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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal trends in concentrations and fluxes of volatile organic compounds above central London" *by* A. C. Valach et al.

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The authors would like to thank the reviewers for their astute comments and suggestions, which have helped in improving the revised manuscript. Responses to the reviewer's comments are below with reviewers' comments followed by a response to each point with the respective revisions to the manuscript in "quotations" unless the changes included the reworking of whole sections. As well as in response to the reviewers' comments, changes have been made throughout to improve the clarity and readability. The manuscript and figures should now be much easier to read and follow. Furthermore, acronyms and formatting have been checked and are now clear and

consistent throughout. Section 3.2.2 has been expanded.

Review 1

General comment 1: My main comment concerns the discussion on the influence of boundary layer dynamics: the possible role of atmospheric boundary layer (ABL) dynamics in shaping the diurnal profiles of species concentrations and their difference between summer and winter is mentioned briefly several times throughout the MS (e.g. in section 3.3.1), but not shown. Only in section 3.1.2 it is mentioned that the ABL was on average 1700 m in summer and 900 m in winter. I think you can discuss much more exactly how ABL dynamics have influenced your observations, and show it using the available data. Just some thoughts on the influence of the ABL from looking at the data: In Fig. 1 several concentrations (acetaldehyde, benzene, toluene, C2-benzenes) show a peak just around 8 a.m., which could be due to the emission into a shallow nocturnal ABL. After 8, the ABL quickly grows, clean air is entrained and emissions are diluted, leading to lower concentrations. The second peak in concentrations of aromatics (around 5 p.m.) could be the result of continuing emissions into a collapsing ABL. Finally, during night time, the ABL is shallow, but also the emissions are low, leading to low concentrations. For a good introduction on the ways in which ABL dynamics influence the relation between fluxes and concentrations of chemical species, see for instance Vilà-Guerau de Arellano et al. (2009). It would be very interesting to see correlations between species mixing ratios and ABL height (which is apparently available from LIDAR observations), in addition to the correlations with temperature, PAR and traffic density in Fig 3. This information could also help to strengthen your argument in Sect. 3.1.2 for the role of ABL dynamics in the seasonal variability and your conclusion (p.6625, l. 2-4) that 'many of the spatio-temporal differences in the observed mixing ratios were attributable to emissions and boundary layer dynamics'.

General response 1: A more extensive discussion and description of atmospheric boundary layer effects on VOC concentrations and fluxes is now included throughout Section 3.1, including the suggested reference. The diurnal summer and winter

boundary layer heights have been added to Figures 2a and b. Furthermore, correlations of averaged boundary layer height and VOC fluxes and concentrations have been investigated and example plots of averaged isoprene fluxes and concentrations with boundary layer height have been added to Figure 3. Only correlations with boundary layer height during summer are shown due to the larger diurnal changes of boundary layer height in summer than in winter. Boundary layer height measurements were only available for 2-3 weeks in summer and winter 2012, as they were part of the short term intensive observation periods of ClearfLo. The benefit of this flux site is that the low measurement height of the tower means that our measurements are always closely coupled with the surface layer, unlike the previous VOC flux study from the BT Tower in London, which had the problem of becoming decoupled from the surface layer during stable night time conditions due to its high sampling height (Langford et al., 2010b).

General comment 2: Throughout the MS, the term 'diurnal averages' of VOC fluxes/concentrations are used, which I think is very confusing. To me, a diurnal average flux/concentration means the flux/concentration, as averaged over all observations during one day, so a single value for each day. I think what you mean is the 'average diurnal cycle' (or 'average diurnal profile' as you write in the caption of Fig. 2), so the diurnal cycle of the flux/concentration, averaged over multiple days. Please check throughout the MS and use the latter term consistently.

General response 2: The term "average diurnal profile" is now used consistently throughout when describing diurnal cycles.

Specific comments:

Comment 1: Title: since large parts of the results section discuss (3.1, 3.1.1) and figures 2 and 4 show diurnal cycles, I would add to the title that you have also looked at diurnal trends. Therefore I would recommend 'Seasonal and diurnal trends in ...'.

Response 1: Title: added "and diurnal".

Comment 2: p. 6603, l. 17-20: the lines about satellite retrievals of VOCs are not necessary for the discussion and could be left out.

Response 2: p. 6603, l. 17-20: This sentence has been removed.

