Geophysical Research Abstracts Vol. 19, EGU2017-16523, 2017 EGU General Assembly 2017 © Author(s) 2017. CC Attribution 3.0 License.



Eddy covariance fluxes of the NO-O₃-NO₂ triad above the forest canopy at the ATTO Site in the Amazon Basin

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Nitrogen monoxide (NO) and nitrogen dioxide (NO₂) (denoted together as NO_x) determine the abundance of the tropospheric oxidants OH, O_3 and NO_3 that regulate atmospheric self-cleaning. The three reactive trace gases NO, NO_2 and O_3 undergo a series of interconnected photochemical reactions and are often referred to as the $NO-O_3-NO_2$ triad.

Ozone deposition is mainly controlled by stomatal uptake, thus contributes to oxidative stress for the plants. Similarly, nitrogen dioxide from above or below the canopy is deposited to leaves through stomatal uptake. NO emissions from soils contribute to above canopy O_3 formation and accelerate OH recycling. Therefore, quantification of the exchange fluxes of these species between the atmosphere and the biosphere are important for atmospheric chemistry and ecosystem research as well.

The eddy covariance method is state of the art for direct measurements of ecosystem fluxes of trace gases. Eddy covariance measurements of NO_x in pristine environments are rare because of lack of availability of instruments with the required precision to resolve concentrations characteristic of these environments.

The Amazon Tall Tower Observatory (ATTO) is located in a pristine rainforest environment in the Amazon basin about 150 km northeast of the city of Manaus. It is the ideal site for studying the biosphere-atmosphere exchange of the NO-O₃-NO₂ triad, being largely undisturbed by anthropogenic sources. During an intensive measurement campaign in November 2015 at the ATTO site, measurements of NO, NO₂ and O₃ were carried out at 42 m above ground level on the 80 m walk-up tower with a fast (5 Hz) and sensitive (< 30 ppt) instrument (CLD790SR2, Eco Physics) for NO and NO₂ and with 10 Hz for O₃ (Enviscope). Additionally, measurements of turbulent and micrometeorological parameters were conducted with a profile of 3-dimensional sonic anemometers and meteorological sensors for temperature, humidity and radiation. Vertical concentration profile measurements of NO, NO₂ and O₃ were available at 8 levels on the INSTANT tower from a reactive trace gas profile system which has been operational at the site since 2012.

From these measurements, we present eddy covariance fluxes of the NO- O_3 -NO₂ triad. We relate the fluxes to the canopy-atmosphere exchange of the trace gases and other scalars using the profile data along the tower. Chemical and turbulent transport timescales of the triad constituents are also presented. Coherent structures and canopy-atmosphere coupling is discussed, particularly in relation to the dynamics of O_3 and its subsequent influence on the NO_x fluxes. As far as we know, these are the first full simultaneous measurements of NO, NO_2 and O_3 fluxes using the eddy covariance method above an Amazonian rainforest.