Eddy covariance fluxes of the NO-O$_3$-NO$_2$ triad above the forest canopy at the ATTO Site in the Amazon Basin

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Nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$) (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-O$_3$-NO$_2$ triad, being largely undisturbed by anthropogenic sources. During an intensive measurement campaign in November 2015 at the ATTO site, measurements of NO, NO$_2$ and O$_3$ 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 NO$_2$ and with 10 Hz for O$_3$ (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, NO$_2$ and O$_3$ 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$_3$-NO$_2$ 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.