Comment 3: p. 6604, l. 1: Seasonal, diurnal and spatial differences?

Response 3: p. 6604, l. 1: added "diurnal".

Comment 4: p. 6604, l. 1: I would mention both VOC fluxes and concentrations here, since you discuss both.

Response 4: p. 6604, l. 1: added "and concentrations".

Comment 5: p. 6612, l. 22: Is Mexico City the only other city for which flux measurements are available for comparison? You also mentioned papers by Park et al. with flux measurements in Houston, TX. Why not compare those with yours too?

Response 5: p. 6612, l. 22ff: An additional comparison of average fluxes and concentrations with Park et al. 2010 has been added (Section 3.1): "Most VOC fluxes and concentrations were comparable to or lower than those previously observed in London (Langford et al., 2010b) and other UK cities (Langford et al., 2009), although C2-benzene fluxes and concentrations, as well as isoprene and benzene concentrations were slightly higher. The discrepancy in isoprene and benzene concentrations is consistent with photochemical loss during transport to the higher measurement height of the previous study. Compared to other cities such as Houston Texas (Park et al., 2010) and Mexico City (Velasco et al., 2005), VOC fluxes and concentrations were lower, apart from C2-benzenes which were comparable or higher, although it must be noted that C2-benzenes in this study represent the sum of multiple VOC species. Unlike the other studies cited, Park et al. (2010) use relaxed eddy accumulation to measure VOC fluxes and hence the data obtained are not directly comparable with measurements made by EC-based methods."

Comment 6: p. 6613, l. 10: If the moments of the peak fluxes coincide with those of

a low ABL it is difficult to tell the effects of emissions and ABL dynamics on the concentration apart. Can you check with data on ABL height how exact this coincidence is?

Response 6: p. 6613, l. 10: This was added as part of Response to general comment 1 and now reads: "The rush hour emission peaks mostly coincide with the boundary layer expansion and collapse and therefore the effect of each factor cannot be separated. The morning concentration peak was slightly higher than the evening peak across traffic-related species even though fluxes tended to be larger during the evening rush hour. Morning emissions enter a shallow nocturnal boundary layer leading to relatively larger concentrations compared with higher afternoon emissions entering a developed boundary layer, leading to relatively lower concentrations. This enhanced dilution effect is found more often during summer when the boundary layer mixing height is higher (Figure 2a). Therefore, the regression analyses below only refer to data from August (cf Section 3.1.2 for comparisons with December). Furthermore, increased photochemical degradation during the day removes VOCs, further contributing to the midday minimum in mixing ratios."

Comment 7: p. 6624, l. 26-27: 'There were observable spatial and temporal variations in relative source impacts at different resolutions such as hour to month.' I find this a too general statement for a conclusion. Can you be more specific?

Response 7: p. 6624 l. 26-27: This has been expanded and changed to: "There were observable spatial variations in flux rates, which result from the varying spatial distribution of emission types and strengths of emission sources, such as vegetation and traffic. Temporal variations in relative source strengths can be seen in the diurnal and seasonal profiles, reflecting the diurnality and seasonality of some of the driving factors."

Technical comments:

Comment 1: p. 6602, l. 5: after 'proton transfer reaction-mass spectrometer', add

'(PTR-MS)', since this acronym is used throughout the text

Response 1: p. 6602, l. 5: added "(PTR-MS)".

Comment 2: p. 6602, l. 15: accounted for -> explained

Response 2: p 6602, l. 15: changed sentence to: "Isoprene, methanol and acetaldehyde fluxes and concentrations in August and September showed high correlations with PAR and temperature, when fluxes and concentrations were largest suggesting that biogenic sources contributed to their fluxes."

Comment 3: p. 6602, l. 17: change into 'Modelled biogenic isoprene fluxes from urban vegetation, using the G95.... ' and remove: ', due to urban vegetation.'

Response 3: p. 6602, l. 17: added "from urban vegetation" and removed "due to urban vegetation".

Comment 4: p. 6602, l. 25: live -> lives

Response 4: p. 6602, l. 25: changed to "lives".

Comment 5: p. 6603, l. 9: additionally act as a source -> act as an additional source

Response 5: p. 6603 l. 9: changed to "an additional".

Comment 6: p. 6603, l. 11: introduce the acronyms NAEI and LAEI here, where they are first used.

