1   **Journal:** ACP

2   **Title:**

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

5   **Author(s):** R. Dlugi et al.

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8

9   **Reply to Anonymous Referee #1**
10   (Received and published: 24 May 2013 - Atmos. Chem. Phys. Discuss., 13, C2742–C2746, 2013)

11

12   We thank this referee for his very detailed and extremely helpful review. Two main remarks
13   are given followed by a number of specific comments:

14   *I have two main remarks: (1) The observational data used in the research is rather limited. I*
15   *realized that this measurements are very difficult to be taken, and the data analysis and*
16   *interpretation is very difficult. The study only used 22 block of 10 minutes. This insures a*
17   *satisfactory quality to calculate mean statistics, but for higher-order moments is not enough to*
18   *obtain robust statistics. Have they additional data set that can be used to further support their*
19   *findings and obtain more reliable statistics? (2) I found the paper with more than 24 figures very*
20   *lengthy and with some repetitions. I will recommend to the authors to shorten the paper and*
21   *remove unnecessary figures. By so doing, the paper will be more accessible to potential readers*

22   The first main remark addresses the robustness of statistics for third moments which appear
23   in our equation (5) – (12). The second asks to revise the paper with respect to

24   a) some repetitions and
25   b) *unnecessary figures*.

26   A Part of these comments is also given by referee #2. But we separately answer to each of
27   these reviews with reference to each other if we think this is appropriate.

28   Reply to the main remarks:

29   It is true that the number of 22 blocks of 10 minutes field data from ECHO 2003 for the
30   further analysis of segregation in the isoprene – OH – system is limited. But, to our
31   knowledge, no comparable additional analysis of such experimental data is published
32   elsewhere up to now.

33   We described this data set and how it was obtained during the ECHO field study together
34   with first steps of an analysis in detail in our paper in Atmos. Chem. Phys. 10. 6215 – 6235.
35   Initiated by the further discussion on these results in addition with some comments given by

36 the reviewers (of this paper in ACP10) and some colleagues (see our acknowledgements) we

37 stepped further into the analysis of these field data from the ECHO – campaign 2003.

38 One of these aspects is to present an analysis of these field data in terms of the theoretical

39 frame also used to model the interactions of turbulence, convection and chemical reactions,

40 e.g. to apply these equations (5) – (12) (and also (1) – (4)) for data analysis. This concept

41 (widely applied in experimental studies of physics and chemistry in the ABL (e.g. Stull, 1988;

42 Sorbjan, 1989; Lenschow, 1982) should provide results for a further analysis of the relative

43 importance of transport / mixing versus chemical reactions on segregation intensity I_s. This

44 procedure also keeps the experimental data rather independent from specific properties of

45 models, and, therefore, allows an intercomparison with results published – for example – by

46 Patten et al. (2001) and Ouwersloot et al. (2001) or – as proposed by this referee – also

47 Vinuesa et al. (2003).

48 Doing this, first to fourth moments of all quantities are calculated. For the first and second

49 order moments we calculated errors and presented the *uncertainty of the covariance* in I_s

50 and for I_s itself in Figs. 9, 10, 12. We now will add the presentation of errors also for the first

51 and second moments in a supplement and for the terms in Eq. 5 and Eq. 6 in an extended

52 Table 3. As the uncertainty in mean values, standard deviations and variances is significantly

53 smaller than for second and third moments and I_s, we did not present these small deviations

54 in figures. But – as mentioned – we will now add this information on numerical values in the

55 text and (e.g. chapter 3.2.4) with references to the new supplement and an extended table

56 as given below. As an example the revised Table 3 will therefore read as follows:

57 Table 3

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}	$< 4 \cdot 10^{-4}$	$\pm 16\,\%$

58 The third moments appear in terms RES (a)) and R_{ij} (b)). R_{ij} is a sum of two terms (eq. (10)),
59 one the product of the mean concentration of OH times the variance of isoprene and the
60 other (C_{ij}) a sum of triple correlations.

