

**Journal:** ACP

**Title:**

The Balances of Mixing Ratios and Segregation Intensity: A Case Study from the Field  
(ECHO 2003)

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**MS No.:** acp-2013-247

**MS Type:** Research Article

**Reply to Anonymous Referee #2**

(Received and published: 5 June 2013 - Atmos. Chem. Phys. Discuss., 13, C3076–C3083, 2013)

This referee gives seven general remarks and a number of specific comments.

- I find this manuscript extremely difficult to read. I find that the presentation lacks focus. The authors provide a high level of detail without clearly guiding the reader through the reasons that understanding the results at that detail level yield important interpretation. I am unable to ascertain the manuscript's testable hypothesis - rather, the introduction's final paragraph simply states the final conclusions. The text also regularly refers the reader to future sections of the manuscript and makes repeated statements. It is therefore my opinion that the manuscript needs a relatively broad overhaul for the AGP readership to properly take home the message; I think the same information could be thoughtfully presented in about half the length and about half the figures.
- For the manuscript to stand on its own, it is my opinion that the reader needs to know more about the actual measurements considered; it therefore seems that there should to be a section outlining items such as (location, time, canopy/vegetation type, canopy density, canopy height, instruments deployed, configuration that the instruments were deployed, pros/cons of that deployment for this analysis, etc. I find it terribly remiss for the reader to need to wait until Section 4 before learning that the canopy's 30m tall and that the single level of instrumentation is located 7m above the canopy. How was the data quality controlled? Were there any stationarity criteria used? Was there any detrending or coordinate rotations imposed? How are averages defined? Why are certain data points missing? What were the overall weather conditions this day? In my opinion, referring the reader to a separate manuscript for these details is insufficient.

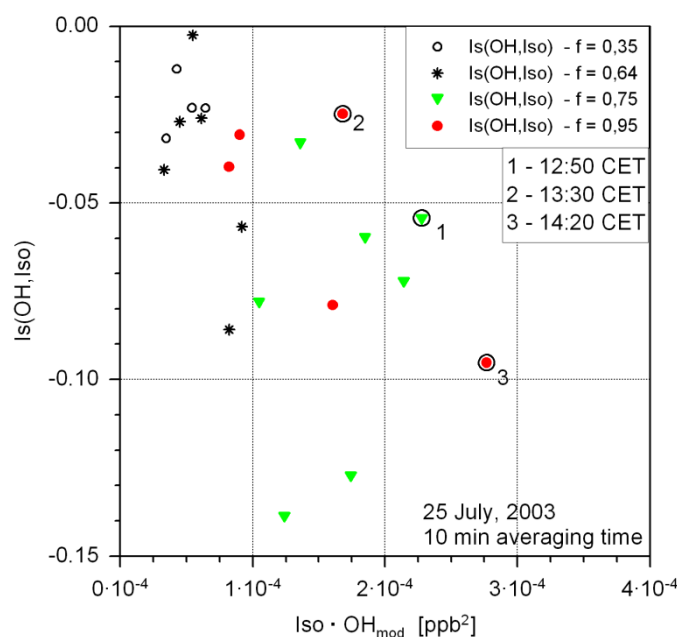
This paper describes the extended analysis of data already published and discussed by Dlugi et al., 2010, ACP, 10, 6215 – 6235. This 2010 paper contains several answers to questions put in the general remarks given above on a number of problems related to the ECHO 2003 field campaign. It is the general procedure that the description of an experiment and first results from these studies, which are used to perform an additional analysis, are not repeated but cited. A short outline of the research done in the past in the text of the revised version with additional material not given directly in the ACP 10 paper in a supplement may possibly help the reader. The overall idea of our study follows the pathway of inductive methods in science from observations to determine and quantify any kind of pattern and to produce a solid set of data for any comparison with hypothesis and theory. This requires an extensive description, analysis and presentation of the results of

measurements and not a restriction. According to the claim of both reviewers, the revised version will get the following structure:

