

Dr. Andreas Hofzumahaus

Editor

Atmospheric Chemistry and Physics

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Dear Dr. Hofzumahaus

Please find enclosed the further revised manuscript. We have addressed all of your and reviewers' recommendations in the revisions.

We have implemented the following major changes which are described in detail in our responses:

- 1) We have completely focused the paper on isoprene and the new title is "Airborne flux measurements of biogenic isoprene over California". The information on other VOCs has been removed resulting in improved coherence of the story.
- 2) We rebalanced the manuscript to emphasize the science in order to fit the ACP scope more clearly. We agree that much of the technical detail was distracting from these scientific findings and had already been included in our earlier methods paper. We therefore omitted or moved much of the technical detail to the Supplementary Information, leaving only the background methodology to facilitate the reader understanding and interpreting the scientific results.
- 3) While the previous versions of the paper could have been interpreted mainly as demonstrating that we can make airborne isoprene flux measurements, our true intention for the paper is to contribute to expanding understanding of what the major sources of isoprene are in California, their magnitude, and how they are distributed and finally why constraining these isoprene fluxes with measurements is important. We have significantly expanded the scientific content with a new figure and discussion in order to improve the scientific interpretation in the paper.

We thank the editor and reviewers for their excellent guidance which was extremely helpful in making this manuscript more focused and interesting for the scientific community reading ACP.

With best wishes

Yours sincerely

Pawel Misztal

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Response to comments by Reviewer 1

We thank once again Don Lenschow for evaluating the paper and providing more comments which we have addressed. We respond below in bold italic.

While generally pleased that the authors have dealt satisfactorily with the comments of my earlier review, I have the following additional comments:

What does the overbar over the wavelet function denote in the wavelet transform given in Eq. (4)?

The overbar denotes an average quantity corresponding to the mother wavelet $\Psi_{p,a,b}(t)$ of a given frequency and finite time. In our case the mother wavelet was the Morlet wavelet. We clarify in the text that $\Psi_{p,a,b}(t)$ is the mother wavelet.

p. 13: I'm still puzzled by the discussion on this page. Namely: "Considering the footprint and wavelet scaling parameters, it is possible for an aircraft flying low at approximately 60 m s⁻¹ to provide meaningful spatial flux representation at the 1-2 km resolution..." You still have to deal with the fact that the eddy sizes that are most important for scalar transport are of the order of the boundary-layer depth. If you are only resolving one or two of these eddies, how can you get meaningful spatial flux representation? You need to resolve of order 10 eddies to get a meaningful sample over a particular flight segment.

We apologize for leaving this lack of clarity in the previous version which may have suggested that we calculated the fluxes over the short period (1-2 km). This is not true, the wavelet transform enables localization of flux in time and frequency to this and smaller resolution but we did the flux calculation over the long segments (e.g. 100 km) that captured all dominant eddies. We now clarify after this sentence. "However, the segment to average the CWT fluxes needs to be sufficiently long to capture all the frequency contributions (e.g. of the order of the PBL depth)". The clear advantage of the CWT method is that its reconstructed discrete flux time series (daughter wavelets) express the reconstructed instantaneous time domain as shown in the cross-scalogram in Fig. 2c where the large eddies are shown to be resolved.

p. 13, l. 3: Why not say upfront here that you used the Morlet function wavelet instead of waiting till p. 14, l. 3? Also, I suggest a new paragraph starting at p. 14, l. 5: Vertical flux...

Thank you for suggesting these changes which we have incorporated.

p. 14, l. 10: ...relatively small compared to the storage term in the temperature budget.

Done.

p. 15, l. 21: (relevant also for conserved species)

Done.

p. 15, l. 24: Is this a horizontal or vertical concentration gradient?

Thanks. The word “vertical” has been added.

p. 20, l. 18: What does "strongest fluxes" mean? Largest mass fluxes?

We now say “largest mass fluxes”.

Once again we thank the reviewer for insights and extremely useful comments which helped us clarify and improve the manuscript.

Response to comments by Reviewer 3

We thank very much the anonymous referee #3 for reading carefully the paper and providing helpful suggestions which resulted in a more science-oriented paper which was our original intention. We respond below in bold italic.

Misztal et al (2014) uses a novel approach to estimate fluxes at the 2-5km scale from aircraft data. The innovation, and applicability of this approach certainly make this appropriate material, however, I cannot recommend it for publication as is, but it should be published after major revisions from the authors.

We appreciate the suggested revisions to change the scope and we have now incorporated all suggested changes.

