Nighttime Chemistry Affects Daytime Air Quality

What happens to ozone and its precursors overnight?

Ozone pollution has three main ingredients: Nitrogen oxides (or NO_x), hydrocarbons (or volatile organic compounds, VOC) and sunlight. At night, in the absence of the sunlight, there is no ozone production, but dark reactions transform the NO_x-VOC mixture and remove ozone. To what extent does the dark chemistry affect ozone and its key ingredients? The answer depends on reactions of two "nocturnal" nitrogen oxides, NO₃ (the nitrate radical) and N₂O₅ (dinitrogen pentoxide). NO₃ oxidizes VOC at night, while reaction of N₂O₅ with aerosol particles containing water removes NO_x. Both processes remove ozone as well.



NO_x cycles with VOC in sunlight to produce ozone



 NO_x reacts with ozone to give $NO_3 \& N_2O_5$. NO_3 oxidizes VOC, while N_2O_5 reacts with aerosol particles to remove NO_x





What did we do during ICARTT?

•Developed a novel, high-sensitivity detector for NO₃ and N₂O₅ based on state of the art laser spectroscopy. This is the first measurement capability for N₂O₅, and the first *in-situ* (i.e., from a single point) measurement of NO₃.

•Deployed detectors on two mobile platforms during ICARTT: NOAA WP-3D research aircraft and NOAA Research Vessel (R/V) *Ronald H. Brown*.

•Characterized NO_3 and N_2O_5 with high spatial and temporal resolution aloft for the first time. Directly compared air masses aloft to those at the surface at night.

•Tracked NO₃ and N_2O_5 as a function of both VOC and aerosol to understand these important nocturnal processes.

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What did we learn?

• Concentrations of NO₃, a strong oxidant, are much larger aloft than at the surface, and therefore far more effective at oxidizing reactive VOC than previously thought.

• The first direct measurements of the reaction of N_2O_5 with aerosol particles showed surprising variability. The correlation with aerosol composition provides evidence for a previously unrecognized link between aerosol and ozone.

• Nitrogen oxide emissions produce ozone during the day but destroy it at night. Quantification of the nocturnal loss processes has identified the factors that influence this balance, including emissions timing, aerosol, nocturnal VOC reactions and the stability of and mixing within the nighttime atmosphere.

What does it mean?

• Nocturnal processes matter! Nighttime processing of O_3 , NO_X and VOC affects the amount of available O_3 and the potential for its formation 2^{-2} from NO_x and VOC on the following day.

• Large increases in NO_3 concentration aloft compared to the surface (where most previous measurements have occurred) suggest greater nocturnal oxidation capacity.

• The composition of aerosol particles affects N_2O_5 reactions, indicating that previously unrecognized factors, such as sulfur and ammonia emissions, may influence regional O_3 levels.

• Updated air quality models may need to account for this newly understood dark chemistry.

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NO,, VOC

Ozone

Day

Transformed

NO_v, VOC

Ozone

Day

Night

The multi-agency ICARTT <http://www.al.noaa.gov/ICARTT/> was formed to study the sources, sinks, chemical transformations and transport of ozone, aerosols and their precursors to and over the North Atlantic Ocean. ICARTT Fact Sheets are designed to present important new science results and findings of high societal relevance to technical non-experts in the community and have been reviewed by an internal committee of peers.