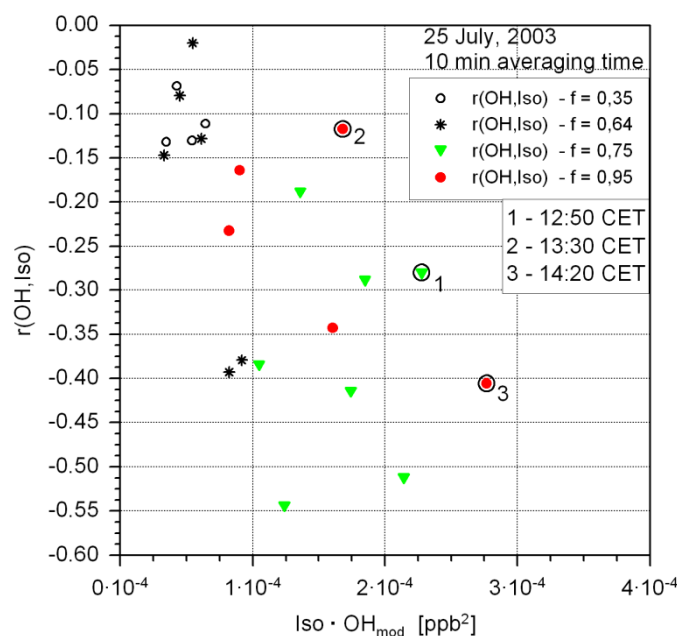
1. Introduction
2. Field site and summery of measurements (short summary, details in a supplement; e.g. instruments, calibration, site description, distribution of isoprene sources)
3. Observed relationships between OH and isoprene
4. Balance equation of the mixing ratio (was Chapter 2)
5. Segregation intensity (was Chapter 3)
6. Balance equation for the covariance and segregation intensity (was Chapter 4).  
(To shorten the paper, former chapters 4.4 and 5.1 will be mainly shifted to the supplement with Figs. 16 – 18. Only Fig. 19 will remain in the paper together with a related discussion.)
7. Reaction and transport (was chapter 5)  
(Fig. 20 will be shifted to the supplement)
8. Summary (was chapter 6)

- I recognize that making measurements of ISO' and OH' is a difficult task, but as presented I find that a single day's data from 10am-2pm with missing data strewn throughout is insufficient to be able to put forward statistically significant conclusions.
- I find the level of effort expended to try to 'shoe-horn' individual data points lying outside the expected range extremely tedious; a feature that implies to me that the campaign failed to measure the quantities necessary to concretely interpret the data presented. I am most disappointed that the effort to massage the data points into the expected range focuses mostly on 'modified' chemistry, and only in the last section does the fluid mechanical aspect really come into the discussion. How is it that things like the potential influence of species entrained from aloft (e.g. Ganzeveld et al, AGP, 2008; Vila et al., JGR, 2011) or spatially organized motions on the scale of the boundary layer depth (e.g. Molemaker and Vila, JAS, 1998; Krol et al, JGR, 2000; Vinuesa and Vila, AE, 2005) are not discussed?

This data set was obtained in a very carefully prepared and performed field study in 2003. Up to now, no other similar data set is published. The variation of radiation input by the influence of clouds influenced the choice of time averaging interval of 10 minutes. We could present 22 data points for  $I_s$  and other quantities. We do not draw any conclusions based on statistics. We sort out the data points as function of functional dependence on different parameter either given by theory or by own analysis. Therefore a detailed analysis and description why several points are outside a certain data cloud is essential. It is also a prerequisite for any information which describes the influence of different processes. The data were analyzed with respect to the influence of chemical reactions because one has to consider the reaction channel between isoprene and OH. Therefore, we had to quantify the OH available for the reaction with isoprene at first. Otherwise we would not be able to discuss the right relationships. This way different data points are separated from each other as function of reactivity term  $f$  for different time intervals and for different special dynamic conditions. For  $I_s$  and  $r$  as function of  $ISO \cdot OH_{mod}$  this is given in the figures below.



84



85

86 Any CBL - scaling cannot be applied. A comparison with the concept published by Vinuesa et al.  
87 (Tellus 55B, 935 – 943, 2003) or others requires that not only surface fluxes of the reacting  
88 compounds, but also entrainment fluxes are available for the calculation of their dimensionless  
89 concentrations respectively mixing ratios (see their eq. 9).

90 The CBL – scaling according to the concept applied also by Vinuesa et al. (2003) should not be  
91 applied to the ABL on 25 July 2003 at this site because we had a cloud topped boundary layer. But  
92 if we calculate  $z_i$  - despite the observed conditions - we need a CBL – height of  $z_i \approx 1500m$  e.g. to  
93 compare with observed variances of isoprene according the concept applied in their chapter 6 for a  
94 bottom- up transported compound for  $c_b=ISO$ .

The bottom of clouds was estimated to be between 650 m at 10:00 CET and 800 m at 13:30 CET and their vertical extent was about 200 – 400 m. Therefore their top was about 1000 m – 1200 m. For this height the calculated variances of isoprene were only in agreement with observed values if the corresponding isoprene entrainment flux would be 40% of the surface flux. Compared to findings by B. Neininger during ECHO 2003 and the results published by Davis (1992, 1994) this is rather unlikely. Therefore, albeit vertical *pumping* by clouds may modify the vertical profiles of scalars and their variance in a comparable way as done by convective transport (in the cloud free (!) CBL), the comparison would be rather qualitative.

In any case, OH is not transported and a dimensionless concentration scale for OH cannot be justified because the OH – flux is only a result of its local chemical reactions! Therefore for the available set of data we cannot perform a robust comparison based on our data and the set of equations published by Vinuesa et al. (2003) or other authors.