As I understand it, the main improvement this paper makes is the application of the wavelet transform method to retrieve isoprene fluxes at the 2km level, and thereby achieve excellent spatial coverage, that at first glance appear to match modeled surface isoprene fluxes well, although inter-comparisons between observationally-derived flux estimates are somewhat inconclusive. This is a broadly applicable technique, which could be useful for validation or comparison with model results. Thus, it represents a significant improvement to current methods. This reviewer appreciated the extensive discussion of uncertainties, as well as the experimental technique.

Thank you for appreciating our work. We think that the earlier version could have erroneously suggested that the observational comparisons are inconclusive. We have expanded the discussion to clarify how the observations provide critical new information on

isoprene sources, distribution, and magnitudes in California. We show consistency of the results with previous branch enclosure studies in the east Sierra foothill oak savannah but the majority of the CA region we covered completely lacked data on regional fluxes of isoprene, thus our results are extremely novel in providing the first observations over an extremely large domain.

There are two main challenges that face the authors. The first is one of focus and information. The title of this paper is 'Airborne Flux Measurements of Biogenic Volatile Organic Compounds over California'. The figures do not suggest that this paper is primarily about BVOC fluxes. Figure one shows the flight tracks, as expected. Figure 2-4 show validation data for the flux calculation. Figure five shows concentration tracks of four VOCs, only two of which get any mention in the paper, and only figure six presents actual flux results, which only involve isoprene, and these results are semi-quantitative. Thus it is confusing because the only VOC flux mentioned significantly in the paper is isoprene, yet three full page maps are devoted to showing track values of VOCs which are not significantly referenced in the paper, only one BVOC flux measurement is discussed, and only in a semi-quantitative manner.

Thus, my main recommendation to the authors is that they decide what they want the paper to be about, and reframe the title and introduction, or add some results.

The reviewer made a very important point and useful recommendation, so, in response to this comment, we have:

- 1) refocused the paper to be centered principally on isoprene.*
 - a) changed the title slightly by replacing "Biogenic Volatile Organic Compounds" with Biogenic Isoprene.*
 - b) omitted the information related to other BVOCs in order not to dilute the main message. The only small exception are ground based isoprene oxidation products (MVK+MAC) from the ground site in the Central Valley to show the significance of small isoprene emissions away from the oak woodlands.*
- 2) significantly expanded the results and discussion to include paragraphs which quantitatively discuss the distribution of ecosystem-based emission factors of isoprene.*
- 3) deemphasize the technical details limiting the included material only to the background methodology which could be valuable for readers in interpreting the results.*
- 4) added a new figure (Figure 6) showing the influence of isoprene and its oxidation products even in the areas where low flux of isoprene is seen (e.g. Central Valley).*
- 5) examined the paper for coherence and clarity and made significant changes to the results and discussion, abstract, introduction, and conclusions, with an intention that the paper is to show the distribution and magnitudes of isoprene sources in California and their significance for regional photochemistry and air quality.*

Summarily: is the paper predominately about the method applied, the results from that method, or a general overview of BVOC and VOC fluxes and concentrations measured from airborne

sources? If the former, then the validation statistics need to be presented (intercomparisons between surface and aircraft isoprene measurements and fluxes) more clearly. If the middle, then only two figures with maps are presented, and little effort is spent to summarize the results. If the last option, then more information about the other VOCs should be provided. In my opinion, in any case, the results are a bit thin, and this is the second challenge that faces the authors.

We thank the reviewer for this constructive criticism which we accept. We have published the method paper already and our intention in this paper was to present and interpret the results from the measurements (the reviewer's middle option). We significantly expanded the result sections with more discussion and another figure, so three figures (5-7) relate now specifically to the results we wanted to present and discuss in this paper.

The second challenge that the authors face is the difficulty of accurately distilling the aircraft data into something that can be understood. As it stands now, the authors only make generic statements (ie flux averages and standard deviations), and show qualitative maps. This is a gap which this paper needs to address. If the authors wish to preserve model intercomparison for another paper, they could at least combine data from the tracks to show isoprene flux measurements, discuss differences in fluxes when tracks overlapped between different days, and over different locations. Instead of saying things like 'low background in the central valley', state what these values are.

As we stated in the text, the comparison with BEFs was semiquantitative in this paper, because it did not aim to make a direct regression of the observations with the model (for which zonal averaging is necessary) but we think that the results presented are fully quantitative and show the valuable results that represent the first observations of the distribution, magnitudes and ranges of isoprene concentrations and fluxes over CA, and we now improve discussion regarding the importance of these new observations.

More specific comments:

Page 6: line 27: Remove this sentence as the referred sections have been removed.

Thanks. This has been done.