61 a) RES is a linear combination of two terms composed of products of second order
62 moments and gradients of mean quantities and three terms (A_{1k}, A_{2k}, TT_k) with the
63 divergence of the wind field and of third moments and gradients of second moments.
64 To explain which terms become important for the final analysis we introduced
65 chapter 4.2. But − concerning the comments of reviewer #1 (but also reviewer #2) −
66 this presentation is revised with respect to
67 1) a more detailed description why a number of terms can be neglected in eq. (5)
68 respectively eq. (9) or finally eq. (12) and
69 2) a further consideration on errors to prove the reliability of our analysis and to
70 describe the influence of uncertainties on the results especially in triple
71 correlations (see above: revised Table 3).

72 According to the requirements given by both referees, the revised version will have the
73 following structure also to shorten the paper and the number of figures:

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

88 The additional information on the experiment will cover several aspects like the following:

89   1) During ECHO 2003 all components of the wind vector (u_k) and the temperature T
90   were measured throughout the canopy (30 m) between 2 m and 41 m above ground
91   in 9 heights with a time resolution of 10 Hz (chapter 3.1, Dlugi et al., 2010, ACP10,
92   6215 - 6235). In addition, 8 psychrometer (with time resolution of about 0.066 Hz for
93   T and specific humidity q) were installed at the same heights except 41 m. Therefore

94   first up to fourth moments of wind velocity components and temperature and their

95   mixed moments (e.g. also third moments like $\overline{u_k' u_l' T'}$) could be calculated.

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

102   But vertical profiles for *mean quantities* with time resolution of about 180s (OH) and
103   600s (isoprene) are available from measurements of others as cited in chapter 1 of
104   Dlugi et al. – (2010, ACP10, 6215 - 6235). Therefore the vertical gradients of time
105   integrated mean values of u_k, T, q and isoprene (ISO) as well as OH are available if the
106   mixed terms (with spatial gradients) are calculated. In addition the covariances
107   (*fluxes*) for momentum, heat, humidity and isoprene as well as OH could be
108   calculated from the measured data. The results for isoprene, OH and heat are
109   presented in the same reference (Dlugi et al., 2010) together with covariances
110   between T or the *sonic temperature* T_s and mixing ratios e.g. of OH, isoprene and
111   HO_2. This gives some more insight into the influences of transport and emission of
112   BVOCs on OH mixing ratio at the measuring height.

113   The following remarks will be presented in a supplement:

114   We often found small negative values of $\overline{T_s' OH'}$ together with small positive values

115   of $\overline{T_s' ISO'}$ or $\overline{T_s' HO_2'}$ (Fig. 9 in Dlugi et al., 2010. ACP10, p. 6228).

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

124   The magnitude of terms TPI_k, $TPOH_k$ and A_{1k} is directly estimated from measured
125   data. This estimate is given in Tab. 3 together with the directly calculated values for
126   term $S \leq 6 \cdot 10^{-8} \, ppb^2 s^{-1}$. We did not mention in the text – but will do in a
127   supplement for the revised version – that the percentage change in vertical gradients

128   of T, q, ISO and OH in the height interval $23m \leq z \leq 41m$ around canopy top

129   ($z=h_c=30m$) is comparable within ±28% during that experimental period. Therefore

130   vertical profiles (and relative changes of local gradients) are comparable. All scalar

131   quantities show maxima inside the canopy in the range $0.77 < z/h_c < 1$ and

132   decreases with increasing height above canopy. Therefore the signs of the mean

133   gradients are the same.

134   The influences of horizontal gradients of $\overline{T}$, $\overline{q}$, $\overline{u_k}$ and $\overline{ISO}$ are estimated from

135   additional measurements at two other towers aligned along mean main wind

136   direction. Results from one of them – the *west-tower* (see Spirig et al. 2005) –

137   describe also the diurnal behavior of isoprene fluxes. OH is controlled only by

138   chemical reactions on a *local* scale of some m^3 as discussed in Dlugi et al. (2010).

139   Therefore the horizontal gradient of OH is purely determined by the horizontal

140   gradient of mixing ratios of chemical compounds acting as sources and sinks as given

141   in Appendix A of the paper under review in eq. (A1).

