Quantifying deposition pathways of Ozone at a rainforest site (ATTO) in the central Amazon basin

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MAX-PLANCK-INSTITUT FÜR CHEMIE

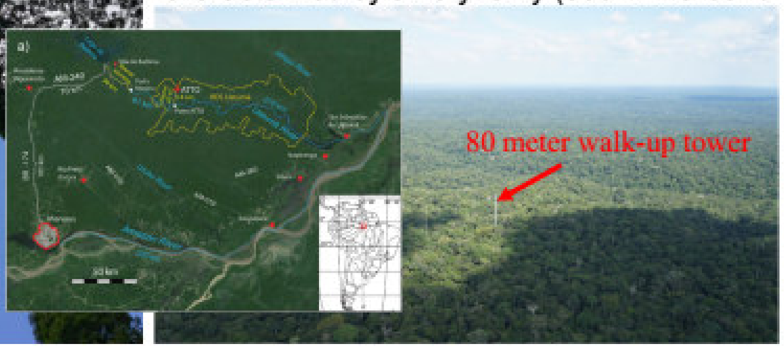
Introduction

- Several recent papers have highlighted the importance of O_3 dry deposition estimates for modelling global O_3, especially over tropical forests. O_3 levels are expected to increase with ongoing deforestation: First, through release of O_3 precursors (NO_x) from biomass burning and secondly by reduced deposition as forest canopies (esp. tropical forest) efficiently remove O_3.
- We present O_3 eddy covariance measurements at four different heights (two above and two within canopy) and quantify the different O_3 deposition pathways (stomatal, gas phase chemistry and surface deposition).

Site

THE ATTO MEASUREMENT SITE SITE

In the Central Amazon Basin, the ATTO (Amazon Tall Tower Observatory) site is located (02°08’38.8”S, 58°59’59.5”W), containing a 325 meter and two 80 meter towers. The site is ideal to perform comprehensive long-term studies regarding forest and atmospheric interaction. The climate is characterized by a very rainy (350 mm around March) and a drier season (ca. 80 mm in September).



During the wet months, the air quality shows almost pristine conditions, contrasted with strong pollution especially due to biomass burning in the drier season. In the north east fetch (prevailing wind direction in the wet season) pristine rain forest extends for hundreds of kilometers.

Fig.1
left: The 325m high ATTO Tower
middle: Location of the ATTO site. The main map shows the access to the site via the road and riverboat connections (background map from Google Earth).
right: View from the top of the ATTO Tower abover the Amazon rainforest

A detailed description of the site is given by Andreae et al., 2015:
https://www.atmos-chem-phys.net/15/10723/2015/

Information about the air masses arriving at ATTO and their seasonality are given by Pöhlker et al. 2019:
https://www.atmos-chem-phys.net/19/8425/2019/

Measurements

- Measurements were carried out at the 80 m walk-up tower.
- 4 levels of O_3 flux measurements: 4, 12, 46 and 81 m.
- 8 levels of profile measurements of O_3, CO_2,H_2O, NO_x: 0.05, 0.5, 4, 12, 24, 38.6, 56, and 79.3 m.

