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Biogeosciences Discussions

Interactive comment on "Concentrations and fluxes of biogenic volatile organic compounds above a Mediterranean macchia ecosystem in Western Italy" *by* B. Davison et al.

B. Davison et al.

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Response to interactive comments from reviewers 1 & 2 on “Concentrations and fluxes of biogenic volatile organic compounds above a Mediterranean macchia ecosystem in Western Italy.”

We would like to thank the reviewers for taking the time to review this article. We have addressed their comments and amended the text accordingly and below responded to comments from both reviewers. The comments have been most helpful in strengthening the paper.

Both reviewers stress the need to highlight the novelty of the work which was understated previously. Sections have been added to the text including the abstract and

conclusions pointing out the rational for the work (to expand on the BEMA work and obtain high resolution isoprene and monoterpene concentration and flux data and greatly improve such measurements for oxygenated VOCs) and its novelty value (measurements made over Macchia vegetation types allowed comparison of 3 PTR instruments and techniques).

We have expanded the modelling section to include calculations of an ecological type basal emission rate for the Macchia vegetation which we derive from our canopy flux measurements. This new value is compared with the emission values from leaf and whole plant measurements made during the present and BEMA campaigns and differences are discussed. We also attempt to optimise the G95 algorithm for the Macchia vegetation type.

Specific comments

Reviewer 2, abstract: We modified the abstract according to the suggestion.

Reviewer 2, page 2185, line 9: Reference removed.

Reviewer 2, page 2187, lines 10-13: Reference included.

Reviewer 2, page 2187, line 29: The Lancaster University, CEH sample line was heated and a section has been added to the text to state this. CNR-UH did not heat their line and according to the tests conducted at the University of Helsinki for a longer and smaller sampling line (length 60 m, inner diameter 4 mm, and flow rate 1 l min−1), line losses are marginal, provided there is no condensation. This may have affected the measurements at night and in the early morning but during this period most data was not used for flux calculations. Although the measurement cabin was air-conditioned, the temperature inside was higher than ambient during the daytime. Hence we believe that condensation did not disturb the daytime measurements.

Reviewer 2, pages 2188-2189 and Table 1: True, the sampling regimes could have been more coherent, but each group had specific VOCs they were interested in moni-

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toring which led to different regimes, though a group of VOC masses was selected for measurement. However, the flux measurement and data analysis methods were essentially consistent. The small discrepancies in the methods gave us some additional information on the sensitivity of the methods.

Reviewer 2, page 2190: Table 2 shows the range for the normalized sensitivities measured by CNR-UH. Each calibration was considered valid until the next one. This was taken into account in the mixing ratio calculations. CEH-LU performed only one calibration and as the drift parameters were not changed the normalised sensitivities should remain valid for the duration of this short measurement period.

Reviewer 2, page 2191, lines 12-15: In the ambient mixing ratio measurements by CNR-UH, the water cluster ion count rate was derived from the signal of water cluster ion isotopes (M39) to extend the lifetime of the detector. In the flux measurements, the water cluster ion signal was measured directly to facilitate the lag time determination. A sentence has been added to the manuscript.

Reviewer 2 pp2195. The acetaldehyde concentrations for Lancaster and CEH have been recalculated with a new correction coefficient and are closer. The original graph used was an earlier edition.

Reviewer 2, page 2198, line 2: Reference has been added.

Reviewer 1 and Reviewer 2, pages 2200-2201: Modelling section has been improved as described in our response to the general comments.

Reviewer 2, Table 1. As previously stated each group had its own sampling regime, and while certain masses were selected for measurement others were also monitored depending on the individual group.

Reviewer 1 and Reviewer 2, page 2202: We have strengthened the conclusions according to the reviewers’ suggestions.

Reviewer 1. In reference to elevated concentrations at the beginning of each sampling

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period. The reviewer states we did not evaluate the evidence of effects of temperature, soil moisture, stomatal conductance, weather conditions etc. and did not name or evaluate the potential “stressors” and thinks it unlikely the small scale effect of instrument setup could affect the larger footprint area. The reviewer is not in a position to make such claims. An analysis of various meteorological factors such as temperature, RH and light did not show any clear correlation across the data set. While there was some agreement between temperature and oxygenated VOC concentrations for part of the data during the beginning of the second sampling period this was not consistent across the whole data set. The leaf level measurements performed throughout the campaign indicated the plants were not showing any signs of stress due to the heavy rainfall during the first period or the higher temperatures of the second period. Damaged plant can emit considerable amounts of VOC and we were therefore left with mechanical plant damage during set up as a possible source of elevated VOC concentrations as no other source could be definitely identified. The texted has been modified.

Reviewer 1: 1. lack of why exactly this study was conducted: what were the goals? objectives?

Objectives were to revisit of BEMA campaign area with better instruments and obtain VDEC canopy flux measurements which are an improvement on BEMA measurements. This also allowed a direct comparison of the PTR-MS. This has been expanded in the introduction.

Reviewer 1: 2. if there were objectives, were they met? if an objective was to improve modelling of isoprene emissions from Mediterranean vegetation, as suggested by text in the introduction, then the results suggest the answer is "no"; if a more general objective was to model other BVOC emissions the answer is "was not addressed".