142   We found empirically $\left(\partial \overline{c_l} / \partial x_k \right) \approx a_l \cdot \sigma_{OH} \left(\Delta x_k \right)^{-1}$ with $\Delta x_k = 3$ m for all reactants

143   (Index *l*) including isoprene. σ_{OH} is given in our Fig. 4 with $0.2 < \sigma_{OH} / \overline{OH} < 0.45$ for

144   OH from Fig. 5. Therefore the calculated mean local vertical gradient of OH (as given

145   in the text) of about $3 \cdot 10^{-5} \, ppb \, m^{-1}$ is larger than the mean horizontal gradient of

146   about $1 \cdot 10^{-5} \, ppb \, m^{-1}$ but still is of the same order of magnitude.

147   Conclusions:

148   - In TPI$_k$ the horizontal gradient has to be multiplied by the horizontal

149   component of the turbulent flux of isoprene which is smaller by one order of

150   magnitude than the vertical component $\overline{w'c_i'}$. Therefore, within an

151   uncertainty of less than 10%, only the vertical contribution remains for term

152   TPI$_k$, e.g. TPI$_3$ (k=3; see chapter 4.1).

153   - For term TPOH$_k$ the calculated vertical turbulent flux of OH is about a factor of

154   3 larger than the horizontal contribution and the total sum is – therefore –

155   less than $4 \cdot 10^{-5} \, ppb \, m^{-1}$. In the related formulation in line 20 of page 12934

156   only *the OH – flux* is mentioned without the explanation that here all three

157   terms are added. Therefore we will revise this sentence. But the conclusion

158   TPI$_k$ ≈ TPI$_3$ ≈ TPOH$_k$ (see Table 3) still remains.

159   - The discussion on the *advection of covariance* A_{1k} by the influence of the

160   divergence of the mean flow field is correct. But the term *advection of*

161   *covariance with the mean flow* A_{2k} in chapter 4.2 (line 4 - 13) needs further

162   discussion. As mentioned in our text we found by the analysis of the data (!)

163   that $R_{ij} \approx RES$ can only be fulfilled together with $S \approx 0$ (!) if also the horizontal

164   derivatives in A_{2k} contribute to RES! Therefore, we propose that our

165   description on page 12935 (line 4 - 13) and 12936 (line 1 - 10) will be

166   extended with respect to the findings described in chapters 4.3.3 (with

167   reference also to Fig. 18, 19) and 4.4 but also 5.1 (line 16 - 24).

168

169 The mean error given in the revised Table 3 (see above) is larger for triple products than for

170 second order terms like covariances. The spatial derivatives of these quantities are

171 estimated according to mixed moments composed of fluctuations of specific humidity q and

172 temperature T (second moments) and u_k, q and T (third moments). For the error analysis, we

173 replaced T by OH and q by isoprene and assumed that the spatial derivatives are the same.

174 For the error analysis of A_{1k} and A_{2k} the relative errors of q and T are replaced by those of OH

175 and isoprene. The same holds for term TT_k. This allows to estimate the influence of different

176 processes on the covariance cov(ISO, OH) and I_s by an order of magnitude estimation

177 (Chapter 4.2 and Appendix B). The finding RES ≈ R_{IJ} (Eq.7, 9) is only possible if the horizontal

178 gradients in A_{2k} significantly contribute to the magnitude of this term (see revised Table 3,

179 number in brackets). Many studies assume that these terms are negligible.

180 b)   The dominant term in R_{ij} is the normalized variance of isoprene. This term has a mean

181   error of only 7%. The second term CH_{is} is dominated by term IV3 from Eq. 6. This triple

182   correlation has a mean error of about 64%, but contributes only by about 10-16% to the

183   budget of I_S in Eq. 12. Therefore the mean error of R_{ij} is only 16% (see revised Table 3).

184   (The term C_{ij} is composed only of third order terms. The Eq. (6) will be extended by the

185   notation of terms (I3 to V3 from Fig. 11) and the same notation will be also written in

186   Tab. 4. The numerical values for these terms have very different orders of magnitude

187   (Tab. 4), and, therefore, only terms III3 and IV3 contribute to the numerical values

188   resulting in eq. (6) or finally in Eq.(12). This simplifies the discussion on errors especially

189   for third order moments.)

