Author Response to Anonymous Referee #1

Julian Weng[1], Yufang Hao[1], Benjamin T. Brem[1], Tianqu Cui[1], Peeyush Khare[1,7], Lubna Dada[1], Kaspar R. Daellenbach[1], Sophie Darfeuil[2], Gaëlle Uzu[2], Jean-Luc Jaffrezo[2], Martin Steinbacher[3], Stefan Reimann[3], Thaleia Gkraikou[4], Konstantina Oikonomou[4], Jean Sciare[4], Martine Collaud Coen[5], Claudia Mohr[1,6], Andre S. H. Prévôt[1], Martin Gysel-Beer[1], Imad El Haddad[1], and Patrik Winiger[1]

[1]PSI Center for Energy and Environmental Sciences, 5232 Villigen PSI, Switzerland
[2]Université Grenoble Alpes, CNRS, INRAE, IRD, G-INP, IGE, 38000 Grenoble, France
[3]Swiss Federal Laboratories for Materials Science and Technology, Empa, 8600 Dübendorf, Switzerland
[4]Climate and Atmosphere Research Center, The Cyprus Institute, Nicosia, Cyprus
[5]Federal Office of Meteorology and Climatology, MeteoSwiss, Payerne, Switzerland
[6]Department of Environmental Systems Science, ETH Zurich, Zürich, Switzerland
[7]Now at: Forschungszentrum Jülich, Jülich, Germany

Correspondence: Patrik Winiger (patrik.winiger@psi.ch)

Manuscript: "A Decadal-Scale Perspective on PM_{10} Composition and its Variability Drivers at the Alpine High-Altitude Research Station Jungfraujoch"

General Comments

Reviewer comment:

This is an interesting and well-written manuscript. The introduction is particularly strong, providing a clear rationale and effectively framing the research question. The paper is carefully written throughout, with a logical organization. Overall, I found the hypothesis of using specific tracers at a mountain site [i.e. NOy/CO for PBLi and w for atmospheric oxidative capacity] to demonstrate and quantify that the influence of the PBL allows for elevated aerosol concentration, while atmospheric oxidative capacity governs the composition of these episodes (in gas and aerosol phase), an interesting and innovative approach. At this point, I believe this paper need further work to clearly demonstrate this approach (additional statistics, etc). The major and minor comments provided below are intended to further strengthen the manuscript and improve its clarity, rigor, and overall impact.

Response:

We thank Referee #1 for the positive evaluation of the manuscript and the constructive feedback improving its clarity and significance. Answers to specific comments are provided below.

Specific Comments

Comment 1

Reviewer comment:

The description of the inlet at JFJ must be clarified. The paper cited (Weingartner et al., 1999) only considered particle below 750 nm. Additionally, the paper looked at number concentration (not mass) of aerosol, and said all assumptions were based on calculation in the submicron sizes. Thus, the "losses below 5%" is not appropriate when considering online mass concentration of PM10. Instead, I would strongly encourage the authors to deeply consider losses in the system using computational or experimental (if available) methods. Here is an example to consider:

Von der Weiden, S-L., F. Drewnick, and S. J. A. M. T. Borrmann. "Particle Loss Calculator–a new software tool for the assessment of the performance of aerosol inlet systems." Atmospheric Measurement Techniques 2, no. 2 (2009): 479-494.

Has an experimental validation of the JFJ inlet been conducted (like these examples: https://www.tandfonline.com/doi/full/10.1080/02786826.2019.1602718#d1e1040 or https://www.osti.gov/servlets/purl/2375529)?

This is especially concerning as later (line 154) it is suggested that negligible number of accumulation (N90) particles is found in the Free Troposphere at JFJ. This is inconsistent with many other mountain sites, which commonly find coarse mode (especially dust) aerosols in the free troposphere. A few examples are provided below.

Shen, M., Qi, W., Liu, Y., Zhang, Y., Dai, W., Li, L., Guo, X., Cao, Y., Jiang, Y., Wang, Q., Li, S., Wang, Q., and Li, J.: Measurement report: Observational insights into the impact of dust transport on atmospheric dicarboxylic acids in ground region and free troposphere, Atmos. Chem. Phys., 25, 16147–16165, https://doi.org/10.5194/acp-25-16147-2025, 2025.

