To Referee #2

We are grateful to you for your interest and comments on this manuscript.

Please find the point-by-point answers to your comments in green.

Please note that the present version of this manuscript reports mixing ratios in ppt and no longer in ppb to show the significant decimal digits.

Please note that, following the referee's comments, we have reformulated/refined the statistical analysis described in Section 2.3, updated the results and discussion accordingly, and have finally merged Section 3.1 with Section 3.2 (now Section 3.1).

General Comments:

The manuscript presents a comprehensive long-term analysis of atmospheric propane at the Monte Cimone WMO-GAW station, based on an impressive 2011–2023 dataset that is also publicly available. The authors deserve congratulations for their sustained monitoring efforts and for making the data accessible to the scientific community. However, I agree with the second reviewer that the manuscript sometimes reads like a "measurements report" rather than a cohesive scientific analysis. The links between sections are often missing, which gives the impression of a series of independent analyses rather than a unified study. Below, I suggest ways to strengthen the narrative and improve the scientific rigor of the paper.

Major Comments:

1. Linking sections 3.1 and 3.2: seasonal trends and long-term trends

The authors mention an increase in the amplitude of the seasonal cycle (Section 3.2). To deepen the analysis, it would be valuable to disaggregate the long-term trend (Section 3.1) by season. Is the increase in amplitude due to higher winter concentrations or lower summer concentrations?

Suggestion: Perform a seasonal trend analysis and discuss how it relates to the findings in Section 3.2. This would provide insight into whether the observed changes are driven by emission variations, meteorological factors, or chemical processes (e.g., OH variability).

Following your suggestion and the questions raised by reviewer#3, we refined the statistical analysis to derive the trend parameters by using daily means mixing ratios instead of raw data to better match the skills of the CCGCRV model developed by NOAA. Moreover, we conducted a sensitivity test running a Monte-Carlo bootstrap data selection. The description of methods was updated in Section 2.3. Finally, the description and the discussion of the results have been merged in a single section (i.e., Section 3.1, present version of the manuscript). Figure 4 was revised by showing trend lines of C_3H_8 seasonal amplitudes and yearly peaks and troughs.

2. Contextualizing trends (2018–2020 and 2021–2023) with extreme values (Section 3.5)

The trends discussed in Section 3.1 (2018–2020 and 2021–2023) should be analyzed in the context of the numerous extreme values reported in 2018 and 2023 (Section 3.5). Could these extreme values be skewing the trends? A discussion on the robustness of the trends in light of these extremes would strengthen the analysis.

Thank you for pointing this out.

As a result of the revised statistical analysis, the two trends previously identified are now less "evident", leading to a slightly different discussion of results. We removed the comments on short term variation of C3H8 on the trend curve between 2018 and 2023.

To better explain the statistical analysis performed, we added to Section 2.3 the following: "The seasonal cycle and trend calculations were done on bootstrap-resampled subsets consisting of 90% of the dataset for 50 iterations."

"The long term trend, the trends on the long-term trend curve (Section 3.1), and trend of seasonal amplitudes (Fig. 4) are estimated with the Theil-sein regression (scikit-learn Python package (Pedregosa et al., 2011)) and Mann-Kendall (pyMannKendall Python package (Hussain and Mahmud, 2019)) testing for significance."

3. COVID-19 impact analysis: accounting for meteorological variability

The analysis of COVID-19 impacts lacks a discussion of meteorological influences (e.g., Petit et al., 2021). Changes in air mass origin or meteorological conditions (e.g., PBL height, wind patterns) could have influenced propane concentrations independently of emission changes.
Suggestion: Include a comparative analysis of meteorological conditions across years (e.g., using ERA5 reanalysis data or backward trajectories for multiple years). The 2022 trajectory analysis is interesting but insufficient for drawing conclusions about interannual variability.

Thank you for pointing this out.

This topic was deeply investigated in our previous paper on anomaly during COVID period, with the conclusion that "The analysis of local wind speed patterns, specific humidity and O_3 monthly diel cycles did not indicate substantial changes in the vertical transport associated with the thermal circulation system in the area. The low O_3 values that characterized MAM and JJA 2020 cannot be attributed to differences in the synoptic-scale circulation compared with the previous five years. "

We added the following to Section 3.4:

"Cristofanelli et al. 2021 observed no substantial variations in the synoptic-scale circulation and vertical transport related to the thermal circulation system at CMN in summer 2020 compared to the previous five years."

4. Potential OH Bias in the Inversion (Section 3.6)

The inversion results (Section 3.6) may be sensitive to the OH concentrations used. Could a potential overestimation of OH lead to an underestimation of propane emissions?

Suggestion: Discuss the uncertainties in OH concentrations and whether there is a seasonal bias in the OH fields used. If possible, perform a sensitivity analysis to assess how variations in OH impact the inversion results.