190 Finally, a revised paper will also cover the following corrections:

191   •   The English language will be improved.

192   •   The Structure of the paper: will be significantly revised according to the suggestions of

193   Referee 1 and 2 in order to provide an improved guideline to the reader.

194   •   The robustness of results and errors of the results will be discussed in detail (see detailed

195   response to general remarks).

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

197   new Supplement.

198

Specific comments:

199

200   **1.** *In the introduction there is some confusion on the definition of the Damkohler number first*
201   *introduced as the time scale of a specific chemical reaction, but later on used as a time*
202   *scale of a chemically active species. I recommend to clarify it.*

203   In a revised version we will clarify that in general the Damköhler number *Da* is
204   introduced *as the time scale of a specific reaction* and that – for the (isoprene + OH) -
205   system within the context of this study – *Da* is always used with respect to the time
206   scale of a reactant (isoprene) with respect to the active species OH.

207   **2.** *Section 2. In Equation (1), and since they focus entirely their research on isoprene and*
208   *the hydroxyl radical, it is perhaps handier and clearer to substitute ci and cj by iso and oh.*

209   We specified c_i = *isoprene* and c_j = *OH* in line 19 on page 12922, because the general
210   description in eq. (5) – eq. (12) makes it easier to follow the derivation. In addition, if
211   we refer to the specific comment 14., one can give a more general formulation,
212   because even if $S \approx 0$ is not valid, only an additional term has to be considered – e.g.
213   for NO and O_3. We will extend the paper by a list with all notations to support the
214   reader.

215   **3.** *Section 2.1.(lines 17 on page 12920 to 3 on page 12921). Quoting them: 'variation of*
216   *only 4.7 % in k_ij'. This leads to 4.7 % difference in chemical reaction rate. Therefore, the*
217   *influence of this variable is of the same magnitude as the effect that is investigated (e.g.*
218   *Fig. 22). This does not seem a valid justification to use a constant k_ij in the analysis.*

219   **a)** If k_{ij} varies by 4.7% – e.g. for a value of $k_{ij}[ISO] \cdot [OH] = 3 \cdot 10^{-4}\ ppb\ s^{-1}$ in Fig. 2 –
220   this is an uncertainty of $1.41 \cdot 10^{-5}\ ppb\ s^{-1}$.

221   **b)** For a variation of 4.7% in Fig. 18 a value of $1.5 \cdot 10^{-4}\ ppb\ s^{-1}$ on the ordinate could
222   be shifted by about $\pm 7 \cdot 10^{-6}\ ppb\ s^{-1}$, which is about ±1 mm on the scale chosen in
223   the online version of Fig. 18 in ACP. To compare with the range of ten data points:
224   They cover a range of about 80 mm.

225   **c)** I_s itself is only influenced by the application of a mean value of k_{ij} in term RE_{is}.
226   To classify these aspects for the reader, we will add the description of the systematic
227   uncertainty in k_{ij} and its consequence in a new supplement, where we will also
228   discuss the results of error analysis for first to third moments.

229   **4.** *Section 2.1. The flux divergences is calculated a residual term and therefore includes*
230   *contributions of the horizontal advection and horizontal turbulent advection. In order to*
231   *avoid misunderstandings ₁will recommend to name it in a different way.*

232   Yes, both terms need to be named in a revised version.

233   **5.** *Section 2.1 (line 27 on page 12921 to lines 3 on page 12922): since the 'flux divergence'*
234   *is actually a residual term, calculated with the mean reaction rate, it is not surprising that it*

235 *has a linear relation with a high correlation coefficient. This could also indicate that the*
236 *observations are wrong. For example, when in this analysis, the mean reaction rate would*
237 *be multiplied by a factor 1000, the 'flux divergence' would be virtual equal to the negative*
238 *of the mean reaction rate since it is the residual term. This would lead to a linear relation*
239 *with correlation coefficient 1. The conclusion that 'advection is not significant in our case'*
240 *can therefore not be drawn on this argument.*

241 The storage term and the flux divergence are of same order of magnitude. The
242 chemical term is smaller than about one order of magnitude. Therefore chemistry
243 influences the flux divergence to a lesser extent than any other mixing or transport
244 process. We therefore revise our statement.

