Atmos. Chem. Phys. Discuss., 8, S12033–S12038, 2009
www.atmos-chem-phys-discuss.net/8/S12033/2009/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Statistical analysis of non-methane hydrocarbon variability at a European background location (Jungfraujoch, Switzerland)” *by* V. A. Lanz et al.

V. A. Lanz et al.

Received and published: 8 April 2009

The questions and comments by referee 2 were helpful to clarify some points in our ACPD-paper. We included these clarifications in the revised version of the paper. Excerpts from the comments by referee 2 appear in *italics*, directly followed by our answer. The involved changes to the manuscript are written in **bold**.

As we understand the main concern by referee 2 is that factor 1, which dominated in wintertime, must not be interpreted as an aged combustion profile (as photo-oxidation is stronger in summer than in winter):

Comment 1: *’[. . .]. Photooxidation is stronger during summer and therefore I would*

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

expect the air to be more aged during this season. [. . .]'

Factor 1 describes aged air masses and this factor is most important in winter (see Figure 4). Indeed, it is true that photochemical oxidation in the polluted planetary boundary layer is much more important in summer than in winter. However, Jungfraujoch is often exposed to the free troposphere in winter. Also during wintertime photochemistry oxidizes primary pollutants in the free troposphere, e.g. when the compounds are emitted into the planetary boundary layer in an other continent, e.g. in North America, and transported in the upper troposphere. We therefore argued that factor 1 most probably represents oxidized air of the free troposphere (FT) and a VOC composition that is related to combustive emissions (fuel, gas etc.). Based on the referee's comment, we added the following sentences to Section 3.3: **'In summer, transport times of polluted PBL air towards Jungfraujoch are strongly reduced due to higher PBL top, enhanced convection and thermally induced circulation systems in mountainous terrain, outweighing the enhanced OH-chemistry on Jungfraujoch: the air masses arriving at JFJ are more (photochemically) aged in winter than in summer (Baltensperger et al., 1997, Nyeki et al., 1998, Zellweger et al., 2003a, 2003b, Henne et al., 2005), which is different for sites that are within the PBL throughout the year. Therefore, it is plausible that a factor representing aged combustion and natural gas distribution (factor 1) is enhanced in winter.'**

Comment 2: *'There are certainly interesting aspects in the data that are touched, such as the correlation of factor 1 with methane or the analysis of potential source regions with back trajectories. But this analysis could have been done also by using concentration data of individual compounds. This would yield potential source regions of real compounds instead of factors the meaning of the latter being highly uncertain.'*

We agree that the individual observations are described in the factor analysis by a linear combination of some 'factors'. Even though these factors are products of a mathematical procedure, they obviously represent some important atmospheric processes, because they allow for a reduction in the very large variability of 8 years observations of 10 compounds measured at Jungfraujoch in a very simple way (using only 4 factors); this is only possible because the procedure makes use of the ratios of the individual compounds and therefore the method allows to obtain more information than the analyses of individual time series. Figure 1 indicates that the superposition of the factors allows us to explain a very large part of the variability. All (calculated) factor profiles are very close to 'real samples' (i.e. they are close to the set of different VOC concentrations at one time in the PC space) and in fact represent characteristic/extreme VOC composition that can be observed in real samples as well (as stated in the current manuscript already on P. 19535, Lines 21–23). However, the challenging part of such an analysis is the connection of the factors to atmospheric processes, such as emissions, transport and atmospheric oxidation which is discussed in the presented paper and explained in more detail in the revised one.

Comment 3: *'I share the opinion of the other reviewer who reckons that more compounds need to be integrated in the factor analysis to make it meaningful.'*

As both referees suggest the incorporation of more trace gases into the PMF calculations we understand that we have not been explicit enough about the selection of the compounds' subset as presented in this paper. We differentiate between the consideration of a) additional organics and b) additional inorganics for PMF:

a) On the choice of organic compounds

We agree that many receptor studies included a larger number of measured species in the factor analysis. The currently chosen dataset for PMF includes all organic compounds measured at Jungfraujoch with atmospheric lifetimes between 2 days and 6 months (P. 19535, Lines 2–5; P. 19542, Line 26; Table 1 on P. 19551) which have been measured during the last 8 years. The concentrations of trace gases with longer lifetimes have different properties which are not studied in this paper. Shorter lived organic species (e.g. MVK) have only been measured during four seasonal campaigns in one year and therefore they were not included in this study. (The results of these campaigns were published by Legreid et al., 2008). Very short-lived compounds (e.g., isoprene) have too low signal-to-noise ratios at this site to interpret their variability, including more persistent substances (such as HFCs) yields factors that do not represent sources but rather long-term trends or hemispheric exchange, because emissions of the latter species were drastically reduced during the past years. Furthermore, compounds with shorter (< 2 days) or longer atmospheric lifetimes (> 6 months) are expected to define their own factors, when included into a data matrix that consists of compounds with intermediate lifetimes (in these cases factor analysis is probably not the best tool for the analysis).