Thank you for your suggestions on the OH bias.

We performed a sensitivity inversion excluding the OH loss term completely. Posterior emissions were reduced to less than half of the reference values (Figure D1 included in the appendix), demonstrating the significant influence of OH chemical loss on the emission estimates. Regarding the concern about OH overestimation leading to emission underestimation, we would like to note that the opposite relationship holds: an overestimation of OH would require the inversion to increase emissions to compensate for excessive simulated loss. The sensitivity analysis confirms that our inversion framework responds appropriately to changes in the chemical loss term. While OH fields are subject to uncertainties of approximately 10–20% (Naik et al., 2013; Wolfe et al., 2019) in current chemical transport models (GEOS-CHEM considered in our study), any systematic bias in OH would propagate linearly into the emission estimates.

5. Methods section: clarifications needed

- Quality Control (QC) Procedures

The QC procedure for propane measurements is not detailed. To ensure confidence in the trend analysis, the authors should provide:

- A table summarizing blank and standard measurements over time.
- Relative standard deviations for standards.
- Any observed instrumental drift and how it was corrected.

Details on the analytical protocol are illustrated in LoVullo et al. 2016. We rephrased and expanded the text in Section 2.1 to include the relevant information:

"The time frame of this study covered the period from January 2011 to December 2023. In situ online measurements were performed at the World Meteorological Organization's

Global Atmosphere Watch (WMO/GAW) global station on CMN (44°12′N, 10°42′ E, 2165 m above sea level). Monitoring of non-methane volatile organic compounds (NMVOC) performed at CMN station is generally representative of emissions occurring in the European continent as reported by Lo Vullo et al. (2016). Measurements of C3H8 were performed with a gas chromatograph-mass spectrometer (GC–MS Agilent 6820 + Agilent 5975C) operating in Selected Ion Monitoring (SIM) mode, preceded by an online sample enrichment using a preconcentration system Unity-2-AirServer-2 (Markes International), following a method described in Maione et al. (2013) and Lo Vullo et al. (2016), according to ACTRIS standard operating procedure (SOP) (https://www.actris.eu/sites/default/files/Documents/ACTRIS-2/Deliverables/WP3_D3.17_M42.pdf) and audited under the GAW programme of the WMO by the World Calibration Center for volatile organic compounds in 2018. Real ambient air samples are collected every second hour, alternated with whole-air calibration mixture (working standard) to correct for any short term instrumental drift, resulting in 12 real air measurements per day. Each month the working standard is calibrated against a certified "30-compounds Ozone precursor mixture" at 500 ppt level in nitrogen from the National Physical Laboratory (NPL-UK). System blanks are evaluated on a weekly basis, with concentrations changing over time but limited well below 15 ppt, with results adjusted accordingly. Total uncertainty for each measurement is calculated as the error propagation of i) the reproducibility of the repeated working standard runs on the same day, ii) the detection limit, and iii) the scale propagation error (derived by the regular NPL/quaternary standard check, additional details in appendix F1). Final QC of the dataset is checked yearly by an external reviewer as part of the ACTRIS-EBAS SOP procedures before submission for data release to the EBAS repository. In addition, C3H8 observations for the year 2022 from JFJ WMO-GAW global station have been used for atmospheric inversion modeling as described in Section 2.5. C3H8 measurements at JFJ are carried out within the framework of ACTRIS activities, following the same analytical protocol for CMN but with different instrumentation (i.e. the Medusa-AGAGE setup (Miller et al., 2008; Prinn et al., 2018)). Measurements of CO and CH4 were performed at CMN according to the methods described in Section A.”

In Appendix A, we added the following:

“Carbon monoxide, and methane datasets:

From 2011 to 2015 CH4 and CO observations were carried out using a GC-FID system, designed according to AGAGE protocol for the GC-MD setup. The calibration of the GC-FID system was performed with a set of 6 NOAA calibration mixtures with concentrations spanning the range of the ambient air values. Quality assurance/quality control procedures were done regularly in compliance with AGAGE protocols by means of GCWerks (SIO) software. From 2015 (for CH4) and from 2018 (for CO), observations have been carried out by using Cavity Ring Down Spectroscopy (CRDS) instruments. From 2018, CO and CH4 observations have been performed at CMN in the framework of ICOS. Within ICOS, observations are carried out in a standardized way for measurement set-up, used materials, quality assurance strategy and data creation workflow. Hazan et al. (2016) and Yver-Kwok et al. (2021) provided a detailed description of the quality assurance programme for ICOS measurements. CH4 observations from 2015 to 2017 have been carried out by CAMM - Italian Air Force in the GAW/WMO framework. The quality assurance programme has been designed based on the recommendation provided by GAW/WMO (https://library.wmo.int/idurl/4/69756). In particular, a multipoint calibration is performed every three months against three laboratory standards provided by NOAA whose mole fractions exceed the range for ambient air. Calibration data are post-processed and calibration coefficients are derived through linear regression and used to correct the in situ air measurements. A specific water vapour correction determined during a system and performance audit by the WMO/GAW "World Calibration Center for Surface Ozone, Carbon Monoxide, Methane, Carbon Dioxide and Nitrous Oxide" was applied to the data (Zellweger et al., 2018). CAMM operators manually screened the data to remove anomalous events related to instrumental/sampling issues or local emissions."