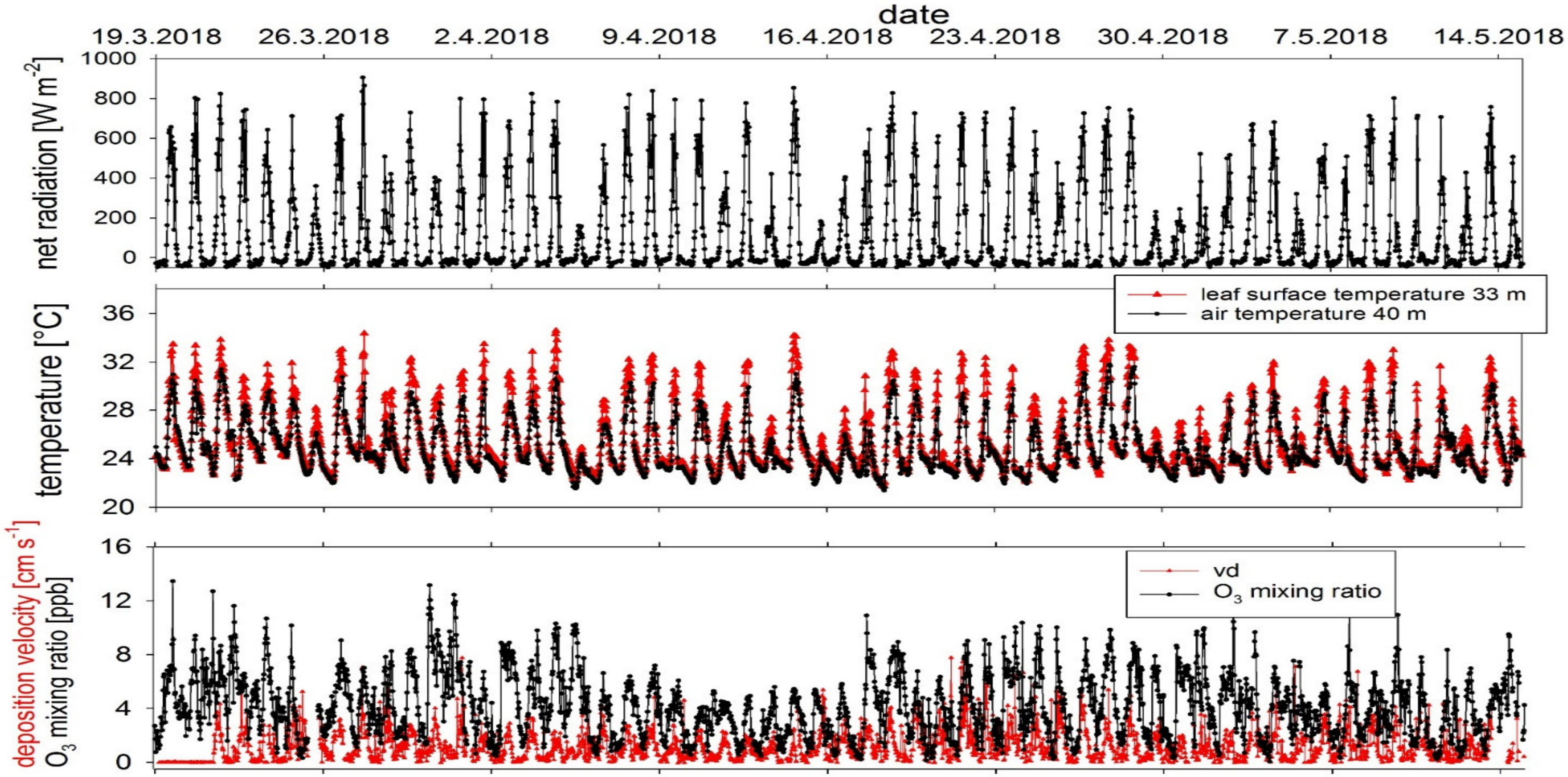
Eddy covariance flux system

- Chemiluminescence-based closed path O_3 analyzers and sonic anemometers both measuring at 10 Hz.

