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# *Interactive comment on* "Ozone, Carbon monoxide and Nitrogen oxides time series at four Alpine GAW mountain stations in Central Europe" *by* S. Gilge et al.

**S. Gilge et al.**

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First we'd like to thank the reviewer for the very detailed and constructive comments! It really helped improving the paper!

General evaluation In this paper are presented continuous data series of trace-gas mixing-ratios (ozone, CO, NO2) collected for several ten years at four GAW stations in the Alps and nearby. Special attention is devoted to long-term trends in yearly or monthly mean mixing ratios over periods of more than 10 years, and discussed in relation to primary emission changes in Europe and at the global scale. ... Finally, as this paper is an interesting scientific contribution and suffers from no major deficiencies,



I recommend its publication in ACP after consideration of minor changes suggested below.

General comments

Paper length The manuscript is a bit lengthy, due to (i) the need of a very detailed description of the data quality assurance methods, (ii) a great number of figures, and (iii) the authors' choice to first present the results (section 3) and then discuss them in a separate section (4). I think however that all these reasons are justified. As I wrote above, data quality assurance is a key element of this study. The figures are well chosen and clearly organized, and all bring interesting information. The chosen sectionning perhaps renders the text a bit longer than it could be, but also makes its clearer. For these reasons I think it would be hard to make the manuscript significantly shorter without loss of interesting information or clarity. Therefore I encourage the authors to make the text more concise wherever possible, but without removing scientific stuff or changing the structure. Use and interpretation of statistical tests In many places in the paper the authors provide results of a statistical test briefly described in Section 2.4. Even I have no doubt the authors interpret the test correctly, I wonder whether using such a statistical test is appropriate in this study. At least, it might be confusing for readers not familiar with statistical tests. I would like the authors consider the four comments below: 1) As far as I know, statistical tests are usually used to control a risk of mistake, and reject results having too high risk of occurrence by chance. In the present study (linear regressions on time series), I would have expected an evaluation of the risk (probability) of inferring the existence of a trend (or more precisely, a degree of linear correlation) although there is actually no correlation (the latter statement being the "null hypothesis" of the test, ie. what is tested in fact). In case of a probability less than 5%, the existence of the found correlation is considered to be statistically significant; it is statistically nonsignificant in the opposite case (by the way, I suggest to change "insignificant" into "non-significant" throughout the paper). Here, the authors use a criterium of probability >95%. This is certainly an equivalent formulation of the test, but this is unusual and moreover they do not explicit the probability of what it is (see my specific comment below). So I encourage the authors to clarify all this. 2) I can understand the use of a statistical test in a normative and/or objective context (eg. in a standardized protocol, an algorithm, etc.) but here the authors present test results as qualitative indications to inform the reader on the robustness of the linear regression results. This information is not ambiguous for significant or highlysignificant results, but in many places the authors mention (and even discuss) nonsignificant trends. I am in trouble with this. What the reader is supposed to think in this case? Do the authors trust in their result, or not? Without further information than "non-significance", the reader can come to no conclusion on the existence of linear correlation. However, in some cases a conclusion might be nevertheless possible and of interest for the reader. If the probability of the null hypothesis (no linear correlation) is 10 3) To avoid such ambiguity, alternatively or additionaly to statistical tests, the authors could provide the 95%-confidence interval associated to the calculated variation rate. In the present discussion paper, uncertainties are sometimes given associated with variation rates (but not always), however, it is not said if these are 95%-confidence intervals or standard deviations. This should be at least clarified, but I also strongly encourage the authors to go further and provide systematically, for each linear regression they mention, the variation rate associated with its 95% confidence interval. In this way the information on the robustness of the result would be more intuitive and less confusing or subject to misinterpretations. REPLY: We followed this suggestion. Whenever necessary, the trend with the 95% confidence interval as uncertainty is given.

4) In Figures 4,5,9,10,13,14, and 18, are the linear trends calculated based on yearly or monthly statistics? This is an important question, because the statistical significance level strongly depends on the number of data points. Significance levels of trends based on monthly statistics might be found greater than for trends based on yearly statistics, although using the same underlying data set. REPLY: Linear trends were calculated on yearly basis, however no different results were obtained using yearly or monthly data for the calculation of the significance of the trends.