Page 9: How long are the flight segments? You mention 100km, but also 20-200km. It would be useful if the authors could report the mean and standard deviation of used lengths in trajectory calculations in the supplementary information.

For the survey flights which are shown in this manuscript we tried to use as long segments as possible and the flight tracks were designed to permit relatively long and straight stretches, because we did not calculate fluxes on the turns. The shorter segments had to be used on the racetrack stack profiles. While we provided the wide range of possible integration lengths for the wavelet method, we typically integrated segments of 100 km or more except when the segments between the turns were shorter. On the other hand, when the straight segment was > 200 km, we would split the segment to avoid diurnal effects. We think that the tracks presented

in Figure 1 can give guidance to the general length of the segments. We have not used the trajectory calculations.

Page 13: In the discussion of wavelets, the authors present the general theory, and then immediately jump to a discussion of the wavelets vs FFT method. It would help immensely to add a paragraph explaining exactly how the wavelet is used in this case to derive the fluxes.

In the first iteration of the response to reviewers, the authors state: “We now state more clearly that for the wavelet fluxes we actually integrate long segments (e.g. 100 km) and based on wavelet decomposition, we reconstruct the time domain for the wavelet co-spectra to yield time series of discrete coherent structures which are subsequently aggregated to 2-km surface fluxes.” I cannot find where this is done, until I read this comment, I thought that the authors were in fact calculating directly 2km fluxes. This statement could be placed into the text almost verbatim, and would make things very clear.

We have included this clarifying statement in the beginning of wavelet section. The wavelet analysis method is new and it induces natural intuition that the discrete fluxes are calculated at discrete time intervals while in fact they come from decomposition of the flux calculated on the long segment. We recognize that our initial lack of clarity led to some confusion during the review. We agree that it would be useful to have step-by-step instructions for calculating the wavelet transform but this has already been nicely described in the references we have provided (e.g. Torrence and Compo, 1998). There is also a tutorial devoted to wavelet analysis available at <http://paos.colorado.edu/research/wavelets/>

Page 14:

For determination of linear flux divergence: Karl et al. (2013) only reported flux divergence values for three tracks. What is done on the other days? Do you use an average?

Yes, we used an average of the flux divergence coefficients on the other days. As we explained earlier in the review, the uncertainty related to the inaccuracy of these coefficients was relatively small (~2%).

Page 15: Why is the error contribution of flux divergence for a reactive scalar like isoprene, lower than the flux divergence of a passive scalar like CO₂? This is confusing since because the Damkohler number is of order 1, and so the chemical timescale is on the order of the boundary layer timescale.

We have now deleted the part of the sentence related to non-reactive tracers to avoid potential confusion. We just meant to say that for the flux divergence dominated by chemical losses, characterizing flux divergence due to chemical losses is at least as important as characterization of the losses due to transport for the non-reactive species. The Damköhler numbers were calculated and discussed as part of the Karl et al 2013 paper, and are not a focus of the current manuscript. Instead, these numbers are simply referenced in our manuscript. The Damköhler numbers were ranging from 0.3 to 0.9 in CABERNET, so the

chemical timescales dominated the vertical flux losses of isoprene which were shown in Karl et al. 2013 to be controlled by OH and we have constrained their magnitudes.

You state that the survey flight specific random error is 5%. What is used to obtain this number? If I estimate using equation 3 from Karl et al, 2013, (citing Lenschow 1994), assuming a flight level of 400m agl (referenced in the abstract), a boundary layer height between 1000 and 2000 m (typical levels as noted by reviewers in comment 19 of reviewer 1), and a sample length of 100km (noted as the average by the authors), errors range between 14 to 17%. . If I'm misunderstanding the equation used to compute the random error, please make more clear what you mean by this value.

In response to Don Lenschow's previous comments (comment #3) we already clarified the random and systematic errors. We apologize that in the first version of the manuscript we used the equation incorrectly to unintentionally suggest the typical survey flight random error to be lower (i.e. ~5% instead of ~15%). This has been corrected.

Line 30: For the flux divergence, you state that it varies by a factor of two. Is this based on the three OH estimates that you have from Karl 2013, or something else? Could you present evidence that the OH levels are similar on other days? The estimated noontime OH levels range from 78 ppq to 1.4ppt, a difference much greater than a factor of two.