Profile system

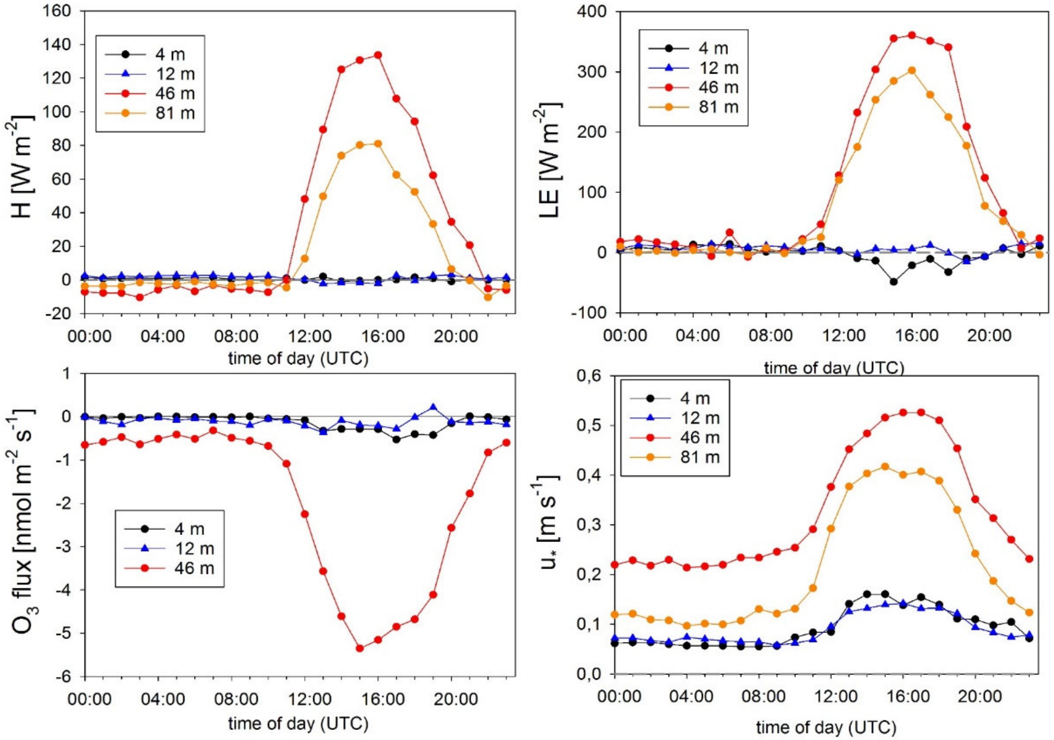
- Valves of the profile system switch every two minutes. The instruments are located within an air conditioned container about 15 m beside the tower. The inlet lines of the three lowermost heights are placed on a near-by tripod to allow undisturbed measurements. The sample air is dried with Nafion.

Overview of measurement period (wet season 2018)



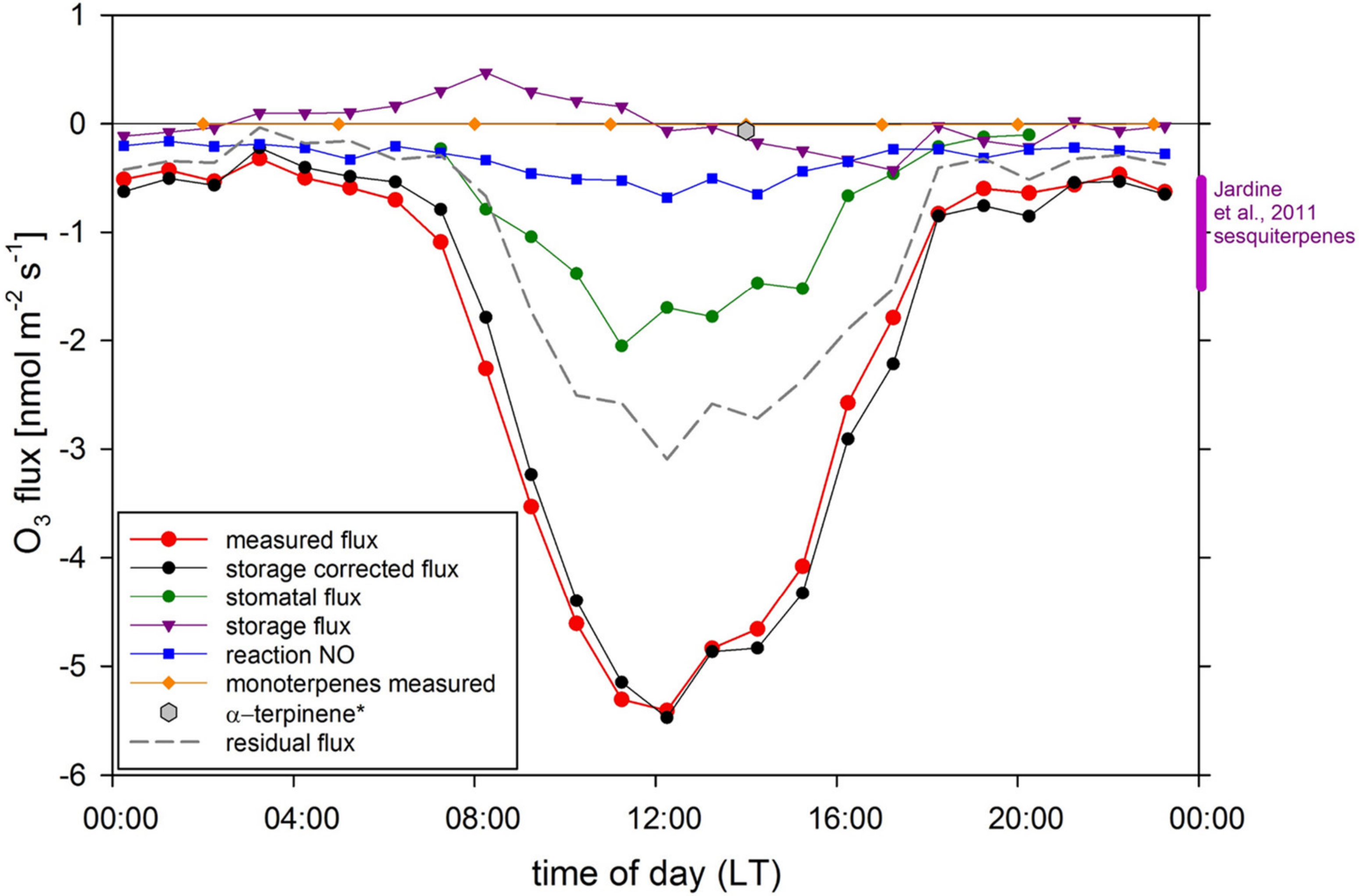
- Ozone mixing ratios are generally very low in the wet season (< 15 ppb for this period).
- There is a period of about 6 days with maximum daytime values between 4 and 6 ppb.
- Deposition velocities are high with maximum values about 8 cm s^{-1}.