On the other hand, e.g. Vinuesa et al. (2003) calculate segregation also for a chemical mixture including a compound RH which has a reaction rate with OH with  $k = 1.8 \text{ ppb}^{-1} \text{ s}^{-1}$  not far from the rate constant  $k_{ij} = 2.3 \text{ ppb}^{-1} \text{ s}^{-1}$  for (ISO + OH). They obtained an average value of the intensity of segregation for the CBL between  $0.2z_i$  and  $0.8z_i$  of  $I_s = -0.17$  (see their Table 3) for the *complex chemistry* case from their LES model runs. Although the conditions are different we will cite and discuss their results and add this information also to Fig. 22. Their second value of  $I_s = -0.23$  is obtained from a parameterization if the covariance (in our eq. (3)) is replaced by our eq. (4) and using results of their LES model. This higher value is compatible to results with a higher correlation coefficient of about 0.95.

As proposed, we will add this information to a supplement of the revised version.

- Due to the limited data available from the ECHO 2003 campaign, the authors lump nearly every term in the conservation equations into a residual while attempting to explain the mechanisms controlling  $c_i$  and  $I_s$ , although I usually don't take issue with this practice, I find that the numerous terms being lumped into the residuals are affected by such a wide variety of influences, that interpreting these residuals becomes extremely convoluted and hides the important ideas.

The “lumping” procedure helps to sort the data in terms of influences by  $R_{ij}$  or RES or both. Although the residuals are affected by such a variety of influences, our figure 19 shows that  $I_s$  is only influenced by the difference of two terms. The third term  $\text{CH}_{is}$  determines the difference and is not the dominant one.

- I find that the manuscript regularly shifts or neglects to document its notation, an additional feature making the reader's interpretation extremely difficult. What's the meaning of  $\sigma(\text{ISO})$  vs.  $\sigma\text{ISO}$  vs.  $\sigma\text{iso}$  vs.  $\text{std}(\text{ISO})$  vs.  $\sigma_i$ ? How do  $[\text{OH}]$  and  $\overline{\text{OH}}$  differ? How are the "s" defined? Where are  $I_3$ -V3 defined? How can the reader be expected to take home the manuscript's primary message when the notation wanders all over the place and/or is never defined?

We add a list of all symbols to a revised version and apply a clear and consistent notation. The terms  $I_3 - V_3$  are the terms of Eq.(6) and will be also added to this equation and to Table 4 to avoid any misinterpretation.

- I also find the English and sentence structure throughout to detract from the manuscript's readability, i.e. commas in incorrect places, heavily strewn with prepositions, run-on sentences, single sentence paragraphs, passive voice, etc. There are certainly aspects of this manuscript that might be useful for the AGP community, but the authors have failed to guide the reader down a clear and convincing storyline. I also question the robustness and applicability of their conclusions across a range of atmospheric stability conditions or chemical regimes. I therefore find myself unable to recommend publishing this manuscript as it was submitted.

In the revised version the paper will be corrected as follows:

The English language will be improved.

The structure of the paper will be significantly revised according to the suggestions of both Referees also in order to provide an improved guideline to the reader.

The robustness of results and errors of the results will be discussed in more detail (see also detailed response to general remarks by Referee 1.).

The size of the paper will be reduced by transferring some material (including figures) into a new supplement

#### Specific Comments:

Lines 165-168 I don't understand the lefthand / righthand value commentary. Write down the approximation as an equation so the reader can see exactly what's being done.

The numerical procedure is described in "Numerical Recipes" by Press et al. (1991), Cambridge University Press. The reference will be added to the paper and the procedure solving finite difference equations will be explained in the supplement together with the discussion on errors.

Line 181 *significantly smaller.* ... How much smaller?

The complete discussion refers to Fig.1. Here it is shown that this term is about 10% or less.

Line 186 *shows that the mean contribution is not significant in our case* ... I disagree. I think it shows that the sum of the storage and advective terms is approximately 20%.

The contribution of advection is addressed by both referees. The storage term and the flux divergence are of same order of magnitude. The chemical term is smaller than about one order of magnitude. Therefore chemistry influences the flux divergence to a lesser extent than any other mixing or transport process. We therefore revise our statement.

Line 208 *... have to be* ... in order for what? I find this discussion terribly circular.

Eq.(8) is inserted into Eq.(3) to obtain the standard deviations normalized by mean concentrations. Here also the correlation coefficient is defined.

