



# Proceeding Paper Sentinel-5P/TROPOspheric Monitoring Instrument CH<sub>4</sub> and CO Total Column Validation over the Thessaloniki Collaborative Carbon Column Observing Network Site, Greece<sup>†</sup>

Marios Mermigkas <sup>1,\*</sup>, Chrysanthi Topaloglou <sup>1</sup>, Maria-Elissavet Koukouli <sup>1</sup>, Dimitrios Balis <sup>1</sup>, Frank Hase <sup>2</sup>, Darko Dubravica <sup>2</sup>, Tobias Borsdorff <sup>3</sup> and Alba Lorente <sup>3</sup>

- <sup>1</sup> Laboratory of Atmospheric Physics, Department of Physics, Aristotle University of Thessaloniki, Campus Box 149, 54124 Thessaloniki, Greece; chtopal@auth.gr (C.T.); mariliza@auth.gr (M.-E.K.); balis@auth.gr (D.B.)
- <sup>2</sup> Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research (IMK-ASF), P.O. Box 3640, D-76021 Karlsruhe, Germany; frank.hase@kit.edu (F.H.); darko.dubravica@kit.edu (D.D.)
- <sup>3</sup> SRON Netherlands Institute for Space Research, Niels Bohrweg 4, 2333 CA Leiden, The Netherlands; t.borsdorff@sron.nl (T.B.); a.lorente.delgado@sron.nl (A.L.)
- Correspondence: mmermigk@physics.auth.gr; Tel.: +30-6973889219
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Abstract: Carbon monoxide, XCO, and methane, XCH<sub>4</sub>, column-averaged dry-air mole fractions (DMFs), observed by the TROPOspheric Monitoring Instrument (TROPOMI) on board Sentinel-5P (S-5P), are validated against those obtained from a Bruker ground-based low-resolution Fourier transform spectrometer, EM27/SUN, operating in the framework and according to requirements of the Collaborative Carbon Column Observing Network (COCCON), in Thessaloniki, Greece, on a mid-latitude urban site. The current operational S5P/TROPOMI observations show very good agreement with the respective FTIR measurements and capture both their seasonal variability and pollution episodes. XCO reported the highest concentrations during the fire episodes in summer 2021, when its daily mean value reached a maximum of  $0.134 \pm 0.015$  ppm. XCH<sub>4</sub> shows a slight annual increase of 0.02 ppm, with the highest concentrations during early 2022 (approximately 1.92 ppm). The satellite  $CH_4$  and CO products have been recently reprocessed with updated  $CH_4$ , CO and H<sub>2</sub>O cross-sections, among other improvements, bringing noticeable changes in the pre-existing biases of S5P products against the FTIR ground-based data. We report that, for this mid-latitude station, mean biases and standard deviations fall well within mission requirements for XCH<sub>4</sub> and XCO ( $-0.01 \pm 0.6\%$  and  $0.62 \pm 4.2\%$  for XCH<sub>4</sub> and XCO, respectively), underlying the significance of satellite measurements as a valuable supplement to ground-based data for the purpose of greenhouse gas monitoring. The results presented in this work for the Thessaloniki FTIR instrument are in strong agreement with FTIR locations in the middle latitudes.

**Keywords:** FTIR; EM27/SUN; COCCON; Thessaloniki; KIT; global warming; TROPOMI; XCH<sub>4</sub>; XCO; greenhouse gases

# 1. Introduction

Climate change and global warming effects are mainly driven by the on-going increase in the abundances of greenhouse gases in the Earth's atmosphere, in both the Southern and Northern Hemisphere, where they are measured using different measurement techniques [1]. Approximately 16% of the total radiative forcing affect can be attributed to methane [2], with a lifetime of over a decade in the atmosphere and a GWP between 28 and 36 over 100 years. Throughout the industrial era,  $CH_4$  has shown an increase in its



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). global annual average of 2.5 times, from 720 ppb to 1800 ppb [3], surpassing that of  $CO_2$ . Carbon monoxide (CO), while not a greenhouse gas itself, strongly affects tropospheric chemistry by removing OH radicals and thus interfering with the oxidation capacity of the atmosphere. Accurately measuring the abundances of these gases as well as studying their variations (spatial and temporal), facilitates the study of their sink/source balance and emission levels and enables the design of the appropriate polices in order to address the global warming mitigation issue.

In addition to the more traditional ground-based network monitoring [4,5], the TROPOMI instrument, on the S5P platform, provides space-borne data of DMFs of the greenhouse gases of interest.

## 2. Methodology

Daily values of reprocessed homogenized TROPOMI CO and CH<sub>4</sub> L2 data were corrected in OFFL, version 02.04.00 (via Copernicus Open Data Access Hub (https://s5 phub.copernicus.eu/, accessed on 2 May 2023). Implementation of the processor update (v. 02.02.00, 1 July 2021) introduces a different type of spectroscopy and changes in the overall biases and can explain the decrease in XCH<sub>4</sub> and XCO bias [6]. A quality assurance filter of 1.0 was implemented for both datasets to ensure cloud-free observations. Validation of these data is provided by both quarterly validation reports [6] by the Mission Performance Center Validation Analysis Facility (http://mpc-vdaf.tropomi.eu/, accessed on 2 May 2023) and recent papers on TROPOMI data validation [7,8].

In this work, CO and CH<sub>4</sub> dry-air column mixing ratios, provided by the EM27/SUN FTIR instrument, were collocated within an hour with respective TROPOMI data from Thessaloniki's overpass, within a radius of 100 km for CH<sub>4</sub> and 50 km for CO.

The OFFL TROPOMI corrected products were used in this study [7,9,10].