From our gradient flights (RF3 in the beginning, RF6 in the middle, and RF7 at the end of campaign) we encountered a range of varying PBL heights and Dahnkoeehler numbers. The slopes from these flux divergence measurements as a function of normalized flight altitude were in the range of -0.21 to -0.31 (20% variation), despite OH densities varying by a factor of 1.6. From these measurements we determine that the height of the PBL is more critical; the idea behind the survey flights was to fly as low as possible, so that the flux divergence term will be proportionally smaller. For the lower range of OH numbers, that the reviewer suggests, the flux divergence term should be even smaller, approaching 0 in the limit. Our upper range of OH densities was 7.2×10^6 molecules/cm³ (RF7, Karl et al., 2013). From this we estimate that (even for doubling OH densities) the systematic error due to the flux divergence term would not exceed 20%, when flying at about $z/z_i = 0.1$. We correct fluxes by 10% (according to the average value from our gradient flights), suggesting an additional upper limit of a bias of 10% under theoretical conditions of extremely large OH values. The range of OH values observed in California (e.g. Mao et al., 2012) shows OH mid-day values typically in the order of 10×10^6 molecules/cm³, suggesting that the range observed during our gradient flights was realistic, and that our flux divergence corrections for all flights was likely not a large source of error.

Page 16:

Line 6: If fluxes are only evaluated over 5km to reduce the error, those are the values that should be shown in Figure 6.

Our point was that whether we average over 5 km directly or first over 2 km (~50% error) and then to 5 km (~30% error) does not matter. In the analysis we average zonally areas >5 km and compare the fluxes so we can compare the data for entire ecoregions. It is more practical to use 2 km flux points.

Page 19:

Line 21: Should figure 5 be referenced here? If so, why not zoom figure 5 so that only the part discussed in the text is shown.

As the comment below suggested, we have omitted the information on all BVOCs except isoprene, so the current figure 5 is showing only isoprene.

Line 24: If these other VOCs are not to be referenced in the paper, remove the other VOCs from Figure 5.

We have done that.

Page 20 Line 18: Since methanol is not mentioned further in the paper, why not remove this sentence?

This sentence has been removed.

Line 25 state what the central valley is, and what the background flux level is.

We state now: "...the low background (0-0.05 mg m⁻² h⁻¹) in the Central Valley of California.

Page 21: It is curious to me that the uncertainty in the instrument aircraft fluxes are equal to the REA uncertainty. How was the REA uncertainty derived? How were those measurements made? I suggest this information be added to the supplement. As noted by the authors, it is unfortunate that there are not more data points to analyze, because it is interesting that one of the two data points is exactly identical to the REA measurement.

We added a brief section to the supplement to describe how REA measurements were made. The error in REA measurement is ~50% for a half an hour sampling period. The wavelet flux at 2 km are related with similar uncertainty. The REA measurements are averaged over consecutive samples, so it is difficult to compare a snapshot flux with an ensemble average over a longer time period locked in space. The comparison is valuable to demonstrate the variabilities at different spatiotemporal scales and that complementary approaches to arrive at a big picture are needed.

Summary: I wish to reiterate: I think that this uses a novel approach and derives some interesting results. However, the way the paper is framed, compared with the contents of the results section, seem to be at odds. I came away from the paper without a real understanding of what the BVOC fluxes look like in California.

That is true that in the early manuscript version we did not do a perfect job with describing and explaining the results and allowed them to be diluted by a plethora of technical material. We hope that the changes we made in response to this review provide a clearer understanding of what isoprene fluxes look like in California and make the paper more interesting for the ACP audience.

Karl, T., Misztal, P. K., Jonsson, H. H., Shertz, S., Goldstein, A. H., and Guenther, A. B. (2013): Airborne Flux Measurements of BVOCs above Californian Oak Forests: Experimental Investigation of Surface and Entrainment Fluxes, OH Densities, and Damkohler Numbers, *J. Atmos Sci*, doi 10.1175/Jas-D-13-054.1.

Lenschow, D. H., J. Mann, and L. Kristensen (1994): How long is long enough when measuring fluxes and other turbulence statistics?, *J. Atmos. and Oceanic Tech.* doi: 10.1175/1520-0426(1994)011<0661:HLILEW>2.0.CO;2.

Torrence, C., and Compo, G. P.: A practical guide to wavelet analysis, B Am Meteorol Soc, 79, 61-78, 1998.

*Mao, J., Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J.-H., Goldstein, A. H., Paulot, F., Beaver, M. R., Crouse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Thornton, J. A., and Brune, W. H.: Insights into hydroxyl measurements and atmospheric oxidation in a California forest, *Atmos. Chem. Phys.*, 12, 8009-8020, doi:10.5194/acp-12-8009-2012, 2012.*

Once again we thank the reviewer #3 for insights and extremely useful comments which helped us clarify and improve the manuscript.

Pawel Misztal

On behalf of authors