Retrievals of peroxyacetyl nitrate (PAN) from FTIR ground-based solar spectra, comparison with GEOS-Chem and satellite data

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Introduction

Peroxyacetyl nitrate (PAN, $CH_3COO_2NO_2$) is the main tropospheric reservoir of NO_x ($NO + NO_2$). PAN is formed when non-methane volatile organic compounds (NMVOCs) oxidation products react with NO_x. Anthropogenic and natural emission sources (fossil fuel combustion, biomass burning, lightning, and response responsible for NMVOC emissions) contribute to PAN formation (Fischer et al., 2014). Its lifetime can reach several months in the upper cold troposphere. This enables the long-range transport of NO_x radicals, under the form of PAN, far from the regions of emission (Tereszchuk et al., 2013; Fischer et al., 2014). The subsequent release of NO_x through the PAN thermal decomposition leads to the efficient formation of tropospheric ozone (O_3), with important consequences for tropospheric oxidative capacity and air quality.

PAN total columns have been retrieved from ground-based high-resolution solar absorption Fourier transform infrared (FTIR) spectra. The developed strategy has been applied to observations recorded at remote FTIR stations of the Network for the Detection of Atmospheric Composition Change (NDACC, visit https://www.ndaccdemo.org/). The resulting datasets are compared with a GEOS-Chem (Goddard Earth Observing System) global chemical transport model (CTM) simulation and with total column time series derived from IASI (Infrared Atmospheric Sounding Interferometer) satellite observations.

Datasets and tools

- **NDACC FTIR observations:** Retrievals of PAN total columns above Jungfraujoch are carried out using SFIT-4 (v0.9.4.4) algorithm implementing the Optimal Estimation Method (OEM) of Rodgers (2000). The retrievals are performed using harmonized layering schemes. 41 layers are defined, with thicknesses increasing progressively from the site altitude (3.58 km) up to 120 km.
- **GEOS-Chem simulation:** This research is supported with an O_3-NO_x-VOC-aerosol standard full chemistry GEOS-Chem global CTM simulation (Bey et al., 2001). We used model version 12.0.2 with MERRA-2 assimilated meteorological fields at $\mathbf{2}^\circ \times \mathbf{2.5}^\circ$ (lat/lon) horizontal resolution and 72 vertical levels, reaching up to 0.01 hPa (approx. 80 km). This version of GEOS-Chem implements the Harvard Emission Component (HEMCO; Keller et al. (2014)) Version 2.1.008 as well as the updates developed and described by Fischer et al. (2014) for the PAN simulation. The simulation extends from 2011 through 2014. The model outputs were saved at a 2-h frequency, and a mass conservative regridding tool (Bader et al., 2017) has been used to interpolate the simulated profiles onto the corresponding SFIT-4 layering scheme.
- **IASI measurements:** IASI is a cross-track Michelson interferometer in the meteorological operation Metop-A, -B, and -C platforms on Sun-synchronous polar orbits, launched in 2006, 2012, and 2018, respectively. It measures the Earth's outgoing radiance in the thermal infrared (IR) spectrum (645-2760 cm^{-1}, with no spectral gaps) and completes a global coverage twice daily, significantly contributing to the monitoring of Earth's atmospheric composition (Clerbaux et al., 2009). The PAN vertical abundances are obtained from the IASI observations by applying v3 of the Artificial Neural Network for IASI (ANNI). The retrieval was applied to each spectrum recorded by IASI/Metop-A (since October 2007) and -B (since March 2013), which represents about 1,300,000 observations per day and per instrument, before prefiltering to scenes with a cloud fraction below 10%. An additional postfilter discards the measurements where the observational sensitivity to PAN is too low to produce a meaningful column.

Poster presented at the IGC10 conference
06-10 June 2022
WashU (St. Louis)

Poster

Reference article (Mahieu et al., 2021)

