

Interactive comment on “Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds” by R. Holzinger et al.

Anonymous Referee #3

Received and published: 30 September 2004

Gradient measurements of volatile organic compounds in a coniferous forest plantation by PTR-MS revealed ion signals of mostly unidentified compounds above the forest canopy. These signals imply maximum concentrations within the canopy region. Larger signals were observed during the day than at night. It is concluded that these signals derive from oxidation of unidentified and highly reactive organic compounds emitted from the vegetation at this site. Fluxes of likely precursor compounds are estimated to be many times larger than previously measured emission rates of monoterpenes. From these experiments the authors conclude that global terpene emissions are probably 10 times larger than current inventories.

These data and conclusions are quite interesting but also rather provocative. The

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suggested underestimation of BVOC fluxes has quite some significance and implications for local, regional and global VOC budgets and atmospheric oxidant and aerosol formation. Therefore, the research leading to these conclusions should be carefully examined. Also, these results are in stark contrast to many, many dozens of carefully performed experiments in a wide variety of diverse ecosystems. Many of these published studies were done by enclosure experiments where oxidants were scrubbed from the enclosure air. Analysis by gas chromatography/mass spectrometry and, more recently, by PTR-MS has yielded the chemical identification of probably > 99 percent of observed emissions. Some recent studies have compared speciated analysis by adsorbent trapping and subsequent GC/MS analysis with results from Total Carbon measurements. Generally, good agreement was found in these comparisons which indicate that most of the terpenes are captured by the chromatography methods.

But, if the conclusions from this study are valid, than we have to assume that possibly 90 percent of terpene emissions were overlooked by all of these studies? These thoughts make me wonder how solid the presented experiments, interpretations and conclusions are.

Taking a closer look, I do see quite a number of questions: Several other previous experiments have found that ozone can lead to the formation of oxidated organic artifact compounds (in particular long-chain n-aldehydes) in Teflon sampling materials/tubing. Do the observed OXx profiles possibly correlate with ozone or water vapor? Have there been tests to study if OXx are formed in the sampling line system, switching valves etc from atmospheric oxidants, changes in temperature or light? Were blanks (with and without ozone) run through the sampling manifold to test for such effects? Are these results reproducible when ozone scrubbers are used as inlet filters? Were any oxidated VOC standards sampled through the manifold to establish loss rates or artifacts? Were calibration functions established with compounds that have comparable volatility and polarity? I realize that none of the OXx are structurally identified and that standards for these OXx probably are not available, but these tests could be performed with gas

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standards of surrogate compounds, for example nopinone, or other aliphatic or aromatic ketones, alcohols, esters or carboxylic acids. Ambient air samples could also be collected with impinger/derivatization techniques and subsequent GC/MS analysis to probe for the (supposedly) high levels of oxygenated products. Another easy verification would be to simply take one of the gradient inlets and ‘sniff’ air from close to the foliage of the plants at this site with the sampling line-PTRMS system, or to conduct enclosure experiments. If indeed, ten times more terpenes are emitted by local vegetation than previous GC analysis, then these compounds most likely will show up in these experiments. How do the authors refute the suspicion that observed ions may be derived from anthropogenic precursor compounds that are transported to the site and possibly temporarily retained in the sampling system?

The flux estimates are based on an interesting and novel approach using canopy sweep time analysis. I have never seen this approach applied to biosphere-atmosphere flux estimates before. Did the authors attempt to compare and validate this approach with alternative, more established methods? This could be done, for example by conducting an intercomparison with eddy correlation isoprene measurements, or possibly, with ozone or CO₂ records from the same site.

In summary, I consider these observations of high interest, but important experimental tests and details are lacking for a fair evaluation. In my opinion, interpretations and conclusions seem preliminary and premature. I do have concerns that these findings may be considered by atmospheric modelers without understanding the rather speculative nature of these results. I recommend that the questions above should be carefully addressed before acceptance of this manuscript for publication.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5345, 2004.

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