Response 6: p. 6603 l. 11: added "(LAEI and NAEI)"

Comment 7: p. 6604, l. 12: m.s.l. -> m.a.s.l.

Response 7: p. 6604 l. 12: added "m a.s.l."

Comment 8: p. 6612, l. 3: diurnal averages -> average diurnal cycles

Response 8: p. 6612 l. 3: changed "diurnal averages" to "Average diurnal cycles" throughout the manuscript.

Comment 9: p. 6613, l. 8: concentrations for aromatics -> concentrations of aromatics

Response 9: p. 6613 l. 8: changed wording throughout this section.

Comment 10: p. 6615, l. 3-4: were seen with -> were seen between, positive correlations with -> positive correlations between.

Response 10: p. 6615 l. 3-4: changed to “between”.

Comment 11: p. 6615, l. 5: pls add a comma between ’temperature’ and ’likely’

Response 11: p. 6615 l. 5: added “,”.

Comment 12: p. 6615, l. 27: Bohnenstengel et al., 2014 -> Bohnenstengel et al., 2015

Response 12: p. 6615 l. 27: changed to “2015”.

Comment 13: p. 6616, l. 4: the equation from Langford et al: which equation?

Response 13: p. 6616 l. 4: added “isoprene temperature response function from figure 9 in”.

Comment 14: p. 6617, l. 16: add ’from those’ between ’than’ and ’areas’

Response 14: p. 6617 l. 16: added “from those”.

Comment 15 and 16: p. 6617, l. 21: add ’that’ before ’compounds’ and “Higher correlations than what? Than compounds with traffic sources?”

Responses 15 and 16: p. 6617 l. 21-22: changed sentences for clarification: “Correlations of VOC/VOC fluxes (R2 = 0.40-0.62, p<0.001) indicated two groups of compounds with good correlations within each group, i.e. compounds related to traffic sources such as aromatics, and oxygenated and biogenic compounds, such as methanol, acetone and isoprene. Correlations of VOC/VOC concentrations (R2 = 0.13-0.84, p<0.001) showed highest correlations between traffic related compounds (R2 = 0.45-0.84, p<0.001) and good correlations between the oxygenated and biogenic compounds (R2 = 0.55-0.69, p<0.001) (Figure 6). High correlations between oxygenated

VOCs could indicate source commonality or formation mechanisms that depend on similar environmental factors.”

Comment 17: p. 6618, l. 1: tended -> tend

Response 17: p. 6618 l. 1: changed to “tend”.

Comment 18: p. 6618, l. 20: delete ’observed’, since it is mentioned twice in this sentence.

Response 18: p. 6618 l. 20: deleted “observed”.

Comment 19: p. 6624, l. 6: What does SNAP stand for?

Response 19: p. 6624 l. 6: added “(Selected Nomenclature for sources of Air Pollution)”.

Comment 20: p. 6625, l. 14: however -> but

Response 20: p. 6625 l. 14: changed to “but”.

Comment 21: p. 6625, l. 15: Where does ’this’ refer to? This study? The previous line?

Response 21: p. 6625 l. 15: Added “study”.

Comment 22: p. 6625, l. 22: there is a typo in the name of the 1st author

Response 22: p. 6625 l. 22: changed to “Valach”.

Comment 23: Fig. 1: Can you increase the size of the green dot, so it is easier to find?

Response 23: Fig 1: The size of the green dot has been increased, a label added and the caption updated: “Map of central London overlaid with the Ordinance Survey grid including the measurement site (KCL) at King’s College (green point) with references to the geography of Greater London and Great Britain.”

Comment 24: Fig. 2: Some use of colours would be very helpful to distinguish between

the different lines, like in figure 4. Besides, the axis labels are too small to read without zooming in.

Response 24: Fig. 2: Layout and font size have been increased to improve the clarity, as well as weekdays and weekends are now in colour (red, blue).

Comment 25: Fig. 5: In the caption, first describe the left and then the right panel. Also here, it would be helpful to increase the font size of the axis labels.

Response 25: Fig. 5: The figure size has been increased, as well as captions and order changed. “Figure 5a. Time series of both measured (grey) and modelled (black) fluxes, as well as PAR and temperature measurements for August and September 2012. Figure 5b. Correlation between modelled and measured isoprene fluxes (mg m-2 h-1) by wind direction using the G95 algorithm with temperature as a third variable, Ordinary Least Squares (OLS) regression lines, 99th confidence intervals, formulae, and R2-value.”