PAN above Jungfraujoch - comparison with GEOS-Chem

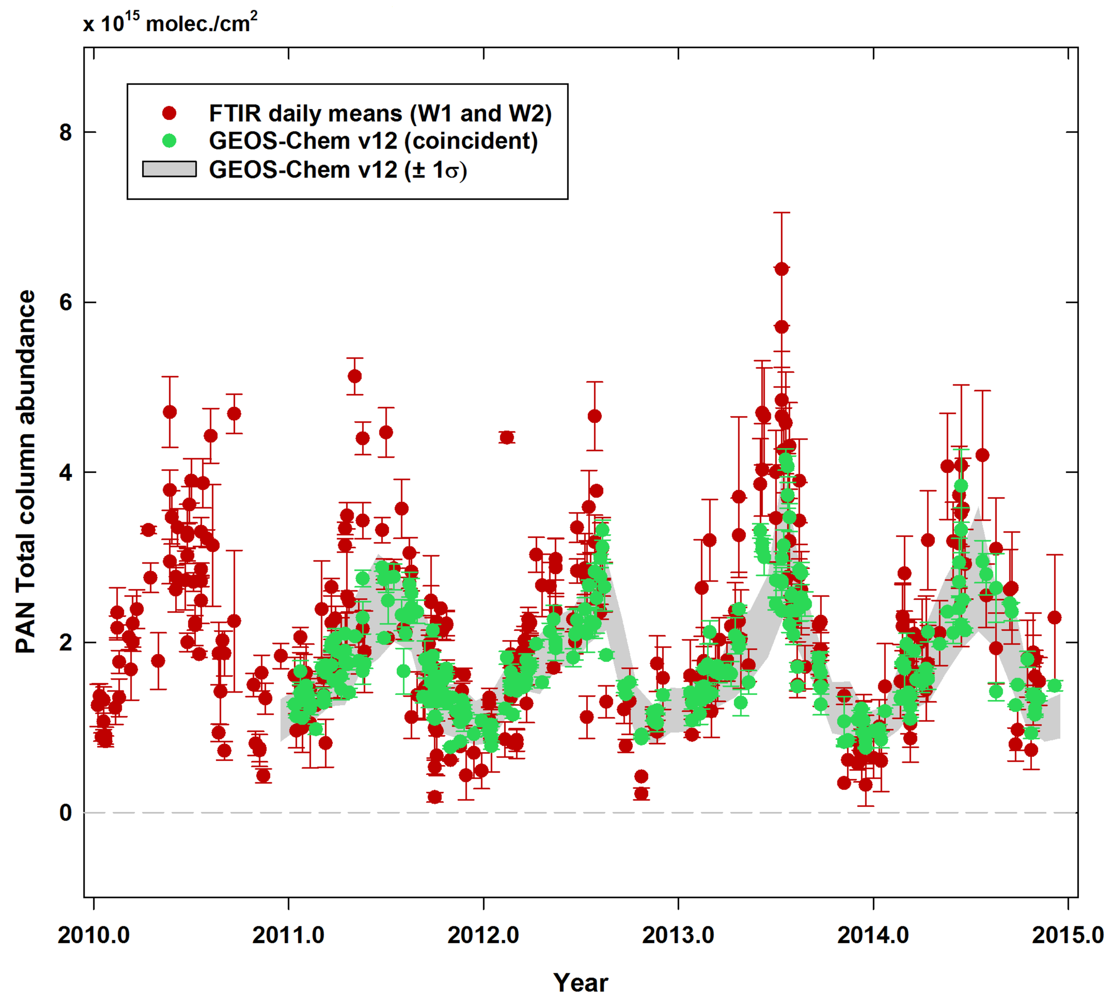

Figure 1: Observed and modeled daily mean total column time series of PAN for the Jungfraujoch station. The modeled time series shows a strong correlation with the observations. The phase of the seasonal modulation is well represented while the amplitude is generally lower, because on the one hand, the low NDJF columns appeared overestimated by the simulation. On the other hand, the peak column values are not captured by the model. From Mahieu et al. (2021).