- 173 Line 213 *on average an inverse relationship (Fig. 5).* To me this inverse relationship is  
174 difficult to see in Figure 5.
- 175 Yes, only for the factor  $f=1$  the relation would clearly be seen. As  $f<1$  there is this difficulty to see  
176 such a relation. We will point out this aspect and propose also to add a graphical presentation (like  
177  $\text{OH}=f(\text{ISO})^{-1}$ ) to this figure to illustrate such a behavior for  $f=1$ .
- 178 Lines 234-235 Isn't this simply stating that for these data points, the reaction with iso-  
179 prene the dominant sink?
- 180 No, this data points are for the significant influence of other reactants than isoprene. Therefore, the  
181 calculation and consideration of available OH for the isoprene reaction shifts the data to the left.
- 182 Lines 236-254 Need to explain why this is effort is being undertaken. I understand  
183 that the authors are attempting to account for other chemistry contributing to  
184 the production/destruction of OH locally at this measurement location, but as  
185 written the reader isn't provided the necessary guidance leading them to this  
186 fact. As it currently reads, one is directed to look back into Appendix A to  
187 understand  $f$  and what it means. Personally, I think the information in Appendix  
188 A is brief enough that it should be included here for improved clarity.
- 189 Yes, this will be done in a revised version
- 190 Lines 257-259 How do the authors know there's a mean sinking motion during this ten  
191 minutes? Was the sonic anemometer deployed perfectly level? Without  
192 providing the reader further information describing how the vertical velocity  
193 measurements were made and/or how the vertical velocity measurements  
194 were processed (coordinate rotations, etc), I'm unable to determine how  $\bar{w}$  is  
195 observed. If there truly is a mean downward vertical velocity for these two  
196 'points', where's the compensating period with a mean upward vertical velocity  
197 as one would expect from passing organized turbulent motions? If there's some  
198 intent to suggest that land-surface heterogeneity is impacting this location,  
199 please explain why the results don't see this downwelling vertical motion  
200 throughout the six-hour period.
- 201 These aspects - how to evaluate sonic wind components for analysis – will be discussed in  
202 chapter 2 with some additional information. By the use of original sonic time series, the special  
203 calibration procedure and the control of the setup by inclinometers the mean accuracy of  $\bar{w}$  is  
204  $\pm 0.007$  m/s. Mean upward motion dominated with occasionally observed periods of 9-12 minutes  
205 downward motion. We cannot interpret these findings (without combined model application and  
206 analysis of all towers) to be caused by either land surface heterogeneity or / and cloud vertical  
207 venting on this day. The local information is not sufficient to interpret the data in terms of such  
208 types of circulation.
- 209 Line 261 ... *cause only a small contribution to  $I_S$*  ... How is small defined in this context?  
210  $I_S$  is small ( $I_S = -0.002$ ) for downward directed advection because  $r$  is small ( $r = -0.02$ ). The product  
211 of the normalized standard deviations  $0.51 \cdot 0.26 = 0.1326$  is small ( $-r \cdot 0.1326 = -0.0026$ )
- 212 Lines 265-266 How is this *direct influence* of the emission source detected?  
213 Unpublished analysis by Spirig and coworkers and us showed that emission fluxes of isoprene  
214 followed temperature according the concept published by Guenther et al., 2006 (ACP 6, 3181-  
215 3210). Ciccioli et al., 1997, showed that the leaf temperature  $T_L$  and its variance control emission.

216 Therefore the variance of isoprene must contain spectral contributions of temperature fluctuations  
 217 of  $T_L$  but also of the storage of isoprene in the canopy which is in the low frequency part of the  
 218 spectrum (less than 0.005 Hz). During the experiment, emissions were directly also measured with  
 219 cuvettes.

220 Lines 270-278 What's the take-home message from this paragraph?

221 Small values of  $I_s$  are either found in downward transported air or in air with reduced turbulent  
 222 mixing above canopy, because the stratification was slightly stable. In a revised version we will  
 223 introduce this chapter with the hint that these small values are found for special dynamical  
 224 conditions.

225 Line 284 With the limited data available, how do the authors know that this upper limit  
 226 is in any way meaningful? What controls this limit? Will the limit be the same  
 227 tomorrow, or the next day?

228 This upper limit estimate is only from extrapolation of the data of  $I_s$  as function of mean reaction  
 229 rate. We find that our largest value (-0.14) is below a possible maximum amount of  $I_s = -0.24$ .

230 Line 308 How do the authors know this is the *lowest possible value*?

231 All results are only for this data set. The lowest possible value from this data set is  $0.38 \cdot 0.23 =$   
 232 0.087. We will add the statement that all results are for this data set.

233 Lines 312-317 I highly disagree with making these comparisons without explaining why  
 234  $I_s$  differs across each study.  $I_s$  is not just a parameter (as the authors discuss  
 235 later in Section 4). All these examples represent different chemical regimes,  
 236 different atmospheric forcing, different emission/deposition.