Figures in general They are all very clear and of good quality, however some are too small and details very tiny. Please enlarge the figures to use the full text width. REPLY: Text in figures has been checked and enlarged where necessary. However, it’s the journal’s choice how large they will appear.

Specific comments

p.19072 l.18-19 "with a tendency to higher ... trends in summer" and l.21-22 "whereas the highest ... in summer, respectively": the statements are redundant and partly inconsistent. Please revise the text. REPLY: The redundant phrasing was taken out and the text was revised

p.19074 l.4-5: the reference to Novelli et al. 2003 could be added to the list of cited papers. REPLY: Followed the suggestion

l.15-17: "Different impacts" of what? This sentence is very vague, please precise. REPLY: Text was revised and the impacts were attributed.

p.19075 l.9 "separate (...) boundary layer and free troposphere conditions": I don’t like the underlying idea that low ground stations are in the boundary layer, and high-altitude stations are in the free-troposphere (at least sometimes). Such statements are common in the scientific literature, but this is an oversimplifying view: âĂć First, this implicitely assumes that the continental boundary layer is a flat structure with more or less the same depth everywhere, and that sufficiently high summits emerge above its top - like islands from the sea. However this image is not true, especially in mountain areas, where the convective boundary layer is very inhomogeneous and show very specific structures evolving along the day. Convective motions above summits and crests can reach altitude much above the top of the boundary layer developing in the same time over the surrounding flat lowlands and inject air from lower layers into the local free troposphere (concept of "mountain injection layer"). Further, even in non convective conditions, strong vertical motion and turbulence might be enhanced in mountain areas due to terrain roughness. âĂć Second, the idea that certain stations are representative of the boundary layer, and other ones of the free troposphere, assumes that the composition of each layer is more or less homogeneous, but this is not the case, especially in the free troposphere. Therefore "boundary layer and free-tropospheric conditions" means little without further precision of time and space scales, as well as altitude. Despite all this, a high-altitude ground-based station might in certain conditions provide measurements representative of the composition of the free troposphere at similar altitude levels above surrounding flat lands, providing one defines carfully what is meant under "free-tropospheric composition", in terms of averaging time intervals and space volumes, altitude range, etc. Finally, I suggest the authors could here change their sentence into something like "... enables to separate local and regional effects, and provide data more or less influenced by the surface, and in some cases representative, for certain time and space scales, of the free troposphere at similar altitude levels above the surrrounding lowlands." REPLY: The reviewer is right and we know that the simple boundary concepts do not hold for mountain areas. We took the suggested phrasing from the reviewer.

p.19076 l.9: It could be precised that the "surrounding countryside" is rather flat and the HPB mountain quite isolated, so that the image of an island emerging above the boundary layer might be more true for HPB in very stable atmospheric conditions, than for the high-altitude sites, embedded in mountain chains. REPLY: We followed the suggestion.

l.24 and 26: Please explain briefly what "global" and "regional" mean for GAW stations. REPLY: A short explanation was added with a link to a WMO-GAW Report.

l.26 "The GAW regional site (...) is freely advected from all sides.": I can understand what the authors mean, but the sentence sounds strange: how could a station be advected? This should be rephrased more properly. REPLY: Obviously, we used the wrong word (advected) and changed the site description accordingly.

p.19078 l.23: Why, with the same technique (NDIR), is the uncertainty of CO measure-



ments at JFJ much smaller than at the other stations? REPLY: The different uncertainties for the CO observations with the NDIR technique can be explained by the different techniques that are applied to compensate for interferences. NDIR CO monitors from Horiba (APMA-360, APMA-370) use 'cross-flow modulation' to compensate for matrix effects in the NDIR absorption measurements. There, the air passes over a heated oxidation catalyst to selectively remove CO from the sample air with a frequency of 1 Hz. Other commercial instruments (e.g. TE 48S) use the gas filter correlation technique. Such instruments have shown reduced performance concerning zero drift in the past and are thus prone to higher uncertainties. The text has been changed accordingly

p.19079 l.14: Please explain what a round robin is in this context. REPLY: We added an explanation to the text.