Betsy, K. B., and Sanjay Kumar Mehta. "Characteristics of dust aerosols within the atmospheric boundary layer and free troposphere over a tropical coastal station." Meteorology and Atmospheric Physics 137, no. 3 (2025): 27.

Tsai, F., Chien, Y.C., Chen, W.N., Notaro, M., Chen, H.Y., Lin, N.H., Hsu, P.C. and Lin, Y.C., 2025. Source and transport of dust to the North Pacific: Observations and analysis from a high mountain. Journal of Geophysical Research: Atmospheres, 130(6), p.e2024JD042415.

Additionally, particle loss may impact the conclusion in line 216 that "on an annual basis, cumulative fine and coarse mode aerosol masses are of comparable magnitude" This mass comparison depends upon the assumption that aerosol transmission losses are not size dependent, which is most likely incorrect.

Response:

We agree with Referee #1 that the JFJ aerosol inlet for online measurements has to be described more thoroughly in this manuscript. This discussion relates to online measurements (particularly online FIDAS PM_{10}), while the filter collection with the HiVol sampler is performed independently according to VDI 2463 BI guidelines, in line with the European standard reference method EN12341 (Hueglin, 2024).

The overall fine- (sub-micrometer) and coarse-mode (above micrometer) particle transmission efficiency is the product of the transmission efficiencies of the sampling head and the inlet line tubing at the JFJ. Experimental characterization of overall transmission efficiency is available only for fine-mode (sub-micrometer) aerosols by Weingartner et al. (1999), who quantified number concentration losses to below 5%. However, both sampling head and inlet line transmission efficiencies have been characterized computationally in the following way (unpublished results):

- Sampling head: computational fluid dynamics simulation similar as described by Petersen et al. (2019). Transmission losses show strong dependency on turbulence and wind speed. Under cloud-free conditions and standard wind speeds (2 to 5 $\mathrm{m\,s^{-1}}$), the experimental results (Weingartner et al., 1999) for fine-mode particles (transmission above 95%) are confirmed. For coarse-mode particles with mass median diameters of 4 µm (which is typical for mineral dust at the JFJ), transmission efficiencies lie around 85%.

- Inlet line tubing: computational calculations show negligible losses for fine-mode particles, consistent with experimental results. For coarse-mode particles with mass median diameters of 4 µm, transmission efficiencies lie around 80%.

Concluding from the computational calculations, overall losses of the JFJ inlet (sampling head and sampling line) for typical coarse-mode particles (mass median diameter of 4 µm) lie in the range of 30% for cloud-free conditions. Overall losses in the fine mode (sub-micrometer) are negligible as reported before (Weingartner et al., 1999). However, especially related to the sampling head, these estimations are strongly subject to environmental parameters: wind speed, turbulence and cloud droplet presence. In the experimental part of the manuscript, these considerations are now acknowledged and discussed (cf. manuscript changes below).

Accounting for potential sampling loss biases through computational calculations in this study is however considered as not expedient by the authors for the following reasons:

- Losses in the sampling line alone, which are straightforward to correct for, as pointed out by Referee #1 and the references provided, are considered to be rather low for all relevant size ranges (e.g. less than 15% for typical coarse-mode particles).

- Losses in the sampling head however, especially related to cloud droplet presence or strong ambient turbulence, are hard to quantify systematically, as they are subject to a strong dependency on a series of environmental parameters. Trying to account for these might introduce substantial biases itself.

- These considerations affect the online aerosol measurements (effectively online FIDAS PM_{10}). All chemical information inferred from filter measurements, and therefore all main conclusions of this manuscript, remain untouched.

- Independently from these considerations, the comparison of gravimetric filter based bulk PM_{10} and fine-mode species with online aerosol measurements provides a consistent picture. For example, gravimetric PM_{10} and online PM_{10} show a very good agreement ($R^2 = 0.94$, Fig. S10), and so does the sum of fine-mode species mass concentrations with online PM_1 ($R^2 = 0.93$, Fig. S22).