237 The values for the correlation coefficients are given in cited references. We did not discuss any  
 238 reasons, but asked the question, why our values are systematically smaller. Hereby we performed  
 239 our analysis and found that our data may be too low but the corrected results are still smaller than  
 240 the correlation coefficients from literature. Model studies often report correlation coefficients in a  
 241 range larger about -0.8. Such high values can be obtained if the correlated quantities are normal  
 242 distributed with small variance. Our data show non-normal distributed data which looks like a log –  
 243 normal distribution in a first guess. Therefore, the correlation between quantities is smaller and has  
 244 a larger variance (See Dlugi et al, 2010, ACP 10, for skewness and kurtosis). It would be  
 245 interesting to compare measured and modeled PDF in further studies.

246 Lines 320-321 Should one expect this result? How does this relationship vary with  
 247 chemical reaction rate? or a reactant's source distribution? or atmospheric sta-  
 248 bility? or turbulence intensity?

249 Fig. 4 gives expressions from the measurements. We performed an analysis from these data  
 250 obtained from measurements above a canopy. We did not expect any result because – following the  
 251 inductive method – we should not assume any relationship in advance. Especially for OH, but also  
 252 other quantities, the turbulent intensities are found in a range also reported by others. The values  
 253 for larger mixing ratios seem to be smaller. The reason for this cannot be simply explained within  
 254 this restricted context.

- 255 Item[Line 338] I don't understand this comment: ... *below the assumption made*  
 256 *for model calculations*. Please explain. What is the typical assumption? Refer-  
 257 ence?  
 258 item[Line 342] Again, ... *often assumed for model studies*. Reference?
- 259 Model studies often report correlation coefficients in a range larger about -0.8. Such high values  
 260 can be obtained if the correlated quantities are normal distributed with small variance. Our data  
 261 show non-normal distributed data which looks like a log – normal distribution in a first guess.  
 262 Therefore, the correlation between quantities is smaller and has a larger variance (See Dlugi et al,  
 263 2010, ACP 10, for skewness and kurtosis). (e.g. Krol et al., 2000, JGR, 105, 6871 – 6884; Vinuesa  
 264 et al., 2003, Tellus 5B, 935 – 949; Ouwersloot et al., 2011, ACP, 11, 10681 – 10704). These are  
 265 results mainly for the isoprene – OH system. In the O<sub>3</sub> – NO – NO<sub>2</sub> system the correlation  
 266 coefficient from measurements better agree to high values around  $r = -0.9$  from model studies (e.g.  
 267 Kramm, Meixner, 2000, Tellus A, 52, 500 – 522). But this system is fundamentally different  
 268 because all three reactants are reacting during transport.
- 269 Line 350 ... *two branches* ... What branches are we discussing? Branches of what?  
 270 This sentence refers to Fig.9 (left). Two branches of the data points are visible.
- 271 Equation 8 Something's awry with this equation. The term  $A_{1k}$  also contains covariance  
 272 see Equation 5. Please explain.  
 273 This is explained in appendix B. If this term would be added, an additional factor  $(1-A_{1k})^{-1}$  would  
 274 appear on the right side of Eq.(8). This would reduce  $I_s$  by less than 10%.
- 275 Lines 450-451 ... *and the mean gradient of OH above canopy - from unpublished*  
 276 *measurements* - ... Unpublished measurements? From where? I was under the  
 277 impression that only a single level of OH was observed at ECHO2003.  
 278 This information is given in Dlugi et al., 2010, ACP 10 and, as mentioned before, will be repeated  
 279 in the supplement of the revised version.
- 280 Lines 452-453 What second term is obtained if isoprene and OH are replaced? Replaced with  
 281 what?  
 282 The terms of Eq.(5) are discussed. The second term  $TPOH_k$  is obtained from the first term  $TPI_k$  if  
 283  $c_i$  and  $c_j$  are replaced.
- 284 Line 457 What product is the same order of magnitude as  $TPI_k$ ? How do the authors  
 285 know this? This entire paragraph seems like conjecture.  
 286 Here we give general description on how the terms were calculated and quantities which could not  
 287 be determined directly were estimated. We also wrote this to referee 1.
- 288 During ECHO 2003 all components of the wind vector ( $u_k$ ) and the temperature  $T$  were measured  
 289 throughout the canopy (30 m) between 2 m and 41 m above ground in 9 heights with a time  
 290 resolution of 10 Hz (chapter 3.1, Dlugi et al., 2010, ACP10, 6215 - 6235). In addition, 8  
 291 psychrometer (with time resolution of about 0.066 Hz for  $T$  and specific humidity  $q$ ) were installed  
 292 at the same heights except 41 m. Therefore first up to fourth moments of wind velocity components  
 293 and temperature and their mixed moments (e.g. also third moments like  $\overline{u'_k u'_l T'}$ ) could be  
 294 calculated.