b) Why not to include inorganic species and methane in the PMF matrix

We agree that the inclusion of inorganic species and methane would increase the number of species in the factor analysis. The latter compounds were included in the presented analysis already as 'external PMF markers' (i.e. the time series of the PMF factors were compared with the time series of the inorganics; P. 19540 – P. 19541, Table 2 on P. 19552, and Figure 5 on 19558). However, we neither included inorganic species (such as NO_x and CO) nor did we include CH_4 in the factor analysis because of the following reasons:

- Based on the concentration ratios of the species we first attributed the factors to different source regions/sources and different atmospheric processes/lifetimes. However, we found it very useful to have independent information in order to critically discuss the attribution of the factors to source regions and atmospheric processes. For this discussion the concentrations of the inorganic species and methane was very useful.

- Entity of chosen organics. The presented data set for PMF (Table 1, P. 19551) consists of primary and predominantly anthropogenic substances. In this respect, the chosen organic gases represent an entity. However, other species have other sources such as the oxidation from other hydrocarbons (e.g. CO in the free troposphere) or

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

other emission sources (such as methane which includes strong biogenic sources). The inclusion of largely biogenic and partially secondary species breaks down the entity of the chosen organics and furthermore bears some conceptual problems: either the secondary portion of carbon monoxide, say, is attributed to a factor representing primary emissions or, conversely, secondary portions of some inorganic species may form their own factor, but the exclusively primary organics might nonetheless be forced by PMF to positive values within the same 'secondary factor'. Such artifacts and more, similar ones might be introduced to the PMF analysis when these inorganic species are added to the organics *a priori*. This was avoided by the current selection of PMF species and making use of the inorganics *a posteriori*. It would be rather unfortunate if primary compounds were mathematically used to reconstruct secondary components and vice versa. By using exclusively the organics for PMF, a straightforward interpretation of the factors is possible.

- Data weighting. A critical trait of the algorithm used in PMF is that each data point is weighted by its uncertainty. PMF is based on an uncertainty weighted least-square approach (Equation 3, P. 19532). This implicitly also means that ideally only compounds that have comparable instrumental errors should be input together into a data matrix for PMF. Different instruments need different calibrations etc. and their errors are often not directly comparable and, therefore, they should not be put into the same PMF data matrix (or a rather highly-subjective weighting of the reliability of the different instrumental errors needs to be introduced). This is different for approaches that do not take data uncertainty into account, e.g. for the simpler setting of a standard PCA (principal component analysis). The concept of PCA however assumes all data points have equals weights. This is not realistic and Paatero and Tapper (1993, 1994) have shown that data-weighting is an advantage of PMF over other techniques of factor analysis.

- Data availability. About 10000 samples of organic trace gases are available for the presented analysis. Since methane (CH_4) was not measured at Jungfraujoch before the year 2005 less than 3000 samples match the other organic samples (see Table 2,

P. 19552). Numeric values are needed for each element in the PMF data matrix.

We realize that the issues above were not discussed in the current manuscript and may have caused some confusion. For clarification of the article we added the following sentences to Section 2.2: **’The organic compounds selected for PMF (Table 1) represent an entity with respect to their origin (primary and predominantly anthropogenic sources) as well as to error calculations (all compounds were measured by the same GC-MS technique). OVOC measurements (including compounds with strong biogenic sources) were only measured during four seasonal campaigns in 2005 (Legreid et al., 2008) and were therefore not included in the study. In this analysis correlations between the inorganic compounds and the PMF factors were used to assist factor interpretation (e.g., see Sect. 3.3).’**

Additional References

Baltensperger U., Gaeggeler H. W., Jost D. T., Lugauer M., Schwikowski M., Weingartner E., and Seibert P.: Aerosol climatology at the high-alpine site Jungfraujoch, Switzerland, J. Geophys. Res., 102, 19707-19715, 1997.

Nyeki S., Li F., Weingartner E., Streit N., Colbeck I., Gaeggeler H. W., and Baltensperger U.: The background aerosol size distribution in the free troposphere: An analysis of the annual cycle at a high-alpine site J. Geophys. Res., 103, 31749-31761, 1998.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19527, 2008.