Comment 26: Supplementary material: A caption for the figure would be useful. Besides, since the supplement consists of only 1 figure, it would perhaps be more convenient to include it in an appendix to the main paper.

Response 26: A figure caption has been added. “Figure A1. Sensible heat fluxes (W m-2) measured from the roof tower of the King’s College London Strand building calculated using 1 to 2.5 h averaging periods and compared with fluxes calculated using the same 25 min averaging period as used for VOC fluxes.”

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/15/C3901/2015/acpd-15-C3901-2015-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 6601, 2015.

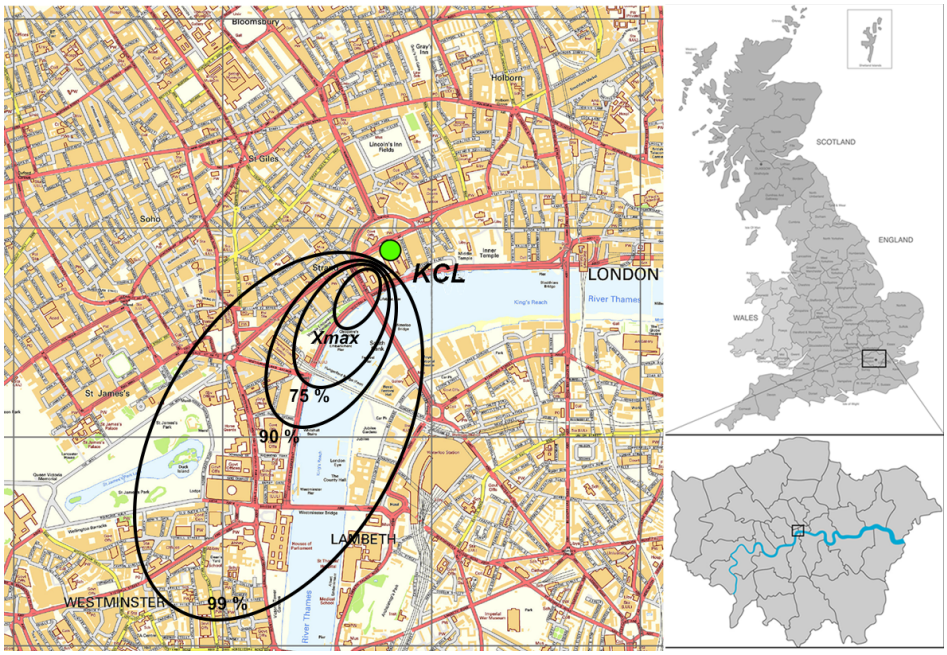

Fig. 1. Map of measurement site in central London

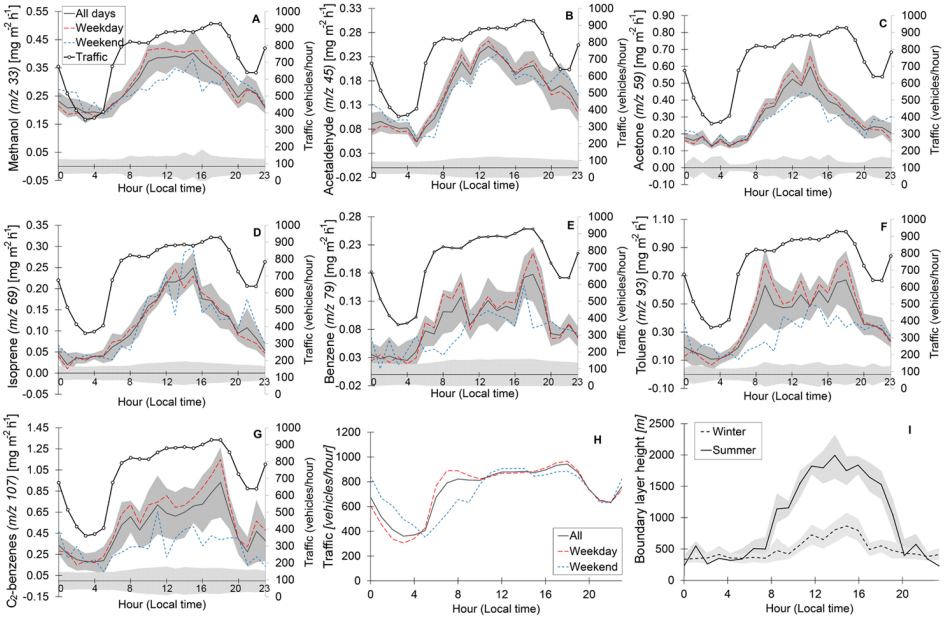

Fig. 2. Average diurnal profiles in local time for selected VOC fluxes

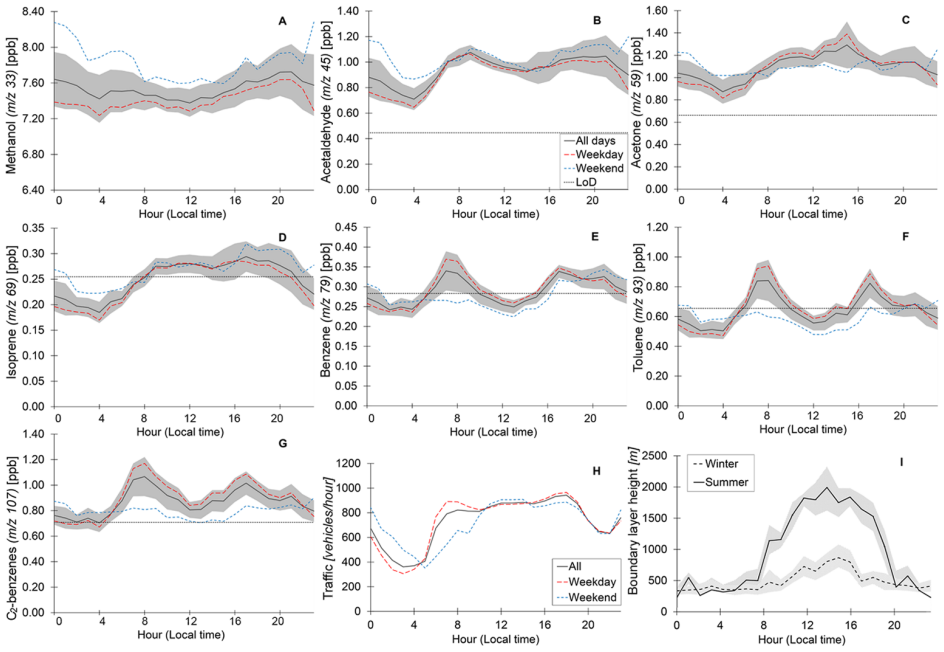

Fig. 3. Average diurnal profiles in local time for selected VOC mixing ratios

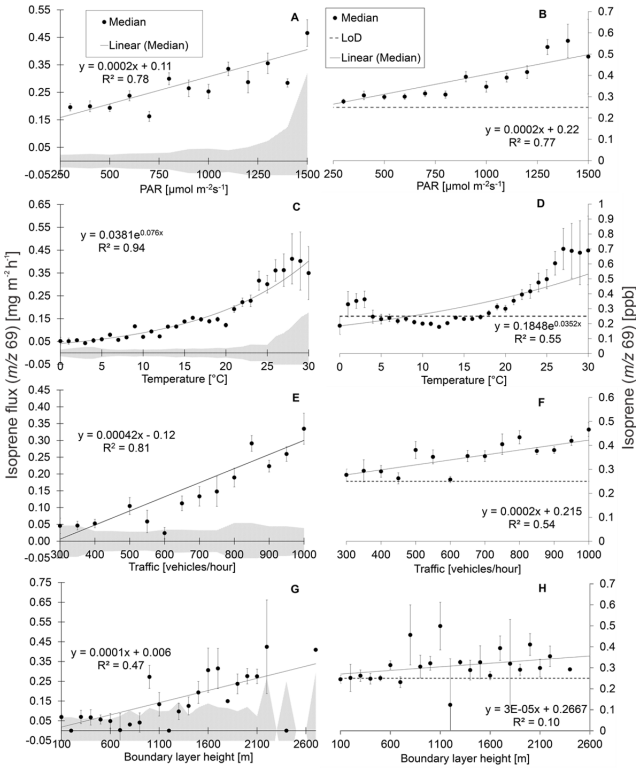

Fig. 4. Examples, using isoprene, of averaged VOC fluxes (left) and mixing ratios (right) as a function of PAR, temperature, traffic density and boundary layer mixing height