Vertical profile of fluxes

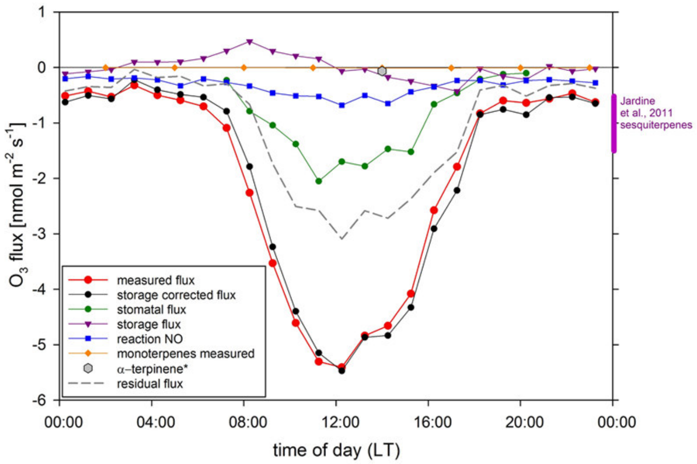


- Soil and understory contribute less than 15 % (mostly less than 5 %) to the above canopy heat flux during daytime (10:00-21:00 UTC).
- Calculating stomatal conductance from the inverted Penman-Monteith method should therefore be justified (>95 % contribution to water vapor flux from canopy).
- They also contribute less than 10 % of the above canopy O_3 flux during daytime (10:00-21:00 UTC).