245 **6.** *Section 3.2.1 (pages 12923, 1 20-23) It will be interesting if a similar relation holds for*
246 *isoperne.*

247 In Appendix A we describe that OH is locally produced and – itself – is not
248 transported! Therefore a definition of a Damköhler number – as applied by Patton et
249 al. (2001) for isoprene with respect to OH – is not meaningful. Formally OH is not
250 transported but if we calculate an effective τ_t for the volume of $1 - 3 \ m^3$ (where OH
251 is produced and destructed) by the wind velocity we end up with $\tau_t > 3 \ s$ for
252 $\tau_c < 0.2 \ s$ (Dlugi et al., 2010, ACP 10). Therefore $\tau_c \ll \tau_t$, and with
253 $k_{ij} = 2.3 \ ppb^{-1}s^{-1}$ and $\overline{ISO} \approx 1 \ ppb$ this leads to

$$\tau_t / \tau_c = D_{iso} > [\text{large number} \ (> 15)] \cdot 2.3 \ ppb^{-1}s^{-1} > 30$$

255 and OH is in the very fast reacting range, as required (line 20, page 12916).

256 **7.** Section 3.2.2. (lines 20-23) Related to the previous point, the authors seem to indicated
257 that entrainment of isoprene (quoting them: " ... some hundred meters above the surface
258 ... ") is an important processes influencing the reactivity behaviour. Van Stratum et al.
259 (AGP 12, 5329-5341) (see Figure 6) presented a budget of reactants where entrainment
260 was a relevant process (at least during the large ABL morning growth). Could they clarify
261 and discuss the role of entrainment in the analysis of the observations?

262 The information on vertical transport was obtained from local measurements of *w* at
263 the main tower. At his day (25 July, 2003) convective clouds modulated solar UV-
264 radiation (e.g. photolysis of O_3 and NO_2) and – according to descriptions in literature
265 for comparable situations (e.g. Stull, 1988) – should have influenced ABL
266 characteristics. The ABL morning growth by heat (and moisture) transfer from the
267 surface is therefore modified by the influence of cloud's downdrafts and updrafts
268 moving through the experimental area. At measuring height we found a mixed
269 influence of shear driven and convective turbulence (see our chapter 5.2.2). We –
270 therefore – cannot quantify the role of entrainment from *CBL – scaling* but only the
271 role of net downward transport in this ABL near the canopy top.
272 During the measuring campaign several flights with a motor – glider performed by Dr.
273 Bruno Neininger, showed that

274   a) the isoprene mixing ratio decreased with height above canopy as in Davis (1992)
275   respectively Davis et al. (1994): *J. Geophys. Res. 99 (D12), 25587 – 25598,* and
276   b) that the variances of ISO and temperature T also decreased with height as
277   described for T e.g. in Stull (1988). We will add this information and a comparison to
278   results by van Stratum et al. (ACP 12) in the new supplement.

279   **8.** *Section 3.2.4 In the comparison with LES results, I was wondering how representative it*
280   *is to compare surface layer measurements influenced by canopy effect with large-eddy*
281   *simulations that are mainly representative for mixed-layer properties.*

282   The results from model calculations and measurements are different and we discuss
283   possible reasons. The paper of Ouwersloot et al. (2011) shows the *horizontal spatial*
284   *correlation between isoprene and OH* in their Fig. 6. We compare their data given to
285   levels down to $h_z = 0$ m with our correlation coefficients for time averaged quantities.
286   Here we suppose that time averaged quantities and spatially averaged quantities can
287   be compared also for this chemical system (see Shu, 1976; Sorbjan, 1989; Stull, 1988;
288   Panofsky, Dutton (1984): Atmospheric turbulence, models and methods for
289   engineering applications, Wiley, N. Y.). It might be that their subscale turbulence
290   parameterization causes a higher correlation (coefficient) near the surface than
291   determined by us from local measurements in some type of a mixed layer (see: Katul
292   et al., 1997; cited in our paper). This can be the case if their pdf's for isoprene are less
293   skewed than found in our measurements (e.g. Fig. 6c, Dlugi et al. (2010), ACP10,
294   6215 – 6235). But they found this behavior (correlation coefficient $r > 0.85$)
295   throughout the ABL (with height h) up to about $z/h < 0.90$ for homogeneous and
296   heterogeneous conditions.