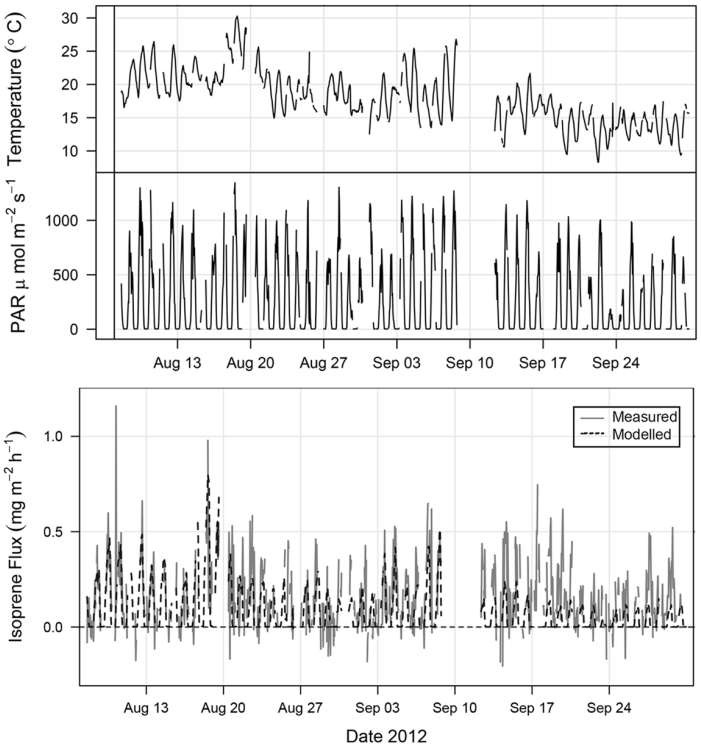

Fig. 5. Time series of both measured (grey) and modelled (black) fluxes, as well as PAR and temperature

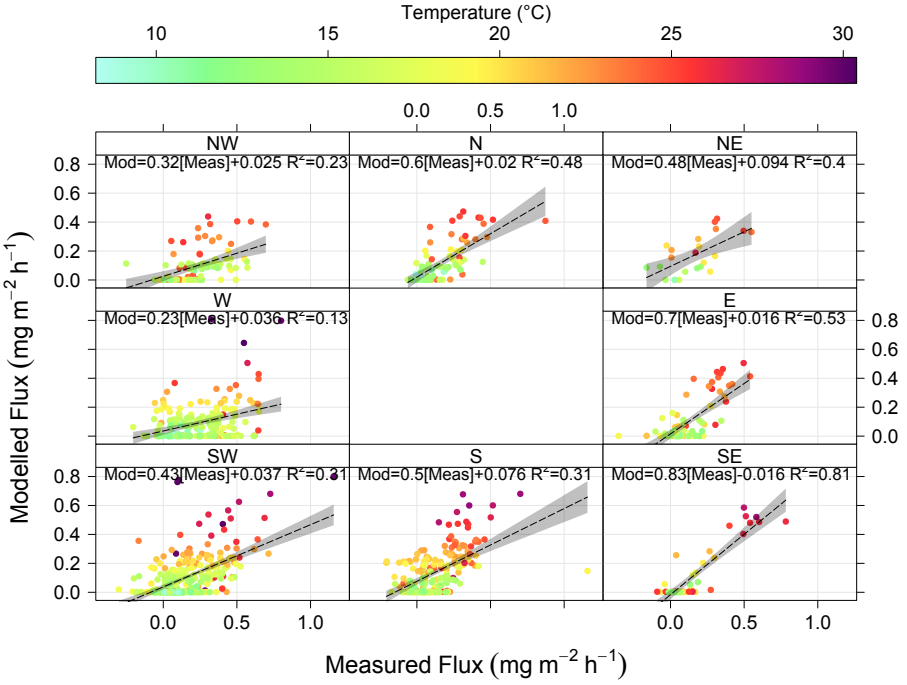

Fig. 6. Correlation between modelled and measured isoprene fluxes (mg m-2 h-1) by wind direction