Partitioning of the total O_3 flux (46 m)



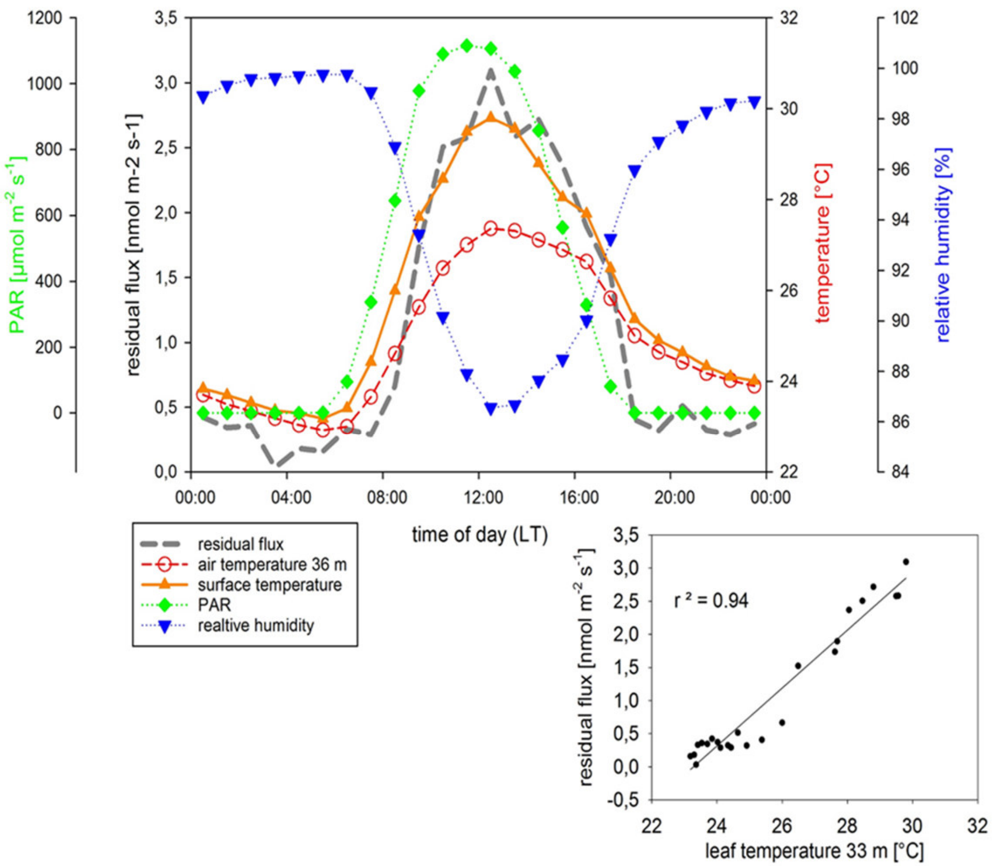
Partitioning of the total flux



- Nonstomatal fluxes are about 50-80 % of the total flux during daytime.
- Storage and reaction with NO contribute less than 10 % each during daytime.
- Measured monoterpenes (α-pinene, β-pinene and limonene) did not contribute significantly.
- α-terpinene, contributing the majority of monoterpene reactivity towards O_3 at ATTO (Yanez-Serrano et al., 2018), is also negligible.
- Sesquiterpenes could explain a large fraction of the flux (Jardine et al., 2011), but concentrations within the canopy at ATTO are not known.

Known sinks contribute about 30 % to 60 % of the O_3 deposition flux. What about the rest?

Potential loss pathways include within canopy chemistry, surface reactions and thermal decomposition (Clifton et al. 2020).

