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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular distributions of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in $PM_{2.5}$ collected at Mt. Tai, in North China in 2014" *by* Yanhong Zhu et al.

Anonymous Referee #2

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General Comments:

Zhu et al. discuss trends in concentrations of particle-phase polar oxygenated organic compounds during one month of summer 2014 at Mount Tai. The dataset presented is interesting, particularly in showing daytime versus nighttime measurements, boundary layer height (BLH) estimates, and a broad range of chemical species concentrations with ~high frequency. The use of principal component analysis (PCA) is also an apt way to summarize potential sources. However, the extent of discussion in the current draft is insufficient for these data and results: each data analysis piece is discussed separately, and cohesion is needed between the BLH estimates, back trajectories, PCA

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factors, and concentration trends. I believe the article therefore requires major revisions before final publication in the form of reorganization of the results and discussion, and additional synthesis of the conclusions.

Specific Comments:

There are several pieces of background information that are missing from the introduction. These include brief discussions (with references) of:

- Boundary layer behavior in complex topography;

- Biomass burning emissions and the new regulations mentioned (Pg. 8, line 26); and

- More about general emissions at Mount Tai.

The methods section is lacking key information. Examples of additional information to be included (can go to supplemental material if desired):

- Details about the VOC concentrations: which species do “VOC concentrations” include?

- Discussion of whether the sampling period is representative of Mount Tai during all seasons, years, etc. (concentrations, BLH, and back trajectories)

- The method for calculating limits of detection for the measured chemical species.

- Uncertainties (specify type; e.g., standard deviation) about the measurements of each chemical species reported

- Meteorological conditions and variations during the study

- Frequency of blanks

- A brief synopsis of data used in this article from Zhu et al., 2017

- In the PCA analysis: is the replacement of values below detection limit with have the value a common convention? I am not familiar with this technique, and it seems like it

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may bias the measurements low.

-Please report a reference for this if possible, and discuss briefly (this can be in the supporting information).

The results and discussion section should be reorganized to offer a more cohesive analysis of all analytical tools/results. Some specific examples include the following.

- A relationship can be drawn between back trajectory clusters and the chemical concentrations/PCA factors. Do dates of influence of particular source regions align with sources/PCA factors? Do the dominant back trajectory clusters change between the first and second halves of the study, which seem to have different chemical features?

- The authors note that there are relationships between the VOC concentrations and those of the polar organic species measured. Please provide an explanation of what this relationship might be: are the higher concentrations of polar organic species at Mount Tai in 2014 a result of the aging of the measured VOCs? Could they have been directly emitted together as primary aerosol particles? Both? Please support with references. If possible and relevant, please also consider individual VOCs.

- A relationship could be drawn between how BLH estimates might alter the effect of long-range transport (back trajectories) on concentrations. Even if the BLH is only above the sampling location during some sampling times, these could be interesting.

The MGly recovery is estimated to be $\sim$50%. Do the authors expect trends in concentration of MGly, then, to be meaningful? Why is the recovery of Gly expected to be so different?

Daytime/nighttime differences:

- The daytime/nighttime analysis gives a summary of the results, but provides little explanation for the observations. How are these trends informative? Please explain the hypothesis about aqueous photochemical reactions (pg. 10, line 22) more thoroughly and with references. Can the similarities between daytime/nighttime concentrations be

supported by looking at diurnal changes in relative humidity, or contrast between high-elevation/summit and low-elevation/base measurements of any kind at Mount Tai?

- The authors suggest that the strengths of nighttime vs. daytime correlations in Figures 2 and 3 explain daytime/nighttime ratios reported (although, confusingly, these ratios are ∼1 for most species). However, the correlations are not clearly different (daytime/nighttime) in either figure. Please find agreement between the daytime/nighttime ratios, Figures 2 and 3 correlations, and the hypotheses about diurnal variations in concentrations/atmospheric processes.

- Figure 3 includes one outlying point at ∼1800 ng m-3 C2 and ∼35 ðİIJĞg m-3 SO42-; what is the result of removing this point? This looks to me to be driving the daytime/nighttime difference. There is certainly a relationship between these two chemical species, but this may not be easily related to the iron-oxalate hypothesis drawn.

Although the BLH discussion is essential to this analysis, uncertainty in estimating the BLH using a model at a mountaintop should be discussed briefly. In addition, results from the Mount Tai Experiment (Kanaya et al., 2013) showed that their sampling site was above the BLH during many days, and within the residual layer some nights. Please contrast the estimates of these two studies briefly.

Could any of the back trajectories suggest that regional emissions from the previous day or two impacted the measured concentrations? Long range transport is suggested to be dominant throughout the study, but perhaps regional emissions have been transported aloft due to topography and/or convection.

