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Atmospheric
Chemistry
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Discussions

Interactive comment on "Summertime contributions of isoprene, monoterpenes, and sesquiterpene oxidation to the formation of secondary organic aerosol in the troposphere over Mt. Tai, Central East China during MTX2006" *by* P. Q. Fu et al.

Anonymous Referee #1

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General comments: This manuscript presents a field campaign to measure secondary organic aerosol (SOA) tracers at the sampling site in Mt. Tai, China. The tracer compounds reported in this study have been well documented in earlier studies from field studies and aerosol chamber experiments. The authors suggest the use of (sum of isoprene oxidation products)/(sum of monoterpene oxidation products) (Riso/mono) as an indicator to estimate the contribution of isoprene and monoterpenes to biogenic SOA formation in various ecosystems. The idea is certainly attractive and reason-able. However, there is a fundamental problem with this approach as the authors used in this manuscript. The spectrum of compounds that the authors have detected in this study is far from complete, especially for monoterpene oxidation products. Indeed, monoterpene oxidation products that the authors have detected are known to be rather minor monoterpene oxidation tracer compounds in ambient aerosols except for pinonic acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). This raises a serious question to whether this ratio has any meanings to it. In order to obtain any meaningful Riso/mono values, the authors need to include organosulfates and nitrooxy-(or nitrated)organosulfates originating from both isoprene and monoterpenes as they are likely to contribute significantly to biogenic SOA in ambient aerosols, especially anthropogenically influenced areas (see e.g. Lukács et al. 2009). The authors rely heavily on the use of surrogate compounds for quantification. This may be acceptable if the focus of the study is to provide a rough estimate of the concentrations of tracers that are newly identified or if the surrogate compound is a homologue of the target compound. However, the quantification is the key for this study; the whole discussion is based on the quantitative results from the chemical analysis yet large part of quantification work is performed using a handful of surrogate compounds. This leaves the impression to the readers that tentative quantification of few compounds using a surrogate compound is sufficient for publication even the focus of the study is the quantitative assessment of the contribution of a large group of compounds to local PM. In addition, the interpretation of the data is very weak. Only the most obvious observations are stated and no connection is made to the atmospheric chemistry of the region. As a result, this reviewer is not able to recommend this manuscript for publication in ACP. The detailed comments are as follows.

Lukács, H., A. Gelencsér, A. Hoffer, G. Kiss, K. Horváth, and Z. Hartyáni (2009), Quantitative assessment of organosulfates in size-segregated rural fine aerosol, Atmospheric Chemistry and Physics, 9, 231-238.

Specific comments: Pp. 16943, line 16: What do the authors mean by “among the highest in the aerosols studied in different regions"? Do the authors mean this study, other studies that the authors are involved or available literature data? Furthermore, how reliable is this ratio when the quantification in this study relies heavily on the use of surrogate compounds? In addition, the authors have determined only five monoterpene oxidation traces that are far from complete. Better quantification attempt is needed for both isoprene and monoterpene oxidation traces as detailed synthetic methods are described for some of major compounds that the authors have detected. I suggest removing this sentence completely.

Pp. 16943, lines 17-18: It is not too clear how high O3, NOx and OH concentrations relate to high isoprene oxidation product/monoterpene oxidation product ratios. Especially, how does high NOx lead to high isoprene oxidation tracer concentration in the particle phase? Here, the ratio of VOC/NO2/NO rather than the total "NOx" is important for the distributions of both isoprene and monoterpene oxidation products. How have the authors determined the isoprene flux? What about monoterpenes?

Pp. 16943, lines 18-19: What is the tracer based method? Is it simply the sum of all detected compounds? If this is the case, it is misleading to call this number as secondary organic carbon (SOC) as the compounds that the authors have determined do not cover a spectrum of compounds that are considered to be both anthropogenic and biogenic secondary organic compounds. Furthermore, a term "monoterpenes" is not exactly correct when the authors have detected mostly a-pinene oxidation products.

Pp. 16943, line 23: This reviewer feels that this statement is unwarranted for above mentioned reasons. The detected compounds do not cover a spectrum of compounds that originates from the oxidation of isoprene and a variety of monoterpenes (including isoprene and monoterpene originating organosulfates and nitrooxy-organosulfates).

Pp. 16944, line 8: This is rather vague. How much is the estimated emission of biogenic VOC globally?

Pp. 16944, lines 9-16: This part of introduction is rather poorly written. I feel it reads better if the authors start from the BVOC emissions including isoprene first then move to SOA.

Pp. 16944, lines 15-16: I failed to grasp the meaning of this sentence. How can 'SOA yields' enhance the 'predicted SOA formation'? Do the authors mean that isoprene oxidation products may contribute significantly to SOA even its SOA yields is typically lower than monoterpenes because of its large emission? The authors need to clarify this point.