p.19080 l.4 "the higher concentrated mixture": Do the authors mean the 40-ppm mixture? REPLY: Yes, this was clarified.

p.19082 l.5: What does the indicated time (1s) stand for? REPLY: This should have been 1-sigma uncertainty range, text was changed accordingly.

p.19083 l.3-5: I guess a "PRM" (also in Table 2) is a standard gas, but could this be precised? Besides, how well does this standard compare with the NOAA standard? REPLY: PRM was replaced by primary reference material. A sentence has been added with the results of comparison of this PRM with the GAW scale at WCC.

l.14-24: It should be more explicitely written here that ozone background concentrations increase with increasing altitude, and that the ZSF ozone data were offset to compensate the altitude difference between ZSF and ZUG, and reconnect appropriately the data series to the previous ZUG data. REPLY: We followed the suggestion and revised the text.

p.19084 l.14-19: Three points should be clarified in the description of the statistical test: 1) The cited reference (Sachs, 1992) is in German and hardly accessible by most readers. Please give an alternative reference in English. If this is not possible, the method should be explained in details. 2) It seems that "r" is the correlation coefficient (Pearson?) of a linear regression, but please, precise it. 3) l.17: the probability of what? (possibly here: the probability of having |t| < ËĘt, where t is an occurrence from a T-distribution centred on zero, representing the null hypothesis.) Please precise this, as well as an interpretation of the corresponding condition. REPLY: The method was explained more detailed, “r” was explained, and the null hypothesis was explicitly given and probability and significance were explained.

p.19085 l.2-5: Why (especially for the longest time series) were linear trends estimated over the whole time periods of data availability, whereas it was said (p.19074, l.10-12) that ozone rapidly increased until the early 1990s then levelled off thereafter. Would not be more relevant to calculate linear trends until e.g. 1995 for the first increase phase, then discuss the second phase from 1995 as it is already the case (Fig.3)? REPLY: We change the sequence of figures 2 and 3 and also the respective text. Trends for the years up to 1995 have been added. In our opinion this improved the chapter.

l.14-15: Why are no summer maxima observed at these sites? Could this be explained by different site characteristics or environments compared to the DACH sites? REPLY: The DACH sites are impacted by regional European emissions causing summer maxima of ozone (photochemical production) whereas the remote sites are not impacted by regional emissions. This has been clarified in the text.

l.28-29 "None of the percentile series show a significant trend.": Is it also the case if the linear regressions are based on monthly percentiles? (See also the general comment on significance levels, item 4.) REPLY: Yes, we checked the significance of the trends when using monthly averaged percentiles and obtained basically the same result.

p.19086 l.23, "ZSF": Should not one read "ZUG" instead (cf. 2.3.4)? REPLY: The reviewer is right and we changed the text.

p.19087 l.4, "logically": Why is it logical that the trend calculated from the baseline data



(Zellweger et al. 2009) is less rapid that from unfiltered data? Please explain briefly. Beyond this, in this sentence "higher" obviously means that the decrease is more rapid, but this is perhaps not the most appropriate adjective for a trend. REPLY: The word “logically” was removed from the text because it is not in the focus of this paper to discuss the effects of data filtering developed in other papers. “Higher” was replaced by “larger”.

l.8, please remove "as they are". REPLY: Done

p.19088 l.14: "anthropogenic impact": I would precise "regional". REPLY: Done

p.19089 l.13-16 and caption of Fig.16: It is not clear how the "relative abundance of gas wheighted by frequency of wind direction" is calculated. Is it obtained as the product of the wind frequency and the mean gas concentration in a given $10^{\circ}$-sector, then normalized by the mean gas concentration over all directions? Please clarify. REPLY: An explanation was added to the text.

