Atmos. Chem. Phys. Discuss., 9, C3538–C3543, 2009
www.atmos-chem-phys-discuss.net/9/C3538/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "VOC measurements within a boreal forest during spring 2005: the role of monoterpenes and sulphuric acid in selected intense nucleation events" *by* G. Eerdekens et al.

Anonymous Referee #2

Received and published: 3 August 2009

Referee Comment on acp-2009-293 – G. Eerdekens et al. VOC measurements within a boreal forest during spring 2005: the role of monoterpenes and sulphuric acid in selected intense nucleation events

General Comments.

The work presented in this manuscript addresses open questions on the formation of secondary organic aerosol. The experimental approach is sound and the data presented is of importance and significance to the scientific community. The manuscript is well structured and well written. Data is largely represented in well arranged graphics even though in some occasions on the verge of being overloaded. In these cases the

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

reader is left alone with sparse captions and not even all figures are mentioned in the text (see below). The interpretation of the data is mostly well established; some statements, however, are speculative and need substantiation. With regards to ammonia the authors revert to data that is not part of this campaign, neither described in the experimental description nor cited properly. The ultimate statement that the work elucidates the "role of monoterpenes in [. . .] nucleation events" EITHER needs experimental substantiation OR Discussion and Title must be rephrased (see below). I have no doubt that the authors will be able to take account of the below mentioned questions and problems/issues in a thorough and satisfactory manner in the on-line discussion and in a revision of the manuscript and I suggest publication in ACP if revised accordingly.

Specific Comments.

Title (see below "ultimate statement")

Introduction

p12784, line 22+: "Several clear aerosol nucleation events. . .". In Riipinen et al. (2007) "clear nucleation" is used in the context of clearly detectable through particle number and growth. Here the authors contrast that with "others" (other events), that occurred synchronously with monoterpene bursts and further "others" correlating with sulphuric acid. Please, clarify if here "clear" means clear of the influence of specific trace gases and if so, do not use the abovementioned citation in this context – or rephrase these sentences to avoid the contradiction.

Experimental

p12790, line: Is rH accuracy 2% absolute or 2% relative to the actual reading?

Results

p12792, line 5: "Such a diel profile has not been observed previously[. . .]" - the authors might want to add "at this site".

ACPD

9, C3538–C3543, 2009

12792, line 15: Fig. 6 appears before Fig. 5 in the text. For assigning indices to the figures use the order of their appearance in the text.

With regards to figure 7 only panel a) and b) are mentioned in the text. Fig 10 only the aspect of labelling burst (P, Q, R) and Fig 10a appears in the text. Similarly panels 11c and 12b are used in the text but not their respective other aspects. Figure 13 is not mentioned at all. Why bother to put all that information in but not using it for your arguments?

12792, line 16: "size [. . .] generally varied between 20 and 110nm". Please, specify what data-derived value is taken for this statement (average size, median size, particle fraction exceeding a certain concentration threshold,. . .)

p12793, line 16+: "There are no grounds to say that the forest soil was a source". This is a statement on a (by design of the experiment) missing evidence for a fact. This is of no scientific value. If this sentence was meant to say what it reads there is no reason to have it in the manuscript. In fact it may be misleading and therefore should be omitted. OR, did the authors carry out experiments that allow a statement on the soil NOT being a methane source? If so, please explicate and substantiate.

p12793, line 23+ "From Fig. 2 [. . .] aerosol concentrations decrease [. . .] to 350-500cm-3 on 19 April. Low levels persist until the 23 April [. . .]" Fact is, that dN/dlogD in fig 2 reaches its minimum of ∼300cm-3 on 18 April, rises sharply to ∼2000cm-3 around midnight, goes just below 500cm-3 in the first half of April 19th and exceeds 3000cm-3 in the evening. There is another sharp rise (10fold!) to numbers close to 3000 just before midnight on 20 April and it does not go below 500cm-3 until May 1st (thus "350-500cm-3 on Apil 19" is incorrect!). This is all rather difficult to get from figure 2 as there are no grid lines. Please, specify "low levels" in the text and give a correct description (with correct numbers) of what is really seen in figure 2.

p12794, line 11+: "[. . .] night-time gradients were usually slightly stronger that those seen by day". This statement is too general as figure 5 does not show clear day/night

ACPD

9, C3538–C3543, 2009

differences in the gradients with the exception of monoterpenes. Substantiate the gradient statement by numerical evidence and prove a general significant difference between day and night using statistical methods.

