

Nocturnal oxidation of biogenic VOC: new insights from nighttime aircraft measurements

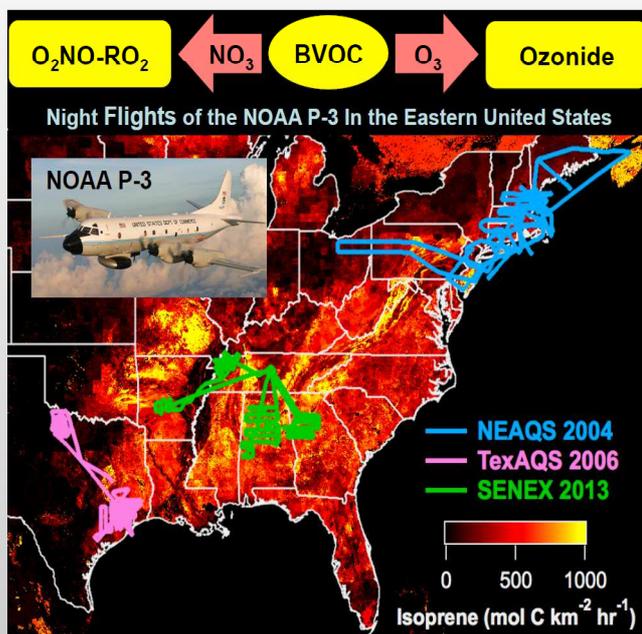
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Biogenic volatile organic compounds, BVOC, represent a significant natural input of chemically reactive species to Earth's atmosphere. They undergo rapid photochemical oxidation via the hydroxyl radical, OH, and much slower oxidation during both day and night through ozonolysis. The presence of air pollution in the form of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) strongly perturbs both the daytime and nighttime oxidation cycles. During daytime, this perturbation occurs through the reaction of peroxy radical intermediates with NO in a well known mechanism that leads to catalytic production of ozone and that may also affect formation of secondary organic aerosol, SOA. At night, the NO_x perturbation occurs through formation of the nitrate radical, NO_3 , which greatly accelerates the rate of nighttime BVOC oxidation in a series of reactions that serve as a large source of both organic nitrates and SOA. The nighttime processes are far more difficult to quantify due to the difficulty of characterizing the interaction of NO_x with BVOC within the stratified nighttime boundary layer structure.



During the past 15 years, the NOAA Chemical Sciences Division has undertaken a program to characterize these nighttime processes through field measurements at ground sites and on tall towers, ships and aircraft. The aircraft measurements represent a unique data set to characterize oxidation processes throughout both the residual layer and the nocturnal boundary layer. This presentation will summarize several key findings from this research program, including an analysis of budgets for isoprene consumption in the residual layer, the potential for nocturnal SOA formation from both isoprene and monoterpene reactions, and an analysis of the transition between NO_x dominated and NO_x limited nighttime chemistry that is taking place as a result of ongoing reductions in U.S. NO_x emissions.