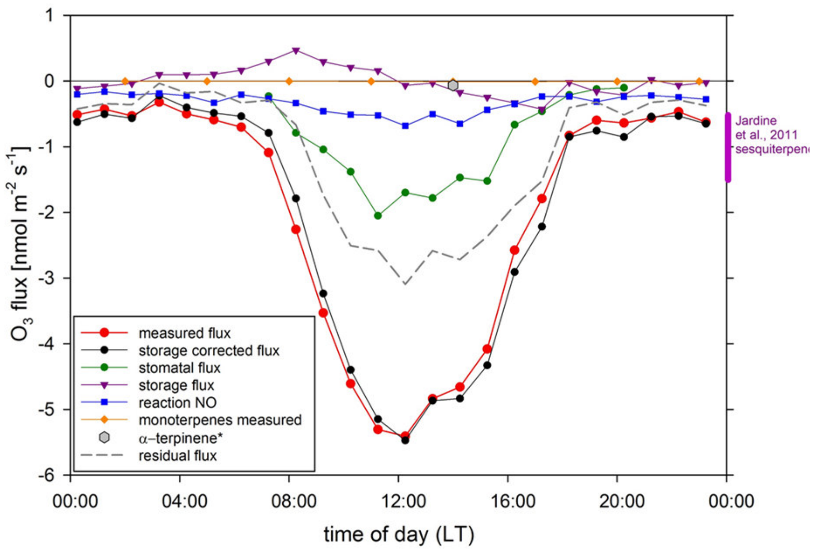


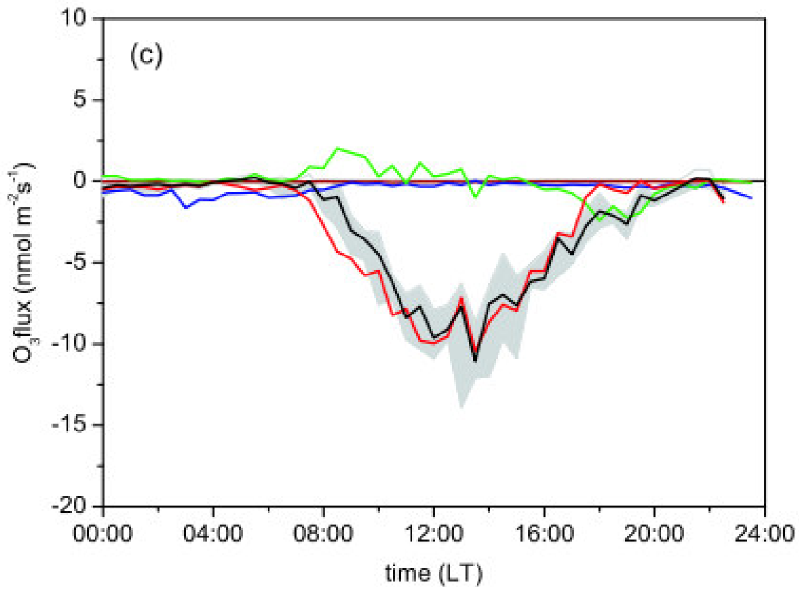
Residual flux correlates best with leaf surface temperature.

Could still be either thermal decomposition or temperature driven VOC emissions.

=> Further analysis should help to disentangle the pathways.

Comparison to Rummel et al. 2007 (rain forest canopy)





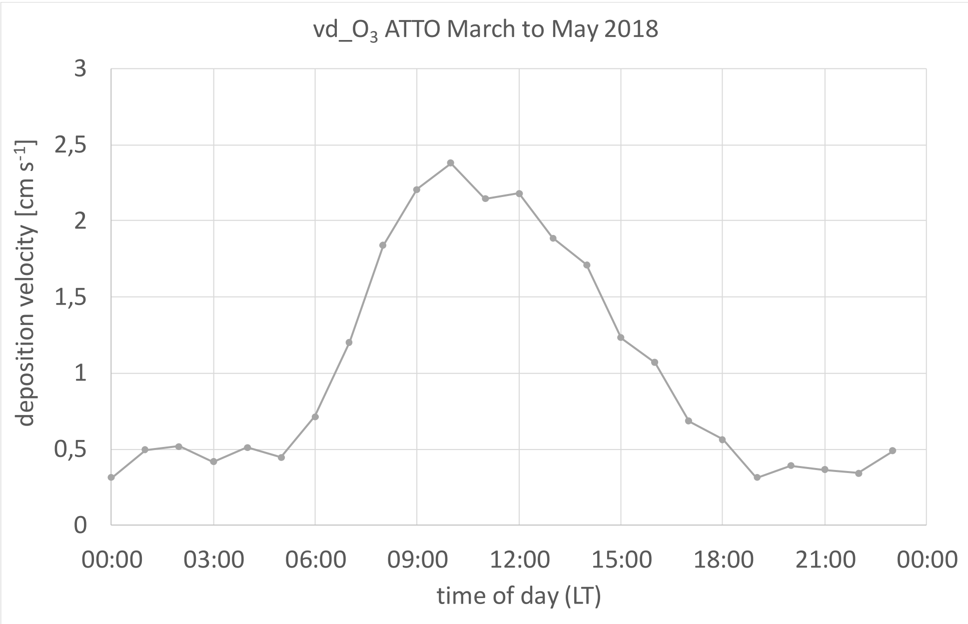
- O_3 fluxes exhibit a similar diurnal cycle and storage fluxes and loss by reaction with NO are of similar magnitude.