One can compare the terms of the interactions of the temperature – velocity field ( $u_k$ ,  $T$ ) (and with less time resolution the humidity – velocity ( $u_k$ ,  $q$ ) and temperature – humidity – field ( $T$ ,  $q$ )) to the terms in eq. (5), respectively eq. (9), or eq. (12). This is done in a way that  $q$  is replaced by isoprene and  $T$  by OH. The compounds isoprene and OH could be only measured with higher time resolution at one height of 37 m (7 m above mean canopy height).

But vertical profiles for *mean quantities* with time resolution of about 180s (OH) and 600s (isoprene) are available from measurements of others as cited in chapter 1 of Dlugi et al. – (2010, ACP10, 6215 - 6235). Therefore the vertical gradients of time integrated mean values of  $u_k$ ,  $T$ ,  $q$  and isoprene (ISO) as well as OH are available if the mixed terms (with spatial gradients) are calculated. In addition the covariances (*fluxes*) for momentum, heat, humidity and isoprene as well as OH could be calculated from the measured data. The results for isoprene, OH and heat are presented in the same reference (Dlugi et al., 2010) together with covariances between  $T$  or the *sonic temperature*  $T_s$  and mixing ratios e.g. of OH, isoprene and  $HO_2$ . This gives some more insight into the influences of transport and emission of BVOCs on OH mixing ratio at the measuring height.

The following remarks will be presented in a supplement:

We often found small negative values of  $\overline{T'_s OH'}$  together with small positive values of  $\overline{T'_s ISO'}$  or  $\overline{T'_s HO_2'}$  (Fig. 9 in Dlugi et al., 2010. ACP10, p. 6228).

This indicates – for example – that warm canopy surfaces tend to emit isoprene which immediately reacts with OH causing a negative correlation between  $T_s$  (or  $T$ ) and OH. This is also shown by the result that a positive (- upward directed -) sensible heat flux is observed together with negative (downward directed) fluxes of OH. The OH – fluxes are only caused by the chemical reactions with isoprene and other compounds (see our Tables 1 and 2). Therefore we used the factor  $f$  in terms of OH – reaction with isoprene versus OH – reaction with all others (measured) reactants. We will repeat these findings from the cited reference in chapter 4.3.2 of our paper.

The magnitude of terms  $TPI_k$ ,  $TPOH_k$  and  $A_{1k}$  is directly estimated from measured data. This estimate is given in Tab. 3 together with the directly calculated values for term  $S \leq 6 \cdot 10^{-8} ppb^2 s^{-1}$ . We did not mention in the text – but will do in a supplement for the revised version – that the percentage change in vertical gradients of  $T$ ,  $q$ , ISO and OH in the height interval  $23m \leq z \leq 41m$  around canopy top ( $z=h_c=30m$ ) is comparable within  $\pm 28\%$  during that experimental period. Therefore vertical profiles (and relative changes of local gradients) are comparable. All scalar quantities show maxima inside the canopy in the range  $0.77 < z/h_c < 1$  and decreases with increasing height above canopy. Therefore the signs of the mean gradients are the same.

The influences of horizontal gradients of  $\overline{T}$ ,  $\overline{q}$ ,  $\overline{u_k}$  and  $\overline{ISO}$  are estimated from additional measurements at two other towers aligned along mean main wind direction. Results from one of them – the *west-tower* (see Spirig et al. 2005) – describe also the diurnal behavior of isoprene fluxes. OH is controlled only by chemical reactions on a *local* scale of some  $m^3$  as discussed in

Dlugi et al. (2010). Therefore the horizontal gradient of OH is purely determined by the horizontal gradient of mixing ratios of chemical compounds acting as sources and sinks as given in Appendix A of the paper under review in eq. (A1).

We found empirically  $(\partial \bar{c}_l / \partial x_k) \approx a_l \cdot \sigma_{OH} (\Delta x_k)^{-1}$  with  $\Delta x_k = 3 \text{ m}$  for all reactants (Index  $l$ ) including isoprene.  $\sigma_{OH}$  is given in our Fig. 4 with  $0.2 < \sigma_{OH} / \overline{OH} < 0.45$  for OH from Fig. 5. Therefore the calculated mean local vertical gradient of OH (as given in the text) of about  $3 \cdot 10^{-5} \text{ ppb m}^{-1}$  is larger than the mean horizontal gradient of about  $1 \cdot 10^{-5} \text{ ppb m}^{-1}$  but still is of the same order of magnitude.

Conclusions:

In  $\text{TPI}_k$  the horizontal gradient has to be multiplied by the horizontal component of the turbulent flux of isoprene which is smaller by one order of magnitude than the vertical component  $\overline{w'c_i'}$ . Therefore, within an uncertainty of less than 10%, only the vertical contribution remains for term  $\text{TPI}_k$ , e.g.  $\text{TPI}_3$  ( $k=3$ ; see chapter 4.1).