In Appendix F, we added a table reporting the precision of the calibration tank used and a plot with the time dependent variation of the daily working standard precision used to evaluate precision of each measurement of propane.

- JFJ Dataset: The Jungfraujoch (JFJ) dataset is used in the inversion but is not described. Clarify the QC procedures, measurement frequency, and any averaging methods applied to this dataset.

The two stations follow the same ACTRIS standard operating procedures and calibration scheme, even though JFJ was -and still is- using a different instrumentation, for which proper citation is reported.

Following your suggestion, in Section 2.1 the text has been modified as follows:

"In addition, C3H8 observations from Jungfraujock (JFJ, Switzerland) WMO-GAW global station have been used for atmospheric inversion modeling as described in Section 2.5. C3H8 measurements are carried out within the framework of ACTRIS activities, following the same analytical protocol of CMN but with different instrumentation (i.e. the Medusa-AGAGE setup (Miller et al., 2008; Prinn et al., 2018)). "

.

- Averaging 2-Hourly C_3H_8 Data to 3-Hourly Bins

The authors mention that 2-hourly C_3H_8 measurements were averaged to 3-hourly resolution for the inversion. However, the methodology is unclear:

- How were measurements assigned to 3-hourly bins (e.g., 00:00–03:00, 03:00–06:00)?

- How were bins with only one measurement (e.g., 04:00 in the 03:00–06:00 window) handled?

Suggestion: Clarify the averaging method and justify its suitability for the inversion.

Following your suggestion, we added the following description in Section 2.5:

“For the inversion, observations from CMN and JFJ were aggregated to a 3-hourly temporal resolution. Fixed 3-hour time bins (e.g., 00:00–03:00, 03:00–06:00) were defined, and all observations within each bin were averaged and assigned to the bin start time. If a bin contained only a single observation, that observation was assigned to the corresponding bin start time.”

Minor Comments:

Abstract: Define "JFJ" (Jungfraujoch) at first mention.

Thank you for pointing this out. We revised the sentence as follows: “..Jungfraujoch (JFJ, Switzerland)..”

Line 143: Define "BB" (biomass burning).

Following your suggestions, we revised the typos related to JFJ and BB.

Figure 2:

- Clarify the names and locations of the sites (ALT, BRW, KUM, etc.) in the caption.
- Explain the two y-axes (the red axis for LEF is confusing as LEF is shown in a different color).
- Clarify what is meant by "CMN trend curve (2 years) or (1 year)".

Following your suggestions, caption of Figure 2 was revised as follows:

” ….. Shaded lines show 95% confidence interval for CMN trend curves with a long-term cutoff value of 1 or 2 years. ALT – Alert (Nunavut, Canada); BRW – Utqiaġvik, formerly Barrow (Alaska, USA); KUM – Cape Kumukahi (Hawaii, USA); SUM – Summit (Greenland, Denmark); MHD – Mace Head (Ireland); LEF – Park Falls (Wisconsin, USA).”

Moreover, shaded lines were added for showing the 95% confidence interval for CMN trend curves calculated on randomly sampled subsets consisting of 90% of the dataset for 50 iterations.

Figure 5:

- Define the seasonal periods (e.g., winter = December–February) in the text.

- Specify whether UTC or local time is used (in other figures as well).

  Annual and seasonal diurnal variations of propane mixing ratio measured at Monte Cimone (Italy) between 2011 and 2023.

Following your suggestions:

- caption of Figure 5 was revised as follows: "….Spring – from March to May; autumn – from September to November; winter – from December to February; summer – from June to August."

- UTC was added to the x-axis title of figures 1, 2, 5, and C2-C5.

Figure 9: Remove the connecting lines during data gaps to avoid misleading interpretations.

Following your suggestions, connecting lines were removed in data gaps.

Conclusion:

This study provides a valuable long-term dataset and important insights into atmospheric propane trends. By strengthening the links between sections, addressing potential biases, and providing more methodological details, the authors can significantly enhance the impact and clarity of their work. I look forward to seeing a revised version that incorporates these suggestions.