Addressing the concern of Referee #1 about N_{90} at the JFJ:

- N_{90} is calculated from number size distributions inferred from mobility size distribution measurements (SMPS). By instrument cutoffs, it does not include coarse particles. Herrmann et al. (2015) have compared several metrics accounting for FT and PBLi influence at the JFJ (including *in-situ* measurements of ^{222}Rn, NO_y/CO and back-trajectory transport modeling) and set these into relation with N_{90}. In that way it was confirmed that under FT conditions at the JFJ (3580 m above sea level), no substantial amount of particles above 90 nm (mobility diameter) are present.

  This might differ from the other mountain sites provided as examples, due to considerably different characteristics in terms of mountain profile, latitude and altitude. For example for the lower altitude mountains Mount Hua (2065 m above sea level) and Mount Lulin (2862 m above sea level), vertical transport strength can likely be considered stronger throughout the year.

- Even when considering the particle size range above the SMPS cutoff, it has been demonstrated at the JFJ that under Saharan dust free conditions (which is actively filtered for in this manuscript), background coarse-mode particles cannot compete with the fine-mode fraction in terms of number concentration (e.g. Fig. B1 in Kammermann et al. (2010)).

Manuscript change:

'A heated inlet (20 °C) with number concentration transmission losses below 5 % for accumulation-mode particles under cloud-free conditions was used for all online aerosol instruments (Weingartner et al., 1999). Transmission losses for coarse-mode particles were not quantified experimentally. However, computational simulations of the sampling head and inlet line indicate overall transmission losses of approximately 30 % for coarse-mode particles with a mass median diameter of 4 µm under cloud-free conditions (unpublished data). These losses depend on environmental conditions, including wind speed, turbulence, and the presence of cloud droplets. In this study, uncertainties associated with coarse-mode particle losses primarily affect online coarse-mode PM mass concentrations, which are, however, additionally evaluate against independent gravimetric PM_{10} measurements. Online PM_1 and PM_{10} mass concentrations were measured using a fine dust monitor (FIDAS 200, PALAS, Germany; Sect. S4). FIDAS PM_{10} show good agreement with gravimetric PM_{10} measurements ($R^2 = 0.94$, Fig. S10). For quantification, the raw FIDAS PM_1 and PM_{10} data were referenced to the gravimetric PM_{10} measurements, as described in Sect. S4.'

Comment 2

Reviewer comment:

Line 99 states that there were 249 composite samples. Yet, if a sample was taken daily for 10 years, we would expect ~3600 filters. The paper suggest that composites include 4 days of filters. Thus, this reviewer expects approximately 900 composite filters. Why are there only 249?

Response:

Only every fourth filter for the time period of 2011 to 2021 was selected, and additionally pooled into composites of four per each sample. The sentence describing the sample selection interval could be misleading in the previous version: 'For chemical analysis, filters for the time period between 2011 and 2021 were pooled into composites of four at an interval of four days each [...]'.

It was updated to a more clear description, while Fig. S1 shows a schematic of the sample selection.

Manuscript change:

'For chemical analysis, filters corresponding to every fourth day for the time period between 2011 and 2021 were selected and pooled into composites of four consecutive dates [...]'

Comment 3

Reviewer comment:

Eliminating times with Saharah dust conditions does specifically eliminate the unique meteorological conditions that allow for this source region. This bias in the dataset should be acknowledged.

Response:

The sentence describing Saharan dust exclusion was adjusted, so that it acknowledges the bias of omitting these conditions, while justifying their exclusion through the large bias imposed through Saharan dust constituents on aerosol and potentially gas phase composition.

Manuscript change:

'Even though contributions of the meteorological conditions allowing for Saharan dust transport are therefore suppressed, excluding these sampling dates is justified as they are subject to strongly elevated loadings of dust constituents, while other aerosol and gas-phase properties could also be impacted.'

Comment 4

Reviewer comment:

Line 78, how has the contribution of local primary emissions changed over the last decade as tourist visits have increased?

Response:

Tourist number have been increasing moderately throughout the study period from 764.000 in 2011 to 1.056.000 in 2019 (a sharp decrease occurred in 2020 due to the measures to counteract the COVID-19 pandemic) (noa). The cited study by Fröhlich et al. (2015) estimated primary organic emissions in 2012/2013, where more than 800.000 visitors were recorded at the Jungfraujoch.