297   **9.** *Section 4.1 (equation 5). The introduction of Equation (5) is very confusing. First they*
298   *mentioned that the advections terms are neglected and thereafter are included (term A2k*
299   *for instance). I recommend to introduce it in a systematic and clearer way.*

300   The advection is given in eq. (5) although **others** neglect this term in their model
301   studies. We will introduce eq. (5) in a text of a revised version without the
302   restrictions mentioned in line 5 – 6 on page 12930 according to this
303   recommendation.

304   **10.** *Equation 10. The use of Cij can bring confusion when comparing with the concentration.* ᴵ
305   *recommend to use another notation.*

306   We will add a list of all symbols in a revised version also with the definition for C_{ij} .
307   A bold letter **C** with indices ij (**C**$_{ij}$) refers to the chemical term (**C**) with triple
308   correlations between compounds i,j with concentrations c_i and c_j . The definition – by
309   a comparison between eq. (6) and (10) – will be explicitly written in the list of
310   symbols to avoid any misunderstanding.

311 **11.** *Section 4.1 (equation 5). The introduction of Equation (5) is very confusing. First they*
312 *mentioned that the advections terms are neglected and thereafter are included (term A2k*
313 *for instance). I recommend to introduce it in a systematic and clearer way. 12- Section 4.1*
314 *(equation 11) Equation (11) does not seem right: the + sign should be a minus. From Eq.*
315 *(8) there is within [] basically RES - kij (Cij + cj ci'2). This results, after division by kij ci in -*
316 *Cij/ci - cj/ci ci'2. So, the + sign should be a minus. Could they check the consistency of the*
317 *sign?*

318 Is answered by 9.

319 **12.** *Section 4.1 (equation 11) Equation (11) does not seem right: the + sign should be a*
320 *minus. From Eq. (8) there is within [] basically RES - kij (Cij + cj ci'2). This results, after*
321 *division by kij ci in - Cij/ci - cj/ci ci'2. So, the + sign should be a minus. Could they check*
322 *the consistency of the sign?*

323 Thank you for this remark. Yes, there is a printing error which occurred by the
324 transfer process and could not be corrected by the ACP administration. Therefore
325 both terms have a negative sign. This error will be corrected in a revised version. The
326 calculations of related data and the presentation in Figs. were also checked and are
327 found to be all correct.

328 **13.** *Section 4.2 (page 12934, line 20). A question that perhaps deserve some attention is if a*
329 *radical fast compound like OH is transported vertically by turbulent motions. Has the OH-*
330 *turbulent flux a physical meaning? What is the accuracy of the measurement of the OH-*
331 *flux?*

332 The OH flux is a net result of the chemical reaction with compounds coming mainly
333 from below to the measuring volume. The calculated flux $\overline{w'OH'} = r_{w,OH} \cdot \sigma_w \cdot \sigma_{OH}$ is
334 mainly determined by $r_{w,OH}$ and to a lesser extent by σ_{OH}. As stated in Dlugi et al.
335 (2010), ACP10, 6215 – 6235, in chapters 3.5 and 5.2.1 the OH – flux *is underestimated*
336 *by -37%* by the influence of the correlation coefficient. A comparison (not published)
337 for the OH – flux for a 40 minute time interval compared to the 10 minutes interval
338 shows a statistical error of 18%. A maximum loss of 13% for fluxes compared to
339 instruments which sample from the same volume and with 10 Hz (instead of 0.2Hz) is
340 theoretically estimated from these measurements during ECHO 2003 which is smaller
341 than our estimate for the statistical error (18%) and a systematic error of -37%
342 (underestimation of fluxes; Tab. 4 of Dlugi et al. (2010) , ACP10, 6215 – 6235).