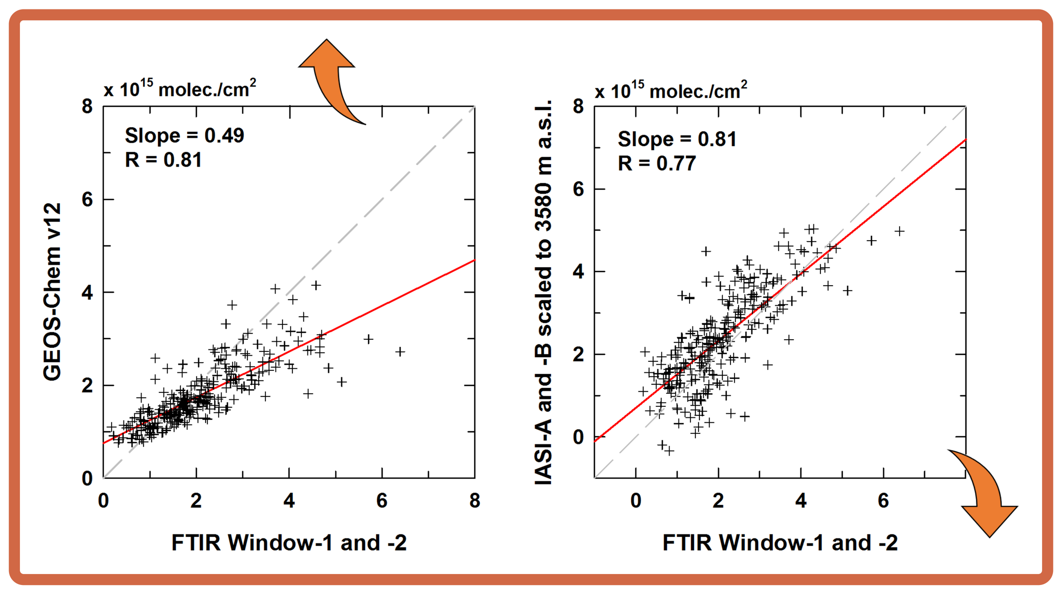

Figure 2: Evaluation of the consistency between the FTIR (W1 and W2 combined) and GEOS-Chem (left) and IASI (right) data. in the case of the FTIR - GEOS-Chem comparaison, a deviation for the extrema, especially for the high values, is shown. The agreement between the scaled satellite columns and the ground-based data gives credit to the scaling method adopted for the IASI columns. From Mahieu et al. (2021).

PAN above Jungfraujoch - comparison with IASI-A and -B

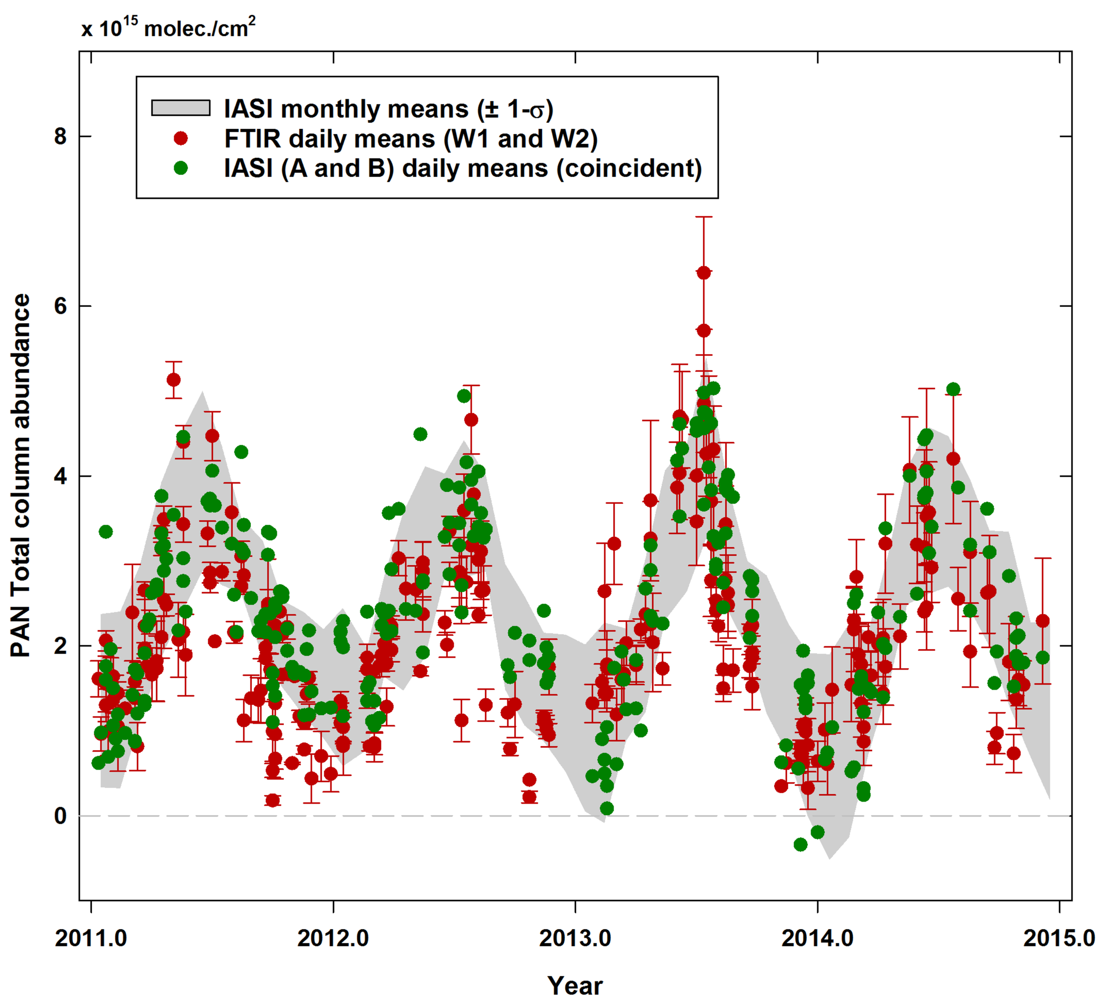

Figure 3: Comparison between IASI and ground-based FTIR total columns above the Jungfraujoch station. IASI observations were taken within 100 km from the Jungfraujoch. The mean altitude of the IASI pixels around Jungfraujoch is 1,352 m a.s.l., more than 2 km below the station altitude. Thus, we used GEOS-Chem simulation as a transfer standard and then scale the IASI columns to the station altitude. From Mahieu et al. (2021).