A moderate increase of primary organic emissions throughout the study period can be expected from tourist related emissions like tobacco smoking (Bukowiecki et al., 2016), while this might be counteracted by reduction in emissions through electrification and reduction of inefficient combustion processes, e.g. through snowcats.

Overall, the contribution of local touristic activities to overall organic aerosol concentrations can still be considered minor and not considerably above the range reported by Fröhlich et al. (2015), which is reflected by the missing effect throughout the COVID-19 pandemic in 2020/2021, when tourist numbers and local activities were strongly reduced.

The text in the experimental section was adjusted to account for these trends.

Manuscript change:

'The contribution of local primary emissions to OA mass concentration at the JFJ lay between 7 to 12 % in 2012/13, predominantly associated to touristic activities (Fröhlich et al., 2015). Increasing tourist numbers might have lead to a moderate increase in direct emissions through tobacco smoking towards the end of the study period, while reduction of fuel consumption of snowcats and electrification might have had a reducing effect. Local influences on mean values of OA properties (as well as most other aerosol constituents) can therefore be considered minor, all year round throughout the entire study period.'

Comment 5

Reviewer comment:

How will potential increasing amounts of wildfire smoke sampled at JFJ impact the atmospheric oxidative capacity, as captured by the humidity ratio? Potentially the CO/CO2 ratio could be used to identify smoke influence. Does the role of smoke impact Figure 9b?

Response:

The detection of smoke events at the Jungfraujoch is subject to ongoing investigations. Due to the complex interaction of regional and long-range transported air masses and large differences in the aging state (even of individual wildfire plumes), a quantification of smoke influences is not straightforward and likely to include a variety of parameters (both gas and aerosol phase). Also, rapidly changing background concentrations at the station need to be accounted for.

Preliminary results indicate that for more recent years (after 2021), the contribution of clearly identifiable wildfire smoke to OA lies in the range of below 10 % (Simon *et al.*, in preparation) on an annual basis, with large peak contributions on individual days. A systematic bias on the conclusions drawn about organic aerosol and particularly Fig. 9b of this study is therefore not expected.

It should be noted however that the humidity ratio ω in this study is used as a proxy for the oxidative capacity history in regionally transported air masses (vertical transport). For a complete disentangling of the drivers of aerosol variability at the Jungfraujoch, it might therefore be important to also account for the effect of different transport regimes such as regional and long-range transport (of e.g. wildfire plumes) more explicitly. The statement which places the approach of the current study into further research needs in section 5 was adjusted accordingly.

Manuscript change:

'Disentangling these contributions will require observations that simultaneously constrain precursor fluxes, long-range material transport (e.g. from wildfires), oxidant concentrations, and chemical pathways, along with model validation.'

Comment 6

Reviewer comment:

Generally, this paper requires more rigor to justify the conclusions. Here are a few examples, where further analysis/statistics could be used to demonstrate the results.

- For figure 3b (plot of CO vs. NOy/CO), there is no clear relationship between the plotted variables, potentially suggestion that CO does not impact the ratio, as the variability (i.e. measurement range observed) in the two variables (NOy and CO) are significantly different
- Line 268. Is this moderate decrease in CO at high humidity ratio statistically significant?
- Generally, the statements pertaining to plots 3b and 3c are speculative and need to be more carefully considered and evaluated.
- Throughout the paper statements such as "correlate well" need to be backed by statistics.
- It is unclear to this reviewer if any relationships are found in Figure 3b and 3c.
- In a similar vein, on line 300 and 311, please define "correlate"/ "correlation" with a statistical value.
- It is also important to quantify term including "strongest dependence", "moderate sensitivity", "not correlated", and "stronger correlation" in lines 313-319.
- Line 339, define using statistics "increase systematically"

Response:

- To 'Fig. 3b': CO is much more long-lived in the atmosphere than NO_y. Therefore, no linear correlation between the variables is expected, although both species originate from emissions in the PBL (mostly combustion processes). Previous studies at the JFJ have used the ratio of NO_y and CO (Zellweger et al., 2003) to account for PBLi strength under the rationale that NO_y accounts for air mass age through wet/dry deposition of NO_y species, while CO accounts for dilution effects. Therefore, even though no clear linear relationship is indicated between CO and NO_y/CO, it was preferred to take CO into account. In this manuscript, this convention is followed to retain consistency with previous works. Future works should however take into account that a small bias likely exist on the side of CO through oxidative effects (as indicated in Fig. 3b).