Contrast with other studies:

- The contrast between this summer 2014 study at Mount Tai and others is informative. However, the ratio used for conversion of TSP to PM2.5 likely introduces large uncertainties. Is this ratio relevant for Mount Tai or the North China Plain? For summer? For 2014? Specify briefly, and consider the degree of confidence that the reader can

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have in these estimated concentrations, including significant digits of concentrations reported. Please note that composition is size-dependent for aerosol particles.

- Please consider the season, year, and mountainous/urban/rural category of these studies (include study year in the comparison table as well).

Biomass burning discussion:

- The biomass burning discussion is interesting, but incomplete. The authors draw the conclusion that, "...from 2006 to 2014, biomass burning decreased by about 80%." This conclusion cannot be drawn from the estimated concentration of a single species (levoglucosan). Many factors could confound this relationship, such as atmospheric oxidant concentrations, or meteorology during the study. Please rephrase and support with additional observations.

- Please include more information about the "emission hotspots" mentioned on pg. 11, line 27, along with references. Are these the locations of biomass burning events? On a related note, please discuss whether there is any indication that biomass burning events decreased between the first and second halves of the study (satellite data, perhaps). Do trends in concentrations match observations in biomass burning events?

PCA analysis:

- Please be more explicit about the methods and the vocabulary used to describe the results. Specifically, in the methods section, the authors should include not only the information at the beginning of section 3.6, but also whether the data were standardized or mean-centered. Are the "weighting factors" the same as the "factor-loadings"? Please label which values are reported in the table.

- A distinction is made between daytime and nighttime concentrations in the PCA analysis, and slightly different factors are identified. Please provide explanations for differences between all of the daytime and nighttime factors. (In the case of the nighttime factor 4, mixed marine and plastic burning emissions are suggested—please explain

further and cite references.) Please consider agricultural activities as a possible emissions source.

Minor Comments (please change with revisions):

The phrase “dicarboxylic acids and related compounds” is overused in the paper, and must be abbreviated for clarity. Please find an appropriate way to do so. An example might be “polar organic compounds (POCs)”.

When reporting values summarizing the campaign data, be clear about whether the value is a mean, etc., in every case.

Throughout the document, please revise for grammar and accuracy of the wording. For example, on pg. 7, line 29, “trends” should be “concentrations”.

Please choose a consistent spelling and format for the following terms: “airmass”, “daytime” vs. “day”, “nighttime” vs. “night”, “back trajectory” vs. “back-trajectory”.

Pg. 3, line 8: Is this really true that dicarboxylic acids and related compounds are typically studied in TSP rather than PM2.5? Please revisit.

Section 3.2 (and throughout): The discussion of the contributors to “dicarboxylic acids and related compounds” would be much stronger with some context (rather than an empirical grouping of chemicals based on methods). What does this category of chemicals represent in the atmosphere? Could it be representative of water soluble organic carbon? Oxygenated organic species in general? Please support this with references.

Top of pg. 8: Please clarify the definition of each of the percentages reported here. Are these all percentages of the total dicarboxylic acids concentration?

There are several scientific language choices that should be reconsidered: “significant” should be used only when statistical significance is demonstrated; “levels” of chemicals is not precise - please use “concentrations”; “considerable amount” is not precise – please use “substantial concentration”, for example.

Where coefficients of determination are discussed, please also report the values within the text.

Please introduce each chemical abbreviation in the article body (e.g., “C2” for oxalic acid, “VOCs” for volatile organic compounds).

Note that phthalic acid and azelaic acid both have primary as well as secondary atmospheric sources.

“Boundary layer height” should be consistently abbreviated to “BLH”.

References

Kanaya, Y., Akimoto, H., Wang, Z.-F., Pochanart, P., Kawamura, K., Liu, Y., Li, J., Komazaki, Y., Irie, H., Pan, X.-L., Taketani, F., Yamaji, K., Tanimoto, H., Inomata, S., Kato, S., Suthawaree, J., Okuzawa, K.„ Wang, G., Aggarwal, S. G., Fu, P. Q., Wang, T., Gao, J., Wang, Y., and Zhuang, G.: Overview of the Mount Tai Experiment (MTX2006) in central East China in June 2006: studies of significant regional air pollution, Atmos. Chem. Phys., 13, 8265-8283, 2013.

Zhu, Y., Yang, L., Kawamura, K., Chen, J., Ono, K., Wang, X., Xue, L., and Wang, W.: Contributions and source identification of biogenic and anthropogenic hydrocarbons to 15 secondary organic aerosols at Mt. Tai in 2014, Environ. Pollut., 220, 863-872, 2017.

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