For term  $\text{TPOH}_k$  the calculated vertical turbulent flux of OH is about a factor of 3 larger than the horizontal contribution and the total sum is – therefore – less than  $4 \cdot 10^{-5} \text{ ppb m}^{-1}$ . In the related formulation in line 20 of page 12934 only *the OH – flux* is mentioned without the explanation that here all three terms are added. Therefore we will revise this sentence. But the conclusion  $\text{TPI}_k \approx \text{TPOH}_k$  (see Table 3) still remains.

The discussion on the *advection of covariance*  $A_{lk}$  by the influence of the divergence of the mean flow field is correct. But the term *advection of covariance with the mean flow*  $A_{2k}$  in chapter 4.2 (line 4 - 13) needs further discussion. As mentioned in our text we found by the analysis of the data (!) that  $R_{ij} \approx \text{RES}$  can only be fulfilled together with  $S \approx 0$  (!) if also the horizontal derivatives in  $A_{2k}$  contribute to RES! Therefore, we propose that our description on page 12935 (line 4 - 13) and 12936 (line 1 - 10) will be extended with respect to the findings described in chapters 4.3.3 (with reference also to Fig. 18, 19) and 4.4 but also 5.1 (line 16 - 24).

The mean error given in the revised Table 3 (see above) is larger for triple products than for second order terms like covariances. The spatial derivatives of these quantities are estimated according to mixed moments composed of fluctuations of specific humidity  $q$  and temperature  $T$  (second moments) and  $u_k$ ,  $q$  and  $T$  (third moments). For the error analysis, we replaced  $T$  by OH and  $q$  by isoprene and assumed that the spatial derivatives are the same. For the error analysis of  $A_{lk}$  and  $A_{2k}$  the relative errors of  $q$  and  $T$  are replaced by those of OH and isoprene. The same holds for term  $\text{TT}_k$ . This allows to estimate the influence of different processes on the covariance  $\text{cov}(\text{ISO}, \text{OH})$  and  $I_s$  by an order of magnitude estimation (Chapter 4.2 and Appendix B). The finding  $\text{RES} \approx R_{ij}$  (Eq. 7, 9) is only possible if the horizontal gradients in  $A_{2k}$  significantly contribute to the magnitude of this term (see revised Table 3, number in brackets). Many studies assume that these terms are negligible.

The dominant term in  $R_{ij}$  is the normalized variance of isoprene. This term has a mean error of only 7%. The second term  $CH_{is}$  is dominated by term IV3 from Eq. 6. This triple correlation has a mean error of about 64%, but contributes only by about 10-16% to the budget of  $I_s$  in Eq. 12. Therefore the mean error of  $R_{ij}$  is only 16% (see revised Table 3).

(The term  $C_{ij}$  is composed only of third order terms. The Eq. (6) will be extended by the notation of terms (I3 to V3 from Fig. 11) and the same notation will be also written in Tab. 4. The numerical values for these terms have very different orders of magnitude (Tab. 4), and, therefore, only terms III3 and IV3 contribute to the numerical values resulting in eq. (6) or finally in Eq.(12). This simplifies the discussion on errors especially for third order moments.)

Therefore, to finally answer this question, the spatial derivatives are calculated in analogy to those from correlations between the fields of velocity, humidity and temperature. The moments itself (and their errors) are calculated from measurements on velocity, isoprene and OH. This is an estimation based purely on observations and the application of balance equations (Stull, 1988). It is common practice to replace trace gases by surrogates as T or q in higher moments and their derivatives. The final result from this approach was given in Table 3 or in the revised Table 3 (see below).

**Table 3 revised**

Term	Range	Mean Error (%)
S	$< 6 \cdot 10^{-8}$	$\pm 30 \%$
$TPI_k$	$6 \cdot 10^{-7}$ to $6 \cdot 10^{-6}$	$\pm 43 \%$
$TPOH_k$	$6 \cdot 10^{-7}$ to $6 \cdot 10^{-6}$	$\pm 48 \%$
$A_{1k}$	$< 10^{-6}$	$\pm 36 \%$
$A_{2k}$	$< 2 \cdot 10^{-7}$ ( $< 10^{-4}$ )	$\pm 50 \%$ ( $\pm 30 \%$ )
D	$< 10^{-10}$	$\pm 60 \%$
$R_{ij}$	$< 4 \cdot 10^{-4}$	$\pm 16 \%$

Lines 466-469 *According to the ergodic theorem we may assume that this spatial gradient is comparable to the time derivative S. It is my opinion that the authors should be required to provide the reader further clarity and explanation regarding*