Pp. 16944, line 22: References are far from complete. I suggest to cite a recently published review by Hallquist et al, 2009 here.

Hallquist, M., J. C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J. Dommen, N. M. Donahue, C. George, A. H. Goldstein, J. F. Hamilton, H. Herrmann, T. Hoffmann, Y. Iinuma, M. Jang, M. E. Jenkin, J. L. Jimenez, A. Kiendler-Scharr, W. Maenhaut, G. McFiggans, T. F. Mentel, A. Monod, A. S. H. Prevot, J. H. Seinfeld, J. D. Surratt, R. Szmigielski, and J. Wildt (2009), The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmospheric Chemistry and Physics, 9, 5155-5236.

Pp. 16945, line 5-6: I failed to grasp the meaning of this sentence. Does this mean 'modeled isoprene concentration is higher at higher altitude than other biogenic SOA precursors' or 'modeled isoprene oxidation product concentrations are higher than other biogenic SOA compounds at higher altitude'? The authors need to clarify this point.

Pp. 16946, line 18: Have the authors synthesized cis-norpinic acid? If so, please provide a reference for the procedure. As far as I know, trans-norpinic acid was available from Sigma-Aldrich in the past but not a cis isomer. The supplier information can be helpful.

Pp. 16946, line 18: If it is trans-norpinic acid, how have the authors achieved the

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positive identification? Are the retention times for both standard and ambient samples the same? The authors need to clarify this point.

Pp. 16946, line 19-21: At the very least, the quantification and identification of methyltetrols and MBTCA MUST be performed using the authentic standard compounds. There is no reason to rely on 'surrogate' compounds for these two as the synthetic procedures for methyltetrols and MBTCA are described well and they are not overly complicated. It is not acceptable to use 'surrogate' compounds for the quantification when the target compounds can be readily synthesized (or purchased for that matter) using standard laboratory apparatuses.

Pp. 16946, line 20: Why have the authors decided to use pimelic acid and pinic acid as surrogates? How have the authors determined likely errors originating from the use of these compounds as surrogates? It is hard to accept them as surrogates as both of them are not homologous compounds to MBTCA and beta-caryophyllinic acid.

Pp. 16946, line 26: Here, the authors state that trans-norpinic acid is used for the recovery test. Have the authors determined cis or trans-norpinic acid in the samples? This reviewer is not aware of mechanisms forming a trans isomer of norpinic acid from the atmospheric oxidation of monoterpenes. The authors need to clarify this point.

Pp. 16946, line 27: The data need to be corrected for the recoveries. Especially, the concentrations of 3-hydroxyglutaric acid and cis-pinonic acid appear to be underestimated at least 30% without the recoveries.

Pp. 16947 onwards: How comparable are these results to the cited studies when the authors have used largely surrogate compounds?

Pp. 16948, lines 10-15: There are a number of other papers reporting these compounds.

Pp. 16948, lines 18-20: I suggest removing this sentence. There are a number of reasons why the concentration of pinonic acid is higher than that of pinic acid in ambient

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aerosols and the vapor pressure may have little to do with this observation.

Pp. 16949, lines 23-24: Pinic acid seems to show a diel pattern in Figure 1. This is consistent with a recently published article by Kourtchev et al. (2009). In addition, both methyltetrols exhibit a clear diel cycle between May 29th and June 3rd. Some discussion of this is needed here.

Kourtchev, I., L. Copolovici, M. Claeys, and W. Maenhaut (2009), Characterization of Atmospheric Aerosols at a Forested Site in Central Europe, Environ. Sci. Technol., 43, 4665-4671.

Pp. 16950, line 2: Do the authors have mechanisms for this reaction? As far as I know, this is still unproven. It is hard to imagine how hydroxy dicarboxylic acid can be formed from the reaction of dicarboxylic acid and OH in the presence of NO.

Pp. 16950, line 23: I suggest changing ’lower-generation’ to ’early generation’.

Pp. 16951, line 7: It is more likely that this originated from a stress (biomass burning) induced emission of sesquiterpenes from vegetation rather than the biomass burning process itself.

Pp. 16951, line 11: This is speculative and should be removed. Why are sesquiterpenes emitted from vegetation fires? Are sesquiterpenes enriched in crop species? The authors need to substantiate this argument with references.

Pp. 16951, lines 13-15: If this is the case, wouldn’t isoprene and monoterpene oxidation products show the same trend? Why is beta-caryophyllinic acid the only compound influenced by biomass burning OC? As the authors stated, pinonic acid has much higher vapor pressure than other compounds detected here and its gas/particle partitioning is more likely influenced by biomass burning OC compared to beta-caryophyllinic acid.

Pp. 16951, line 23: Please provide references.