- Higher O_3 fluxes in Rondonia are due to higher O_3 values due to more biomass burning in that region.

- Instead the deposition velocities are very similar (see next plot).

Fig. 8 from Rummel et al. 2007:
"Measured O_3 flux (red), O_3 storage within the column 0–53 m (green), net "chemical flux" according to Reactions (R1) to (R3) (blue), O_3 flux at the forest soil surface (brown), and O_3 flux corrected for storage (black with IQR)."
Comments: R1-R3 refer to the cycling of NO_x and O_3. The site was situated in Rondonia which was more severely influenced by biomass burning.

Consistently high deposition velocities above (amazonian) rain forests



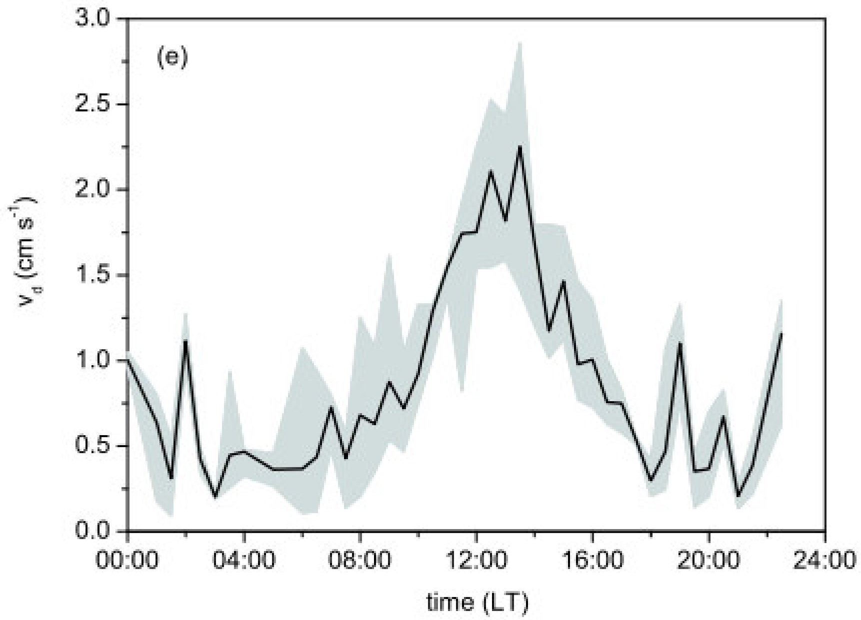


Fig. 8: from Rummel et al., 2007 "O_3 deposition velocity of storage-corrected flux"

Mean peak deposition velocities ~2.3 cm s^{-1} have been observed in the wet season 2018 at ATTO (2018) and in the wet season 1999 (Rummel et al., 2007). The magnitude of values and the diurnal cycle are astonishing similar.

Summary and conclusions

- Measurements above tropical forest reveal high O_3 deposition velocities.
- Only part (~20-50 %) is due to stomatal deposition.
- There is some contribution from storage flux and reaction with NO.
- Reactions with monoterpenes cannot explain missing deposition.
- The residual flux correlates well with the surface temperature.
- Deposition pathways like thermal decomposition or reaction with sesquiterpenes are therefore potential candidates that need to be investigated in more detail.

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Acknowledgement:

This work has been supported by the Max Planck Society (MPG). For the operation of the ATTO site, we acknowledge the support by the German Federal Ministry of Education and Research (BMBF contract nos. 01LB1001A and 01LK1602B) and the Brazilian Ministério da Ciência, Tecnologia e Inovação (MCTI/FINEP contract 01.11.01248.00) as well as the Amazon State University (UEA), FAPEAM, LBA/INPA, and SDS/CEUC/RDS-Uatumã.