p12795, line 20: "[. . .] 3nm particles [. . .]" in event 1. In figure 6 event 1 seems to start only with significant particle numbers for particles larger than 6nm whereas the bursts on April 25th, 26th and 27th grow from particles <3nm (which were not taken into account for event 2). Can event 1 be truly classified as nucleation event? In a real nucleation event with the total particle concentration bursting as high as 8000cm-3, how could dN/logDp[3-6nm] be at most a few hundreds per cm3? It seems that a potential nucleation event happened somewhere else and that airmass passed the site somewhat later, when the bulk of the particles had already reached a bigger size. Please comment and clarify.

p12797, line 5+: The authors mention ammonia measurements that are not described and not cited. Who measured ammonia (is the person co-author) and how was ammonia measured (Experimental) – if ammonia is relevant, provide the full information.

p12798, line 21+: "[. . .] event 1 was strongly correlated to changes of wind direction and humidity [. . .] and characterised by strong correlation with sulphuric acid [. . .]" It does not seem that the authors calculated linear regressions between the parameters they claim to be strongly correlated. Therefore the use of mathematical terminology is somehow misleading. (also in Abstract, p12783, line6, in Discussion and Conclusions p12803, line 6 and at several other places throughout the manuscript) This is even more striking for event 2 where they claim a "clear correlation" between monoterpenes and "the events" (particle number?) (Results p12802, line 6+, but also Discussion and Conclusion p12803, line 28+). Furthermore they state a correlation of the particle burst with CO2, NO2 and many, mostly unknown VOCs and an anti-correlation with ozone. Non of these correlations is substantiated by putting the time-series into mathematical relation with e.g. particle number concentration, which would allow for a measure how strong the parameters correlate. The use of the term correlation in this context

ACPD

9, C3538–C3543, 2009

of the co-occurrence of particle bursts and monoterpene concentration increases (and others) is misleading as it suggests a causal connection. This, however, is neither established mathematically nor substantiated by chemical analysis of the aerosol particles or monoterpene oxidation products.

p12799, line 14+: “The angular deviation of the wind with height became more apparent after midnight with deviations of 15-30° between different levels." Wind directions at which levels were taken into consideration of this? Figure 2 shows the wind speed at 8.4m is <1ms-1 during event 1, data from 4.2m is not displayed at all. At low wind speed wind direction becomes meaningless particularly when influenced by obstacles. So if wind measurements on all heights are considered then the angular deviation might not be a significant parameter. Please comment and clarify how the angular deviation was derived.

p12800, line 26+: No m69 and m71 data is shown here. The claimed correlation between m69 and tolouene (m79 signal) is not shown. Assigning m69 to isoprene and connecting isoprene emissions to local anthropogenic sources is highly speculative. The authors may want to show data and present striking evidence that the rise in m69 is due to traffic related isoprene emission or similar sources. If this cannot be substantiated the paragraph needs to be revised thoroughly.

The ultimate statement (as advertised in the manuscript’s title) the work elucidates the “role of monoterpenes in [. . .] nucleation events” is based on the following indirect evidence: In event 2 particle bursts and strong increases of monoterpene concentrations are observed simultaneously. “Event 2 bears some resemblance to [pinene ozonolysis] studies” (p12805, line 18+) by Bonn and Moortgat (2002). In those laboratory studies concentrations of monoterpenes and ozone were 500ppbv, non-volatiles nucleated and semi-volatiles were able to condense on preformed particles and caused an increase in particle size and volume. There may be similarities in the dynamics of some physical parameters of the aerosol in those laboratory experiments and the here presented field studies but the authors fail to

ACPD
9, C3538–C3543, 2009

* substantiate that monoterpene oxidation is of any significance for particle formation and growth under the observed circumstances and concentrations

* show the appearance of monoterpene oxidation products in the air masses of event 2

* prove that monoterpene oxidation products (non-volatile and semi-volatile) show up in the aerosol and contribute significantly to the particulate matter (lack of chemical analysis of the aerosol particles).

This does not mean that monoterpenes do not play a role in event 2 but the presented data does not essentially elucidate the role of monoterpenes neither in such selected events nor in general. The authors need to emphasise the hypothetical character of their lines of argumentation (p12805, line 16 – p12806, line 11) in the Discussion and Conclusion section, in the Abstract and in the Title and address the abovementioned issues.

Technical Corrections

Results

p 12792, line 8: replace “these” with “those” as it refers to other work.

References

p12811, line 8+: Reimann et al. (2000) Atmos.Environ 34 (not volume 30)

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 12781, 2009.