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Pp. 16951, Hierarchical cluster analysis (HCA): How have the authors performed the HCA analysis? Detailed information about the procedure must be given. Pp. 16952, line 5 and lines 13-14: Pinonic acid and pinic acid may also originate from ozonolysis of alpha-pinene. Pinonic acid is unlikely to be formed from the oxidation of beta-pinene.

Pp. 16952, line 15: I suggest changing higher-generation’ to ’later generation’.

Pp. 16952, Enhanced contribution of isoprene oxidation products: I am not convinced that the ’Riso/mono values’ determined in this study can be used anything meaningfully when only a small group of rather minor alpha- or beta-pinene oxidation products are determined. The oxidation of both isoprene and monoterpenes are rather complex and their product distributions are strongly influenced by ambient conditions (i.e. T, RH, oxidants, NO/NO2/HO2/RO2 etc.). The authors may compare the results obtained in this study to the results from other regions but it goes a little too far to suggest ’Riso/mono values’ to be used for estimating the contribution of isoprene and monoterpenes to biogenic SOA formation in various ecosystems when only a limited number of compounds are determined using ’surrogate’ compounds.

Pp. 16952, line 24: It is misleading to state ’monoterpene oxidation tracers’ as the authors have determined only a small group of alpha- or beta-pinene originating oxidation compounds.

Pp. 16953, lines 15-16: Do the authors mean isoprene is the ’missing’ large source of organic aerosol in the FT?

Pp. 16953, lines 17-19: More measurements are needed at different locations to substantiate the authors’ claim.

Pp. 16953, line 20: What do the authors mean by ’enhanced SOA formation’? This is simply ’higher concentrations of isoprene oxidation products’.

Pp. 16953, lines 24-26: This sentence is unclear. Is it a mass concentration or a number concentration? Is it the highest in China or the world? Are there any connections to the accumulation mode particles and the high concentration of isoprene oxidation products?

Pp. 16954, line 4: Are they concentrations or mixing ratios? The mixing ratios (or concentrations) are not a good indicator for the completeness of the reactions under atmospheric conditions. How have the authors determined the conversions of isoprene and monoterpenes without initial mixing ratios for them?

Pp. 16954, line 6: This part contradicts the authors' earlier statement (Pp. 16949, lines 23-24). Indeed, the temperature can be important for the gas/particle partitioning but the argument put forward by the authors to rationalize higher isoprene tracer concentrations in the nighttime samples than the daytime samples is unsubstantiated. If this is the case, why should monoterpene oxidation products behave differently? 2-Methyltetrols are known to be present predominantly in the particle phase and are unlikely to be influenced by temperature yet they also show higher concentrations in the nighttime samples according to Table 2. If you pay close attention to Figure 1, the opposite trend (i.e. higher isoprene oxidation products during the daytime) can be seen between May 29th and June 3rd. It is evident that the higher nighttime average concentrations of isoprene SOA tracers summarized in Table 1 are likely caused by the extremely high concentrations observed on June 20th. Furthermore, are the differences statistically significant, especially for monoterpenes?

Pp. 16954, lines 12-26 and Figure 5: It is hard to see any relationship between the mixing ratios of O3 and NOx, and Riso/Rmono from Figure 5. It is much more informative to show scatter plots when there is a relationship between two variables. This part is largely a collection of random information and it leaves readers to interpret the data presented in this study. Both OH and O3 were high during the sampling period. How do they relate to high Riso/Rmono. Does the ratio of OH to O3 relate to the compound distribution? How does the ratio of NO to NO2 change? Does high NO relate to the presence of some compounds? Does high O3 relate to high temperature?

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Pp. 16954, lines 29: Were air masses passing through the sampling site significantly influenced by cloud chemistry? Alternatively, have the authors determined higher isoprene oxidation products when the sampling site was covered in polluted cloud? The authors need to clarify this point.

Pp. 16956 Estimated contributions of BVOCs to secondary organic carbon: The authors need to clearly state that the numbers presented here are rough estimation and contain large uncertainties.

Pp. 16957 line 4: Why should the Mt. Tai data be consistent with the data obtained in North Carolina?

Pp. 16957 line 18-Pp. 16958 line 7: This section is largely a descriptive summary of the manuscript rather than conclusions.

Pp. 16957 line 24-Pp. 16958 line 3: It is hard to draw a conclusion from the authors' data if the high OC or pollutants had any influence on the gas/particle partitioning of SOA. Conclusions need to be drawn solely from what the data actually shows.

Pp. 16967 Fig. 1: It helps the readers to differentiate the day and night samples if the authors could use e.g. a black filled circle for the night time samples.

Pp. 16971 Fig. 5: 'Concentration' should be 'mixing ratio'

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 16941, 2009.