l.18 and Fig.17 (right panel): Does the wind distribution in this figure mix data from both ZUG and ZSF? This would make little sense, as ZUG lies on the top of the mountain and ZSF on its southern slope. I expect the influence of the topography and in turn the wind angular distribution are very different at these two stations. In this case, two figures for ZUG and ZSF should be shown and discussed separately. REPLY: Only data from “Schneefernerhaus “were shown in the original manuscript. Since the relative ozone distribution follows perfectly the wind distribution, figure 17 (showing ozone distribution of SNB and ZUG/ZSF) was withdrawn.

p.19091 l.2 "footprint area": I am afraid this is not understandable by all reader, please explain. Also, the term "catchment area" (ie. the area from where the emissions influencing the station are caught) might be better. REPLY: We followed the reviewer’s suggestion and changed the text accordingly.

l.15 "except for summer where the factor is 1.2": As JFJ is situated in a very touristic area, do the authors think that enhanced local traffic in summer, especially during week-ends, could play a role? REPLY: We think local touristic traffic does not play a strong role. Otherwise, the weekly NO2 variation should show a maximum at the weekend. Since the JFJ is a touristic area all over the year, there should not be an obvious difference in seasons unless only in summer and due to the intensified vertical mixing air mass from the local, traffic polluted valley can reach the altitude of JFJ

p.19092 l.2-14: How robust are the discussed trends? REPLY: The text has been changed by adding trends with confidence intervals were necessary.

l.7-8 "the shift in ... individual sectors": this sentence is unclear to me, please rephrase. REPLY: “overall” added to clarify.

l.9 and 14: "significant" might be confusing here. Is the term used in its statistical or general meaning? REPLY: “statistical” has been added.

l.21 "in the range between insignificant and -5%/yr": a significance level and a variation rate are inconsistent with each other, please rephrase. Beyond this, it assumes that a non significant result should be interpreted as an absence of trend. This is not true, see the related general comment. REPLY: We have changed the text accordingly.

l.24 - p.10093, l.20: This discussion assumes that proportionality should be expected between the changes in European NO2 emissions and ambient concentrations at the stations. This is scritly valid only if there is zero background concentration at the hemispheric scale and if all sources influencing a station have changed in the same proportions. This is not the case, actually. Could the authors discuss the link between emissions and expected concentrations further? In particular, is there a non-negligible large-scale background of NO2 due to reservoir species of NOx (HNO3, PAN, etc.), and if so, how is it changing on the long term? REPLY: The reviewer correctly points out that concentration and emission trends can only be directly compared if there is zero background and if different local sources show similar trends. We assumed that indeed the back-ground is small, mainly based on two observations: (1) the percentile distri-



butions at JFJ show a consistent downward trend also in the small percentile classes (same for Hohenpeissenberg, if the values from the first 2 years are not considered), and (2) the weekly cycles with up to factor 2 enhanced values on working days in all seasons except summer. Both observations indicate low background contribution to the observed trends. However, exception is the summer season as discussed in the paper and here indeed background influences might compensate the small trends observed in other seasons. But annual mixing ratios and their trends are least impacted by the low summer values. Thus, there are no indications for substantial background contributions which might have reduced the trends in the mixing ratios. Furthermore, we assumed that local sources are mostly related to combustion and show similar trends. We added some of this discussion to the text, however, based on the evidence from observations as discussed before. A calculation of the impact of reservoir substances from measured time series of PAN and other compounds would be a different study and beyond the scope of this paper.

p.10093 l.24: Again, "significant" is a confusing term in the context of this paper. REPLY: “Significant” has been removed

p.19094 l.1-2: "mainly due to the annual cycle of (...) OH radicals": could the authors cite a reference? REPLY: A reference was added.

l.28 - p.19095, l.3: This paragraph is a bit confusing. If there is no decrease of the vertical mixing, how to explain the increase of the CO vertical gradient? Beyond this, HPB and JFJ are quite far from each other: could one really infer a conclusion on the evolution of the vertical CO gradient? I think vertical comparisons should be made between closer sites, eg. ZUG and HPB, or JFJ and a NABEL site in Switzerland. REPLY: In the light of CO’s long atmospheric residence time HPB and JFJ are close together. Maybe for this comparison a NABEL site would be better, but the paper is dealing with the results from the DACH sites. The comparison between HPB and ZUG is difficult because of the limited data availability from ZUG. Since there is no trend in vertical gradient of short lived NO2 and an increasing trend in CO there is no hint towards increasing vertical mixing. With increasing vertical mixing the difference in mixing ratios of primary trace gases between HPB and JFJ would become smaller.