#### 3. Results

In the following section, the comparison between the methane and carbon monoxide total columns from EM27/SUN ground-based measurements and space-borne TROPOMI data is presented. Daily means of both FTIR and TROPOMI dry-air column mixing ratios are presented (Figure 1) for clear/partially clouded sky conditions for XCH<sub>4</sub> (a) and XCO (b). Also, in Figure 2, the relative mean bias of XCH<sub>4</sub> (a) and XCO (b) for the standard (green line) and corrected (orange line) products are compared. TROPOMI observations capture the time series of FTIR measurements for both products, and in the case of XCO, this peaks during summer 2021 as a consequence of fire episodes.

Furthermore, in Figure 3, the relative bias is shown (for both XCH<sub>4</sub> and XCO) correlated to the distance of S-5P pixels from the FTIR station, which is located in the city center. XCH<sub>4</sub> reveals a decrease in relative bias when the distance from the FTIR station increases (Figure 3a). The relative bias of XCO follows almost the same pattern as XCH<sub>4</sub> with the distance. However, some outliers during summer 2021 indicate the long-distance transport of XCO due to the large fires that occurred in Athens and North Evia at this time. TROPOMI captures these fire episodes at a long distance away from the city center of Thessaloniki, around 35–50 km (Figure 3b).

The relative mean biases of TROPOMI XCH<sub>4</sub> and XCO against FTIR measurements were calculated and are presented in Table 1 together with total averaged values of S-5P products.

Good agreement was found between the Thessaloniki COCCON site and respective measurements of other FTIR stations at mid latitudes, such as those of NDACC in Bremen, Karlsruhe, Zugspitze or Garmisch. For methane, Bremen's relative mean bias (for a biascorrected product) is  $0.12 \pm 1.5\%$ , where as the Zugspitze and Garmisch biases reach  $-0.22 \pm 1.07\%$ , and  $-0.01 \pm 0.83\%$ , respectively [6]. An annual increase, though small, is observed for methane concentrations for all sites. The mean relative bias in the case of XCO for the NDACC stations in mid-latitude areas is found to fall well within the mission requirements, with a good agreement with our site. In particular, the de-striped mean

relative bias of Bremen, Zugspitze and Garmisch is  $0.84 \pm 5.64\%$ ,  $-0.32 \pm 7.74\%$  and  $6.42 \pm 9.09\%$ , respectively. It should be noted that the bias of NDACC vs. S5P comparison uses a wider time collocation window of 3 h (vs. 1 h in this work).

**Table 1.** Relative mean biases of TROPOMI XCH<sub>4</sub> and XCO against FTIR measurements and total mean values of S-5P products.

X-Gas	<b>Relative Mean Bias (%)</b>	S-5P Mean (ppm)
XCH <sub>4</sub>	$-0.01\pm0.6$	$1.87\pm0.01$
XCO	$+0.62\pm4.2$	$0.09\pm0.01$



**Figure 1.** Daily mean of dry-air column mixing ratios measured by TROPOMI (dark red) and FTIR (blue) under clear-sky and cloudy atmospheric conditions, with associated spatiotemporal standard deviation. (a) XCH<sub>4</sub>, (b) XCO.



**Figure 2.** Relative mean bias of collocated TROPOMI column-averaged dry-air mole fractions of methane (XCH<sub>4</sub>) and carbon monoxide (XCO) compared to EM27 FTIR ground measurements in Thessaloniki from January 2019 until June 2022. Both standard products and corrected products are shown in the above figures. (a) XCH<sub>4</sub>, (b) XCO.



**Figure 3.** Relative mean bias vs. distance of collocated TROPOMI column-averaged dry-air mole fractions of methane (XCH<sub>4</sub>) and carbon monoxide (XCO) compared to EM27 FTIR ground measurements in Thessaloniki from January 2019 until June 2022. The color bar indicates the date–time index in both figures. (a)  $XCH_4$ , (b) XCO.

## 4. Conclusions

The TROPOspheric Monitoring Instrument (TROPOMI) captures the temporal XCH<sub>4</sub> variability, both the seasonal cycle and the summer increase. Both datasets report a slight annual increase, and the total averaged values of TROPOMI and FTIR measurements are  $1.878 \pm 0.018$  ppm and  $1.879 \pm 0.015$  ppm, respectively. The bias-corrected product (albedo correction) provided by the new algorithm [6] improves the correlation between the satellite and the ground-based FTIR instrument (Figure 2a). We observe the lowest bias (September 2020) in long-distant orbits far from the location of Thessaloniki's FTIR station, around 75–80 km (Figure 3a).

Regarding XCO column observations, both ground-based and satellite measurements capture the short-scale carbon monoxide temporal variations. Higher XCO is observed for spring and winter (attributed to incomplete fossil fuel combustion and industry), while the highest values of FTIR measurements, representing the fire episodes during summer 2021 in Greece (fire episodes in a suburban forest area in Thessaloniki and air mass transport from Athens and North Evia), are also captured by TROPOMI observations with values over 0.135 ppm. The total averaged values of TROPOMI and FTIR measurements are 0.093  $\pm$  0.01 ppm and 0.092  $\pm$  0.008 ppm, respectively. The new algorithm improves the bias between the satellite and the FTIR spectrometer, and we observe a small decrease between the relative bias and the distance in the case of XCO (Figure 3b).

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Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

**Data Availability Statement:** The EM27/SUN FTIR spectrometer data from Thessaloniki, Greece, are available upon request (mmermigk@physics.auth.gr and darko.dubravica@kit.edu). The S5P/TROPOMI observations are publicly available from the Copernicus Open Access Hub (https://scihub.copernicus. eu/, ESA, 2021, accessed on 22 March 2023).

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