This is dealt with in the discussion – canopy fluxes were obtained and compared with BEMA ‘bottom up’ models. This expands the isoprene and

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monoterpene datasets available for model verification and greatly improves the limited data for oxygenated VOCs. PTR-MS were compared and showed good agreement once different response times were allowed for, for both concentrations and fluxes. Modelling was not a prime objective of this part of the project or this paper.

Reviewer 1: 3a. lack of interpretation: assuming that the measurements are correct, no attempt was made to interpret them beyond documentation. - What drives methanol or acetone emissions in this ecosystem? temperature? light?

We did not think it necessary to discuss correlations between the VOCs measured and the various meteorological parameters measured such as light and temperature as this area of research has been well documented in the past for isoprene and monoterpene emitters. Guenther et al. (1993) and later work clearly shows such a correlation and refinements of the algorithm has been used for many years. The reviewer is correct that such correlations are less clear for methanol emissions. No obvious drivers could be inferred from the measurements implying a complex relationship with several potential pathways of methanol production. The objective of this project was to obtain flux measurements from Macchia vegetation. Mechanism studies of methanol production within the plants and its emission would be better suited to a laboratory based study which would allow control of the various external parameters which are likely to affect the production pathways.

Reviewer 1: 3b. stomatal conductance? soil emissions? plant developmental status? it is not enough to cite the literature in which these questions were addressed; YOU need to address them!

Stomatal conductance measurements made were on selected days but showed no clear correlation and this has now been stated in the text.

Reviewer 1:- why are the modeled BVOC emissions so far off the measurements? issues with the model setup? issues with onsite LAI or isoprene/monoterpene emitter density? issues with the measurements?

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The modelled data has been recalculated using the revised basal emission rates which varied throughout the measurement period rather than an average for the whole period. This provides a better fit between the measured and modelled data.

Reviewer 1: - why are all fluxes negative on the night of 9-10 May? A fluke? Would have all nighttime fluxes been negative if the stability or friction velocity criteria are relaxed? if deposition fluxes are considered real, why did you not discuss them?

We can only be confident about fluxes measured when the criteria are satisfied and most night time fluxes did not satisfy the criteria. We have state these in the text and added references.

Reviewer 1: The statement "Note however, that night time flux measurements are often associated with large degrees of uncertainty due to the stable atmospheric conditions and low wind speeds that often occur at night." is misleading, because you said earlier that fluxes made under stable conditions were discarded (why was this done anyway?).

We state “Most of the night time flux data were rejected” and in the text have further explained and referenced the micromet criteria for excluding fluxes based on stability. We can only be confident about the fluxes measured when the criteria are satisfied,

Reviewer 1: Also, your text suggests that "uncertainty" means incorrect. However, your data shows a clear auto-correlation, hence at least a qualitative correctness. Got something new here you may want to comment on?

The auto correlation may be driven by common met parameters such as wind/turbulence conditions, which are interrelated and affect the apparent flux but have no bearing on actual emissions, which is why all fluxes behave similarly.

Reviewer 1:- why do you discard BVOC flux measurements when there is no clear maximum in the covariance function between vertical wind speed and humidity? That just means there is no measurable water vapor flux; there may still have been a BVOC

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flux; and even if the BVOC-w covariance function does not show a maximum, that just means there is no measurable flux, not necessarily that the flux calculation method is inappropriate.

The water vapour maximum was only used if no maximum was identified in the PTR-MS signal. If no maximum was apparent in either data then there was no measurable flux and so no data to report. Texted altered to clarify this.

Reviewer 1: It seems very unlikely that the pump acquiring the sample would have had such large fluctuations that it renders the lag time estimate so erroneous as to make it necessary to discard the data. All non-exact lag time estimates simply lead to an underestimate of the real flux (refer e.g. to B. Baker et al., 1999).

While true, the possibility of condensation and variable lag times is a major reason to discard doubtful fluxes- a flux that is known to be wrong (too small) without knowledge of the size of the uncertainty is not very useful.

Reviewer 1:- if you discard data for the said reasons, that principally results in a "minimum detectable/ acceptable flux" in your setup; what is the value of that?

Not strictly true – the flux could still be large but uncertain – the concept of minimum detectable flux is not very helpful here if we know that an uncertain flux (because of uncertain lag time) is always going to be biased low Does the review want a numerical value which is variable due to dependence on several varying factors or are they being philosophical? A minimum detectable flux is not easily defined being dependent on the sensitivity of the concentration measurement, and on the wind/turbulence conditions, which in general are interrelated. As the flux can be bidirectional, the concept of ‘minimum detectable flux’ is perhaps meaningless other than to be able to put an uncertainty on each flux measurement.

reviewer 1:- what is "new" in your data? the discussion of BVOC abundances and fluxes does not present new insights.

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This has been further emphasised in the introduction and conclusion. Canopy-level fluxes measurements for the vegetation of the area has been achieved using corroborative PTR evidence for VDEC fluxes, which is new. Our use of these fluxes to calculate a basal emission rate for the footprint area is new and these values when compared with the emission rates from leaf and plant studies show the need for further improvement in the model parameterisation and for further measurements.

Technical corrections We thank Reviewer 2 for pointing out these mistakes. We amended the manuscript accordingly.

Interactive comment on Biogeosciences Discuss., 6, 2183, 2009.