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Agilent J&W HP-PLOT Al_2O_3

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Environmental

Multiannual Observations of Acetone, Methanol, and Acetaldehyde in Remote Tropical Atlantic Air: Implications for Atmospheric OVOC Budgets and Oxidative Capacity

Environmental Science & Technology, **46**, 11028-11039 (2012)
K. A. Read *et al.*

Tags
LOWOX, HP-PLOT Al_2O_3, 6890N GC, environmental, air analysis

Abstract
Oxygenated volatile organic compounds (OVOCs) in the atmosphere are precursors to peroxy acetyl nitrate (PAN), affect the tropospheric ozone budget, and in the remote marine environment represent a significant sink of the hydroxyl radical (OH). The sparse observational database for these compounds, particularly in the tropics, contributes to a high uncertainty in their emissions and atmospheric significance. Here, we show measurements of acetone, methanol, and acetaldehyde in the tropical remote marine boundary layer made between October 2006 and September 2011 at the Cape Verde Atmospheric Observatory (CVAO) (16.85° N, 24.87° W). Mean mixing ratios of acetone, methanol, and acetaldehyde were 546 ± 295 pptv, 742 ± 419 pptv, and 428 ± 190 pptv, respectively, averaged from approximately hourly values over this five-year period. The CAM-Chem global chemical transport model reproduced annual average acetone concentrations well (21% overestimation) but underestimated levels by a factor of 2 in autumn and overestimated concentrations in winter. Annual average concentrations of acetaldehyde were underestimated by a factor of 10, rising to a factor of 40 in summer, and methanol was underestimated on average by a factor of 2, peaking to over a factor of 4 in spring. The model predicted summer minima in acetaldehyde and acetone, which were not apparent in the observations. CAM-Chem was adapted to include a two-way sea–air flux parametrization based on seawater measurements made in the Atlantic Ocean, and the resultant fluxes suggest that the tropical Atlantic region is a net sink for acetone but a net source for methanol and acetaldehyde. Inclusion of the ocean fluxes resulted in good model simulations of monthly averaged methanol levels although still with a 3-fold underestimation in acetaldehyde. Wintertime acetone levels were better simulated, but the observed autumn levels were more severely underestimated than in the standard model. We suggest that the latter may be caused by underestimated terrestrial biogenic African primary and/or secondary OVOC sources by the model. The model underestimation of acetaldehyde concentrations all year round implies a consistent significant missing source, potentially from secondary chemistry of higher alkanes produced biogenically from plants or from the ocean. We estimate that low model bias in OVOC abundances in the remote tropical marine atmosphere may result in up to 8% underestimation of the global methane lifetime due to missing model OH reactivity. Underestimation of acetaldehyde concentrations is responsible for the bulk (~70%) of this missing reactivity.

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