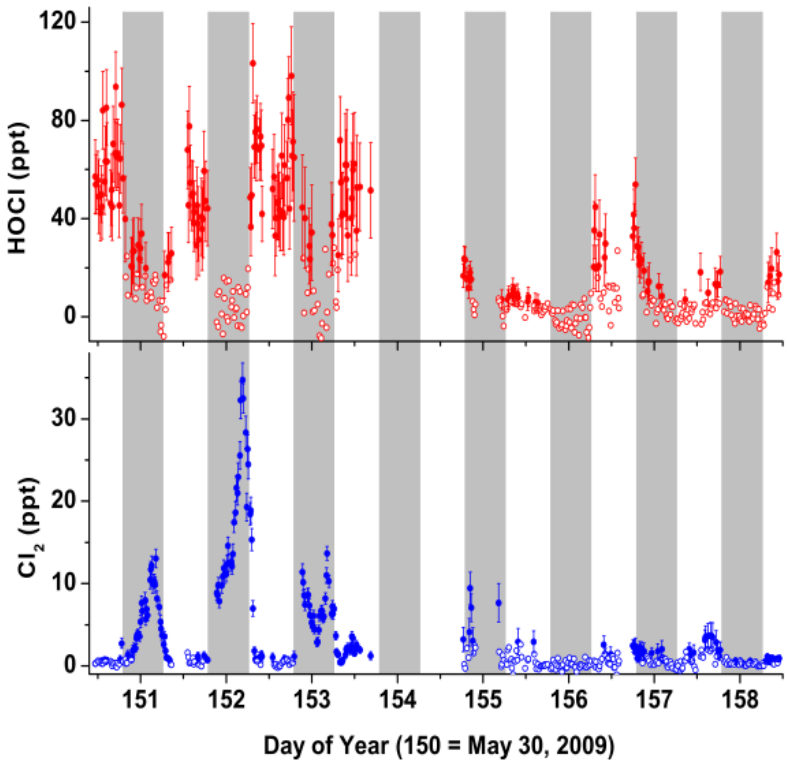

Figure 1. HOCl and Cl_2 mixing ratios at CVAO during May 30 - June 7, 2009. Closed circles are data points above the detection limit, and open circle points are below detection. Gray shading indicates nighttime. Error bars are +/- 1 standard error.