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Atmospheric Measurement Techniques Discussions

Interactive comment on "A dynamic plant chamber system with downstream reaction chamber to study the effects of pollution on biogenic emissions" *by* J. Timkovsky et al.

Anonymous Referee #3

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This submission describes a newly constructed gas exchange system apparently designed primarily to assess the reaction products arising from the ozonation of biogenic VOCs, and to estimate the yields of various reaction products. The experimental setup is well described and some preliminary data to assess system performance is presented.

The focus of any submission to Atmospheric Measurement Techniques should be the description of a new technique or apparatus which can't be briefly described in a paper reporting scientific results. The apparatus described here, consisting of two plant enclosure systems and an ozone reaction chamber, is described in about a page, sup-

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plemented with longer descriptions of the analytical tools employed (PTF-TOF-MS and a GC with cyrofocusing) neither of which is new or unique. The system for exposing plants to ozone is essentially a more elaborate version of the system used by Karl et al. (Atm. Chem. Phys., 2005) to assess whether oxygenated compounds observed after ozone fumigation of loblolly pine were primary (direct plant emissions or the result of ozone reacting with leaf or chamber surfaces) or secondary (resulting from ozonolysis of primary plant emissions). [At the very least, this paper should be cited.] To be sure, the system described here is far more elaborate and the inclusion of GC-PTR-TOF-MS represents a significant analytical improvement, but the basic concept of varying the positions for introducing ozone and drawing off sample for analysis is not new.

Although the system was apparently designed primarily to investigate the products of BVOC ozonolysis and not the controls over the emission of the BVOC per se, several shortcomings are apparent in the design. In particular, the light levels (130-150 micromol/m2/s at the middle of the plant chamber, but it's not clear where this is with respect to the plants themselves) are quite low and presumably limit quite strongly any light-dependent BVOC emissions, thus making more difficult the identification and quantification of reaction products. While it's not stated, it may be that these relatively low light levels were necessary lest the non-temperature controlled leaf chambers overheat under a higher radiation load. Certainly, the use of desiccators as plant chambers, while perhaps convenient, hardly represents the state-of-the-art. Well ventilated, temperature-controlled enclosures, composed of a suitably inert material (ideally glass) are feasible, and would allow far greater control over BVOC emissions. A temperature-controlled reaction chamber would also be useful for determining the temperature dependences of product yields. The flow rates used, relative to the volume of the enclosures, were quite low, implying a flushing time ($\sim$4*ln(2)/(Flow/Vol)) of nearly 30 minutes. The low flow rate may have been necessary to generate sufficient BVOC concentrations downstream for subsequent analysis (especially given the low light in the chambers), but also exacerbates any problems associated with wall reactions or losses. The GC-PTR-TOF-MS system has the significant advantage of allowing the

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separation of individual monoterpene species (and other compounds sharing the same m/z), but it would be helpful if samples for traditional GC-MS analysis (either on-line or by the use of adsorbent tubes) could also be obtained so that the compounds could be positively identified. The presence of such a large number of unidentified products may be inevitable at this stage of our understanding, but further attempts to identify them would be welcome.

The lack of agreement between yields obtained here for the ozonolysis of beta-pinene and those previously reported (Table 2) is a little disconcerting, and I didn't find the explanation terribly satisfying. On the other hand, the increased number of identified products may prove useful, particularly if further identification is possible.

I do not mean to imply that the instrumentation described is not an advancement in attempts to determine ozonolysis products and yields. The various shortcomings pointed out by the authors (low sensitivity, system cleanliness, wall reactions of losses, lack of an OH scavenger) (and they should be congratulated for being straightforward and honest with the reader) can be improved upon and I look forward to seeing some very useful data arising from this system in the future. These sorts of measurements are extremely challenging and this sort of system provides a greater level of control than large smog chambers often used.

However, I do not find the described system sufficiently unique or complicated to justify publication in AMT. When the authors gather a set of publishable data using this system, the apparatus can be adequately described in the Methods section of another, more suitable, journal.

In general, the paper is well organized and the language is clear.

p. 9011, line 11 ". . . downstream of the. . ."

p. 9015, line 6 I found this sentence a little hard to understand

p. 9019, line 19 The fact that BVOC emissions are often light dependent and increase

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during daylight hours is well-known and the subject of a large number of papers; these three references are a strange sub-set to cite

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Interactive comment on Atmos. Meas. Tech. Discuss., 6, 9005, 2013.