

## ***Interactive comment on “Biogenic volatile organic compound emissions during BEARPEX 2009 measured by eddy covariance and flux-gradient similarity methods” by J.-H. Park et al.***

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The comparison of EC and gradient flux methods for VOC fluxes and especially the study of possibilities of using gradient flux method that enables determining fluxes of several or tens of VOCs with a quadrupole mass spectrometer are clearly important for the VOC community. The measurements have been done well with great care; however the data treatment provides insight on the qualitative, but perhaps not on the quantitative agreement of these two flux methods. Here the value of gradient flux scaling parameter  $K$  has been determined from the same set of measurements as the value on average that scales the gradient flux results to the EC fluxes. The authors call

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these universal K values and argue that they should be used rather than in K values from measurements not related to VOC e.g. from fluxes of CO<sub>2</sub> or for some other variable that does not react during the flux transport processes, however the authors also show that sources and reactivity of the VOCs differ. It is no surprise that the gradient flux values agree well with the EC flux values that they have been scaled with, it is a circular argument, *Petitio Principii*, not test of proof of the accuracy of the gradient method. Flux quality control e.g. by testing that the half and hours are stationary and estimation of potential flux errors is appreciated. Also the analysis of the high quality night time flux data is very valuable. I recommend publication of this very good and useful manuscript in ACP after minor corrections presented in detail below.

The authors use the term flux for eddy covariance flux as well as for flux in general. Please correct 'flux' to 'EC flux' at least on page 25088, lines 14 and 17 and page 25095, line 5.

Introduction: P25083, line 13. Presently also the use of time of flight mass spectrometers enable direct EC flux determination of unlimited number of VOCs, e.g. Ruuskanen, Müller, Schnitzhofer, Karl, Graus, Bamberger, Hörtnagl, Brilli, Wohlfahrt, Hansel, Eddy covariance VOC emission and deposition fluxes above grassland using PTR-TOF, *Atmos. Chem. Phys.*, 11, 611–625, 2011. Please correct the text accordingly.

P25083, line 20: Flux gradient method was not initially introduced by Goldstein et al., the only one referenced here. Many comparisons of indirect gradient fluxes with the fluxes from the direct eddy covariance method have been done in the 1980's. Please also reference them, one possibility is an overview by Baldocchi, Hincks, Meyers, *Measuring Biosphere-Atmosphere Exchanges of Biologically Related Gases with Micrometeorological . . .*, *Ecological Society of America*, 69: 1331–1340. Please add reference.

P25084, line 1: In addition to different source profiles, the fluxes and thus gradient K values are influenced by chemical reactions mainly leading to loss of reactive VOCs in during the transport from emission to the measurement point, e.g. Rinne et al., *Effect*

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of chemical degradation on fluxes of reactive compounds – a study with a stochastic Lagrangian transport model, Atmos. Chem. Phys., 12, 4843-4854, 2012.

Methods: Page 25085, line 25. Please clarify to text: Were the moments contaminated by the generator removed from the dataset? If not, why?

Page 25090, line 27: correct spelling 'mesasurements' should be 'measurements'

Page 25091, line 5: Please clarify how was the storage affect taken into account? Where the gradient flux measurements during the morning hours 6-8 o'clock corrected for the storage that was over 50% of the EC flux for methanol and monoterpenes? Please add how much the storage accounted for in the night. Please add: What criteria were used to filter values due to noise from real flux from the gradient flux values?

Results: Page 25092, line 10: Please rewrite: 'Diurnal patterns of... .. peak in the morning...' Consider changing to 'Mixing ratios of... ..were highest in the morning...'

Page 25093, line 10 and Figure 5: are the measurements above the noise level? Please add detection limits of each m/z to methods or Table 1.

Page 25094, line 10: Please consider editing: starting the section where 'Fluxes of the additional 14 measured BVOC species were determined..' (Page 25096, line 3) by stating that 'Fluxes of the other 14 species selected for vertical gradients (should be vertical gradient measurements) were not measured...'

Page 25094: The authors derive K from methanol, isoprene-MBO and monoterpene measurements so that it would fit the sources and sinks of also the other 14 VOCs better than CO<sub>2</sub> flux. However, the evaluation of sinks e.g. chemical loss is discarded. More importantly the authors show that methanol has a different source profile than the isoprenoids (Fig 4), and appears to be emitted from the forest floor. Please add discussion on: Why is the universal K derived from the three different VOCs and how much does it differ from the K derived from CO<sub>2</sub> and water vapor?

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Page 25096: Please add to text information on the reliability of the gradient fluxes, all values derived might not be due to a flux, but due to noise in a low signal: Did the small positive and negative fluxes of  $m/z$  71, 113, 155 pass the quality controls and were the mixing ratios also above detection limit?

Page 25099: Degeneration of organic matter e.g. soil litter is also a well known source of methanol release in the understory. Could the sources of methanol emissions be dominated by release from plants through stomata (T and PAR driven release) during the day and litter decay (T driven release) in the night?

Page 25100, line 4: Add references.

Page 25101, line 18: please remove the circular statement of 'excellent agreement' of EC and gradient fluxes derived from EC measurements.

Fig. 7: Please edit the figure colors, so that the Kuniv line is darker also in legend than the shaded area in a B&W print. Please change std to percentiles e.g. quartiles to present the variation of the K values. Use of std requires normally distributed data, and the K values clearly are not

Fig. 9: Please check, do the vertical bars denote standard error or deviation from the mean? Please change std to percentiles (see comment on Fig. 7.).

Fig. 10: Are the fluxes derived from gradient method or both methods? Please clarify to the caption.

Fig. 11: Please check the legend. Change to consistent form e.g. 'Compound ( $m/z$ )', also in the other figures.

The total hourly mean BVOC diurnal flux in Fig. 10 is valuable, hopefully in the future the authors will continue on the determination deposition of oxidation products and consider devoting measurement time on the for the direct eddy covariance method.