- To 'Line 268': With respect to CO absolute mixing ratios, counteracting effects might be at play: increase through stronger vertical transport of more fresh air masses at high NO_y/CO, while depletion through higher oxidative capacity history at high ω. Rather than looking at absolute mixing ratios, it is more indicative to compare relative CO discrepancies at a certain NO_y/CO-level between high and low ω conditions. A Mann-Whitney-U-test for the two highest NO_y/CO-bins in Fig. 3b was computed and the p-value was added to the manuscript to highlight statistical significance: $p = 0.00030$. In order to account for the relative rather than absolute change, the wording used in the manuscript has been changed from 'decreased' to 'exhibits a moderate depletion at high ω'. Also the wording for the case of O_3 has been changed and a respective p-value of $p = 0.0014$ has been added.

- We agree with Referee #1 that further care should be taken for interpretation of the behavior of CO and especially O_3. In the manuscript, these species take in supporting roles besides the more indicative NO_x/NO_y and VOCs. We still believe that their behavior deserves mentioning, as especially in the case of O_3, previous studies exist that have linked its seasonality to photochemical reactivity. The statements about CO and O_3 were therefore re-formulated to a hypothesis character, which could be taken up in future works. Also, further statistics were provided to assure significance of the observed trends (cf. above). Example: 'Possibly related to that, CO, whose primary atmospheric sink is oxidation by OH (Zheng et al., 2019), exhibits a moderate depletion at high ω (cf. the binned local median trend lines in Fig. 3b, Mann-Whitney-U-test of data points in two highest bins: $p = 0.00030$).'

- As far as related to plots and data of this manuscript, all statements of correlations have now been backed up by statistical values (coefficient of determination or partial Pearson correlation coefficients).

- C.f. the comments to points 1 and 3 above.

- To 'Lines 300 and 311': As the correlation of PM_1, eBC, WSOA and sulfate with NO_y/CO is conditional on ω, delivering a simple correlation coefficient or coefficient of determination would be misleading. To back up the wording by statistics, partial Pearson correlation coefficients, controlling for the humidity ratio ω were added (e.g. $r_{PM_1,NO_y/CO\cdot\omega} = 0.43$ and $r_{eBC,NO_y/CO\cdot\omega} = 0.36$).

- To 'Lines 313 to 319': quantitative expressions were added to the sentences, e.g. '[...] sulfate shows moderate ω-sensitivity (almost doubling at $\omega > 3\,\mathrm{g\,m^{-3}}$ compared to $\omega < 3\,\mathrm{g\,m^{-3}}$), and WSOA exhibits the strongest dependence (increasing fivefold at $\omega > 3\,\mathrm{g\,m^{-3}}$ compared to $\omega < 3\,\mathrm{g\,m^{-3}}$).'

- To 'Line 339': The coefficients of determination (R^2) was added to the statement for both anthropogenic marker examples.

Comment 7

Reviewer comment:

This review does not agree yet agree with the statement in line 413 “results emerges with clarity”.

Response:

We thank Referee #1 for this comment. We intended this sentence to emphasize a central mechanistic finding emerging from our 11-year, process-resolved analysis, rather than to make a general claim about the clarity of the results. To retain this emphasis while expressing the conclusion more qualitatively, we have revised the sentence to read as follows in its context:

Manuscript change:

> ’The 11-year record presented here provides a rare process-resolved view of aerosol evolution at the interface between the PBL and the FT. By leveraging the unique setting of the Jungfraujoch and the comprehensive chemical characterization over more than a decade, we directly track the formation and transformation of secondary (organic) aerosol during atmospheric transport, isolating the governing processes.
>
> A key finding becomes evident: the atmospheric oxidative capacity experienced by PBLi air masses during transport to high altitudes is a primary driver of the observed secondary aerosol formation.’

Minor comments

Reviewer comment:

Figure 3b and 3c: Consider starting the y-axis at 60 ppb for CO and 35 ppb for O_3. This adjustment would improve the readability of the plots by reducing the amount of unused white space and emphasizing the variability in the data.