p.19095 l.16 "-0.84 ppb/yr": This result is difficult to compare with the values above. It should be also given in %/yr. REPLY: This was cited from a paper. But we also added the %-change.

l.16-20: These two sentences are confusing, please clarify. REPLY: These sentences have been rephrased.

l.21-22: This seems contradictory: how could the low sites in Switzerland (I guess, on the northern side of the Alps?) be more impacted by Italian emissions than JFJ? REPLY: They aren't necessarily on the northern side of the Alps, but probably closer to sources. The text has been rephrased for clarity.

p.19096 l.2 "as presented in Sect.3": The authors could precise: in Fig.9. REPLY: Done

l.11-12 "depending on source areas": It is vague. Where are these source areas? REPLY: Since CO is a very long lived trace gas, it's difficult to localize the source areas.

p.19097 l.9 "declining": do the authors mean "lower"? REPLY: Yes, text has been changed.

p.19098 l.3-5: Again, one cannot infer the absence of trend from a non significant result, but this idea is underlying beyond this sentence. This should be rephrased. REPLY: The text has been rephrased.

p.19099 l.13: In the cited references, are the found trends positive or negative? REPLY:The found trend is negative. The text has been changed accordingly.

l.22 "higher elevated atmospheric composition": Do the authors mean "atmosphere composition at higher elevations"? Higher than what? REPLY: Text has been changed for clarification.



p.19100 l.5-12: See above my specific comment on p.19092, l.24. REPLY: Please consider our answer to the above mentioned point.

l.19 "results are not consistent": It is not clear which results are referred to. REPLY: The text has been changed for clarification.

l.29: The study by Kaiser et al. 2010 is not in the reference list. Please precise if it is a paper in preparation. REPLY: The text has been changed accordingly.

p.19111, Fig.2: Are the averaged values calculated over a common time period? Please precise which one(s). REPLY: Yes, it's from 1995 to 2007. A respective remark is added to the figure caption.

p.19127, Fig.18: To be consistent with the structure of Section 4, the panels for NO2 should appear in second raw. REPLY: Done

Technical corrections

p.19074 l.27-29: This sentence looks badly constructed ("mapping", "but are not influenced"?). Please rephrase. Moreover, is "Therefore" appropriate? I see no clear causal relatioship with the preceeding sentence. REPLY: The meaning of the sentence has been clarified.

l.28: "larger" missplelled. REPLY: Done

p.19075 l.21 "Current": "Up-to-date"? REPLY: Changed

p.19079 l.15: For clarity, "as occasional checks" could be moved to the end of the sentence. REPLY: Done

p.19083 l.9: Please rephrase to read "The station was audited ..." REPLY: Done

l.14: Unexpected " after 100ppb. REPLY: Removed

l.19: "Zugspitze" misspelled. REPLY: Done

p.19087 l.3-5: The opening parenthesis just before "JFJ" (l.3) should be logically closed by the one just after "Zellweger et al., 2009" (l.5). Please remove the parentheses in between. REPLY: Done

p.19089 l.12, "Fig. 17-18": One should probably read "Fig. 16-17" instead. REPLY: Done

p.19092 l.10-11 "different from JFJ": "unlike at JFJ" might be better. REPLY: Done

p.19096 l.21: "has been" could be removed. REPLY: Done

p.19097 l.8: This sentence looks badly constructed ("The circumstances ... is supported ..."), please rephrase. REPLY: Done

p.19099 l.8: I would use "Although" instead of "As". REPLY: Done

l.11 "constant": "unchanging"? REPLY: Done

p.19101 l.14: bad reference, please modify to read "doi:10.1029/2007JD009751". REPLY: Done

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