Long-term trend analysis

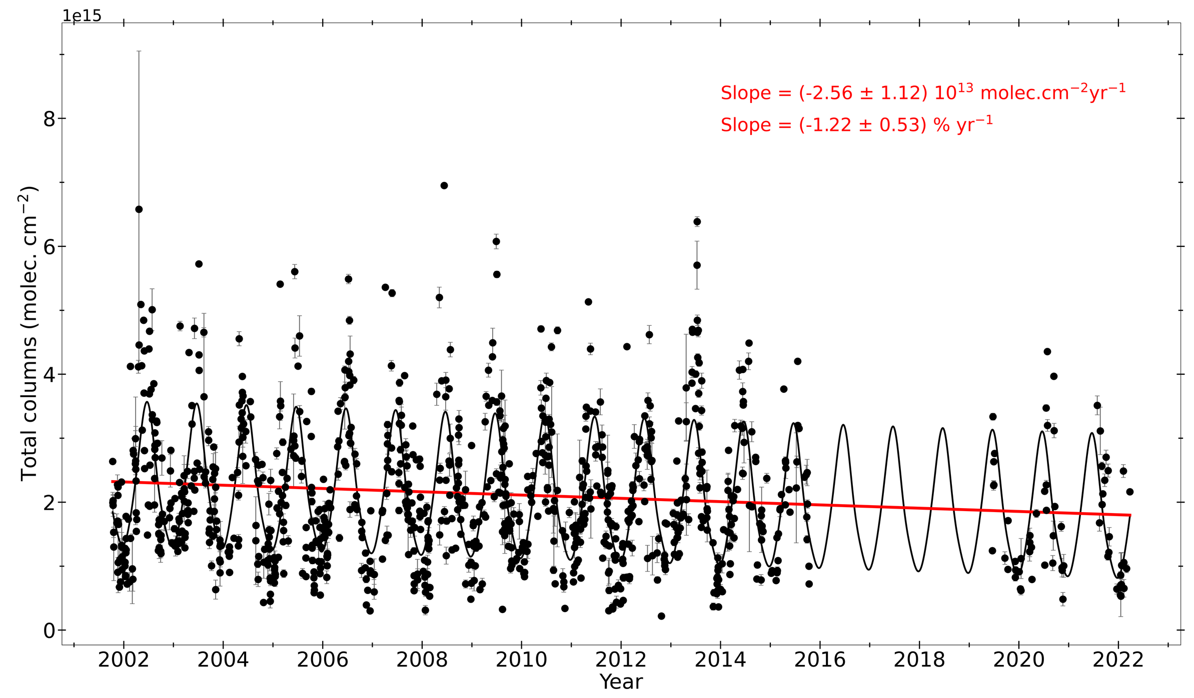

Figure 4: PAN total columns above Jungfraujoch from October 2001 to March 2022. W1 and W2 combined. The agreement between W1 and W2 was lost for few years due to the change of the instrumental setup. This period (October 2015 - June 2019) has been removed.

Conclusions and prospects

- Absorption features are broad, unstructured, and weak, forcing the setup and definition of wide windows for the proper retrieval of PAN. Total columns characterize essentially the troposphere.
- PAN significant seasonal modulation: minimum in winter and maximum in summer.
- Total column time series characterized by significant seasonal modulations and ranges of magnitude consistent with IASI observations and a global GEOS-Chem simulation.
- Some underestimation of the PAN burden by the model.
- Prospects for the production of global multidecadal time series of PAN.

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Acknowledgments

The University of Liège team has been primarily supported by the Fonds de la Recherche Scientifique (F.R.S.-F.N.R.S., Brussels, Belgium; grants J.0147.18 and J.0126.21) and by the GAW-CH program of MeteoSwiss (Zürichm Switzerland). E. Mahieu is a senior research associate with the F.R.S.-F.N.R.S.
The MERRA-2 meteorological data products used for driving the GEOS-Chem simulation have been provided by the Global Modeling and Assimilation Office at NASA Goddard Space Flight Center.

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