References:

Petit, J.-E., Dupont, J.-C., Favez, O., Gros, V., Zhang, Y., Sciare, J., Simon, L., Truong, F., Bonnaire, N., Amodeo, T., Vautard, R., and Haeffelin, M.: Response of atmospheric composition to COVID-19 lockdown measures during spring in the Paris region (France), Atmospheric Chem. Phys., 21, 17167–17183, https://doi.org/10.5194/acp-21-17167-2021, 2021.

References

Cristofanelli, P., Arduni, J., Serva, F., Calzolari, F., Bonasoni, P., Busetto, M., ... & Putero, D. (2021). Negative ozone anomalies at a high mountain site in northern Italy during 2020: a possible role of COVID-19 lockdowns?. *Environmental Research Letters*, *16*(7), 074029. DOI 10.1088/1748-9326/ac0b6a

Hazan, L., Tarniewicz, J., Ramonet, M., Laurent, O., and Abbaris, A.: Automatic processing of atmospheric CO_2 and CH_4 mole fractions at the ICOS Atmosphere Thematic Centre, Atmos. Meas. Tech., 9, 4719–4736, https://doi.org/10.5194/amt-9-4719-2016, 2016.

Hussain, M. and Mahmud, I.: pyMannKendall: a Python package for nonparametric Mann-Kendall family of trend tests, Journal of Open Source Software, 4, 1556, https://doi.org/10.21105/joss.01556, 2019.

Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Greally, B. R., Mühle, J., and Simmonds, P. G.: Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, 80, 1536–1545,505 https://doi.org/10.1021/ac702084k, 2008.

Naik, V., Voulgarakis, A., Fiore, A. M., Horowitz, L. W., Lamarque, J.-F., Lin, M., Prather, M. J., Young, P., Bergmann, D., Cameron-Smith, P., et al.: Preindustrial to present-day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry andClimate Model Intercomparison Project (ACCMIP), Atmospheric Chemistry and Physics, 13, 5277–5298, 2013.

Pedregosa, F., Varoquaux, G., Gramfort, A., Michel, V., Thirion, B., Grisel, O., Blondel, M., Prettenhofer, P., Weiss, R., Dubourg, V., Vanderplas, J., Passos, A., Cournapeau, D., Brucher, M., Perrot, M., and Duchesnay, ˙E.: Scikit-learn: Machine learning in Python, Journal of Machine Learning Research, 12, 2825–2830, 2011

Prinn, R. G., Weiss, R. F., Arduini, J., Arnold, T., DeWitt, H. L., Fraser, P. J., Ganesan, A. L., Gasore, J., Harth, C. M., Hermansen, O., Kim, J., Krummel, P. B., Li, S., Loh, Z. M., Lunder, C. R., Maione, M., Manning, A. J., Miller, B. R., Mitrevski, B., Mühle, J., O'Doherty, S., Park, S., Reimann, S., Rigby, M., Saito, T., Salameh, P. K., Schmidt, R., Simmonds, P. G., Steele, L. P., Vollmer, M. K., Wang, R. H., Yao, B., Yokouchi, Y., Young, D., and Zhou, L.: History of chemically and radiatively important atmospheric gases from the Advanced Global Atmospheric Gases Experiment (AGAGE), Earth Syst. Sci. Data, 10, 985–1018, https://doi.org/10.5194/essd-10-985-2018, 2018

Wolfe, G. M., Nicely, J. M., St. Clair, J. M., Hanisco, T. F., Liao, J., Oman, L. D., Brune, W. B., Miller, D., Thames, A., González Abad, G., et al.: Mapping hydroxyl variability throughout the global remote troposphere via synthesis of airborne and satellite formaldehyde observations, Proceedings of the National Academy of Sciences, 116, 11 171–11 180, 2019.

Yver-Kwok, C., Philippon, C., Bergamaschi, P., Biermann, T., Calzolari, F., Chen, H., Conil, S., Cristofanelli, P., Delmotte, M., Hatakka, J., Heliasz, M., Hermansen, O., Komínková, K., Kubistin, D., Kumps, N., Laurent, O., Laurila, T., Lehner, I., Levula, J., Lindauer, M., Lopez, M., Mammarella, I., Manca, G., Marklund, P., Metzger, J.-M., Mölder, M., Platt, S. M., Ramonet, M., Rivier, L., Scheeren, B., Sha, M. K., Smith, P., Steinbacher, M., Vítková, G., and Wyss, S.: Evaluation and optimization of ICOS atmosphere station data as part of the labeling process, Atmos. Meas. Tech., 14, 89–116, https://doi.org/10.5194/amt-14-89-2021, 2021.

Zellweger, C., Steinbacher, M., and Buchmann, B.: System and Performance Audit of Surface Ozone, Carbon Monoxide,Methane and Carbon Dioxide at the Global GAW Monte Cimone, Italy, June 2018, WCC-Empa Report 18/1, Dübendorf, Switzerland, 2018.