- 391 application of this theorem to their particular situation. Also, I think the  
392 reference should be Liepmann (1952), not Lippmann.
- 393 The requirement to shorten the paper let us conclude that we should add the information given for  
394 line 457 in a supplement and avoid the hint to Liepmann (1952). We replace only time averaged  
395 and spatially averaged parameter.
- 396 Line 469 ... *and in Fig. 10  $S$  is small.* If you're going to refer to the time derivative as  $S$ ,  
397 then  $S$  needs to appear somewhere in the figure or in the figure caption.
- 398 The figure will be revised in a way that  $S$  is directly given in the capture.
- 399 Line 477-479 *The turbulent transport is also one term in the chemical part of the flux balance*  
400 *and is calculated directly from measured quantities at  $z_R=37m$ . This term is*  
401 *generally below  $\pm 10^{-5}$  ppb  $m\ s^{-1}$  ...* A couple points: 1) The turbulent transport  
402 term involves the vertical gradient of the third-order moments. How are these  
403 calculated from a single observation level? 2) Where's the figure showing that  
404 these data are shown to be in the stated range?
- 405 See our explanation given for line 457. We did not prepare a figure for terms of RES from these  
406 estimations.
- 407 Lines 500-503 What's  $I_3$ ?  $II_3$ ?  $V_3$ ?
- 408 The sentence explains what is  $I_3 - V_3$ . In addition, we will add the notation below the terms of Eq.6  
409 and in Table 4 for clarity in the revised version.
- 410 Line 507 ... *higher by a factor of two respectively four in the morning hours ...* I don't  
411 understand this sentence structure.
- 412 This paragraph will be formulated in a clearer way to point out that the mixing ratios in the  
413 morning hours are higher than later on. It might be helpful, to add a figure showing this to the  
414 supplement in the revised version.
- 415 Lines 534-535 ... *many features of  $I_S$  ...* What features? What are we talking about here?  
416 Given that most everything being discussed is calculated as a residual from the  
417 other, I'm not surprised that ups and downs of one are reflected in the other.
- 418 The whole paragraph will be shortened in a revised version.
- 419 Line 539 *Two branches ...* Again, what kind of branches are we discussing?
- 420 We are again discussing branches of separated data points in Fig.12.
- 421 Line 585 *The latter can only be determined as a mathematical residuum ....* Perhaps this  
422 is true for the experimental data being discussed here, but otherwise I must  
423 question the validity of this statement.
- 424 No comment.
- 425 Lines 711-714 What point is being made by presenting this linear regression? Is there some  
426 implication that this functional form should apply above all canopies? Or for all  
427 chemical regimes? Please inform the reader what they should take home.

428 At first, the linear relationship is for data in Fig.19.  $I_s$  is not a simple function of the normalized  
429 variance of isoprene but is influenced also by other transport processes expressed by  $RE_{is}$ , which  
430 tend to reduce this influence of variance.

431 Line 734 *This is done...* To what does 'this' refer?

432 An analysis is done with further ...

433 Lines 754-755 Why can't a typical sweep/ejection cycle be established for this current data  
434 set? What's different?

435 Only isoprene is transported through a field of locally varying OH.  $I_s$  is significantly influenced by  
436 the normalized variance of isoprene which can be advected. Therefore a measure of isoprene  
437 variance,  $M_{21}$ , can be related to the residual transport term  $RE_{is}$  but also the normalized variance.  
438 But a relation with the turbulent transport of the isoprene flux cannot be detected in the data.

439 Lines 806-810 *A comparable spatial variability of  $H_v$  may be possible for ECHO2003 ...* Does  
440 this sentence intend to state that the ECHO2003 measurements are affected  
441 by heterogeneous sources of heat and isoprene? If so, this leads back to my  
442 earlier comment regarding mean vertical velocity.

443 Due to the spatial heterogeneity of the Jülich landscape, we mentioned this possibility. In a revised  
444 version, we will add additional information in the supplement about the site. On the other hand, a  
445 quantitative analysis of these mesoscale transport phenomena is not done yet and is far above the  
446 scope of this paper.

447 Lines 827-829 Patton et al. (2001) reported a value of the stability parameter ( $h_c/L$ , where  $L$  is  
448 the Obukhov length) of -0.4 for their simulations. This seems far from what the  
449 community would call 'free-convection', i.e. shear production remains  
450 important. Also, for the 'average' case presented here (using the reported  
451 values of  $u_* = 0.39$  m/s and  $H = 0.085$  m K/s), I calculate that  $h_c/L$  is  
452 approximately -0.5 – not terribly different from that presented in Patton et al.  
453 (2001). Something therefore seems awry with this entire discussion.

454 Patton et al. 2010 reported on page 95 that  $H=0.43$  K m s<sup>-1</sup>. This is comparable to  $H=413$  W m<sup>-2</sup>.  
455 This means free convection. If one takes his value  $h_c/L = -0.4$  from page 96 and estimates a heat  
456 flux the result is  $H=0.85$  K m s<sup>-1</sup> as given by your estimation. If we take that value for granted, then  
457 the results agree with our analysis in a better way. We will present this relationship also in the text of  
458 a revised version and refer to your comments.