Figure 3, 4, 6, and 7 – Consider a different more distinct color bar. It is difficult to differentiate blue and purple, which is the most commonly used colors on all plots.

Response:

The y-axes of Fig. 3b and c were adjusted. The color bar range across all figures was narrowed to make differences in the data easier to see.

References

Geschäftsbericht 2024, https://www.jungfrau.ch/geschaeftsbericht-2024/downloadcenter.

Bukowiecki, N., Weingartner, E., Gysel, M., Coen, M. C., Zieger, P., Herrmann, E., Steinbacher, M., Gäggeler, H. W., and Baltensperger, U.: A Review of More than 20 Years of Aerosol Observation at the High Altitude Research Station Jungfraujoch, Switzerland (3580 m asl), Aerosol and Air Quality Research, 16, 764–788, https://doi.org/10.4209/aaqr.2015.05.0305, 2016.

Fröhlich, R., Cubison, M. J., Slowik, J. G., Bukowiecki, N., Canonaco, F., Croteau, P. L., Gysel, M., Henne, S., Herrmann, E., Jayne, J. T., Steinbacher, M., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Fourteen months of on-line measurements of the non-refractory submicron aerosol at the Jungfraujoch (3580 m a.s.l.) – chemical composition, origins and organic aerosol sources, Atmospheric Chemistry and Physics, 15, 11 373–11 398, https://doi.org/10.5194/acp-15-11373-2015, 2015.

Herrmann, E., Weingartner, E., Henne, S., Vuilleumier, L., Bukowiecki, N., Steinbacher, M., Conen, F., Collaud Coen, M., Hammer, E., Jurányi, Z., Baltensperger, U., and Gysel, M.: Analysis of long-term aerosol size distribution data from Jungfraujoch with emphasis on free tropospheric conditions, cloud influence, and air mass transport, Journal of Geophysical Research: Atmospheres, 120, 9459–9480, https://doi.org/10.1002/2015JD023660, 2015.

Hueglin, C.: Technischer Bericht zum Nationalen Beobachtungsnetz für Luftfremdstoffe (NABEL) 2024, Tech. rep., EMPA, 2024.

Kammermann, L., Gysel, M., Weingartner, E., and Baltensperger, U.: 13-month climatology of the aerosol hygroscopicity at the free tropospheric site Jungfraujoch (3580 m a.s.l.), Atmospheric Chemistry and Physics, 10, 10 717–10 732, https://doi.org/10.5194/acp-10-10717-2010, 2010.

Petersen, R. C., Hallar, A. G., McCubbin, I. B., Ogren, J. A., Andrews, E., Lowenthal, D., Gorder, R., Purcell, R., Sleeth, D., and Novosselov, I.: Numerical, wind-tunnel, and atmospheric evaluation of a turbulent ground-based inlet sampling system, Aerosol Science and Technology, 53, 712–727, https://doi.org/10.1080/02786826.2019.1602718, 2019.

Weingartner, E., Nyeki, S., and Baltensperger, U.: Seasonal and diurnal variation of aerosol size distributions (10<D<750 nm) at a high-alpine site (Jungfraujoch 3580 m asl), Journal of Geophysical Research: Atmospheres, 104, 26 809–26 820, https://doi.org/10.1029/1999JD900170, 1999.

Zellweger, C., Forrer, J., Hofer, P., Nyeki, S., Schwarzenbach, B., Weingartner, E., Ammann, M., and Baltensperger, U.: Partitioning of reactive nitrogen (NO_y) and dependence on meteorological conditions in the lower free troposphere, Atmospheric Chemistry and Physics, 3, 779–796, https://doi.org/10.5194/acp-3-779-2003, 2003.

Zheng, B., Chevallier, F., Yin, Y., Ciais, P., Fortems-Cheiney, A., Deeter, M. N., Parker, R. J., Wang, Y., Worden, H. M., and Zhao, Y.: Global atmospheric carbon monoxide budget 2000–2017 inferred from multi-species atmospheric inversions, Earth System Science Data, 11, 1411–1436, https://doi.org/10.5194/essd-11-1411-2019, 2019.