343 For the calculation in this paper we did correct for this systematic error! The accuracy
344 of the measurements of w is ±0.007 ms^{-1} by the procedures described by Dlugi et al.
345 (2010). For the OH – mixing ratios we found a mean relation
346 $OH'/std\ dev\,(OH) > 4.2$ as error of a single measurement for 0.2 Hz (as given in
347 Dlugi et al. (2010)). We will add this information and a short description of calibration

348   procedures to measure wind components in the supplement, because also referee 2
349   asked for such details.

14. *Section 4.2 (page 12935, line 20). Although the large-eddy simulation loses accuracy*
351   *within the atmospheric surface layer, I think it can be interesting, at least qualitatively,*
352   *(and for the sake of completeness of the discussion) to include a comparison with the co-*
353   *variance budget presented by Vinuesa et al. (Tellus 558, 935-949, 2003) for the NO-N02-*
354   *03 triad to determine if the vertical distribution and the order of magnitude of the different*
355   *contributions of the co-variance equation is similar.*

356   In this paper we analyze the reaction between isoprene and OH from available
357   measurements (see our *general remarks*). These were *point measurements*! This
358   analysis is done also with respect to an influence of other reactants on the *available*
359   *OH* for this reaction with isoprene. A comparison with the concept published by
360   Vinuesa et al. (Tellus 55B, 935 – 943, 2003) requires that not only surface fluxes of
361   the reacting compounds, but also entrainment fluxes are available for the calculation
362   of their dimensionless concentrations respectively mixing ratios (see their eq. 9).
363   As pointed out before (see point 7.), the *CBL – scaling* according to the concept
364   applied also by Vinuesa et al. (2003) should not be applied to the ABL on 25 July 2003
365   at this site because we had a cloud topped boundary layer. But if we calculate z_i -
366   despite the observed conditions - we need a CBL – height of $z_i \approx 1500\ m$ e.g. to
367   compare with observed variances of isoprene according the concept applied in their
368   chapter 6 for a bottom- up transported compound for c_b=ISO.
369   The bottom of clouds was estimated to be between 650 m at 10:00 CET and 800 m at
370   13:30 CET and their vertical extent was about 200 – 400 m. Therefore their top was
371   about 1000 m – 1200 m. For this height the calculated variances of isoprene were
372   only in agreement with observed values if the corresponding isoprene entrainment
373   flux would be 40% of the surface flux. Compared to findings by B. Neininger during
374   ECHO 2003 and the results published by Davis (1992, 1994) this is rather unlikely
375   (see: Comment 7). Therefore, albeit vertical *pumping* by clouds may modify the
376   vertical profiles of scalars and their variance in a comparable way as done by
377   convective transport (in the cloud free (!) CBL), the comparison is rather qualitative.
378   In any case, OH is not transported and a dimensionless concentration scale for OH
379   cannot be justified because the OH – flux is only a result of its local chemical
380   reactions! Therefore for the available set of data we cannot perform a robust
381   comparison based on our data and the set of equations published by Vinuesa et al.
382   (2003).
383   On the other hand they calculate segregation also for a chemical mixture including a
384   compound RH which has a reaction rate with OH with $k = 1.8\ ppb^{-1}s^{-1}$ not far from
385   the rate constant $k_{ij} = 2.3\ ppb^{-1}s^{-1}$ for (ISO + OH). They obtained an average value

386   of the intensity of segregation for the CBL between $0.2z_i$ and $0.8z_i$ of I_s = -0.17 (see

387   their Table 3) for the *complex chemistry* case from their LES model runs. Although the

388   conditions are different we will cite and discuss their results and add this information

389   also to Fig. 22. Their second value of I_s = -0.23 is obtained from a parameterization if

390   the covariance (in our eq. (3)) is replaced by our eq. (4) and using results of their LES

391   model. This higher value is compatible to results with a higher correlation coefficient

392   of about 0.95.

393   **15.** *Connected to the previous comment, the diffusion term seems to have a different*

394   *meaning and order of magnitude in the research presented by Patton et al. (2001) and*

395   *Vinuesa et al. (2003) (see for instance Figure 7). In the LES studies, the term is repre-*

396   *senting a dissipation at the smaller scales and it is comparable in order of magnitude to*

397   *the other terms in the co-variance equation (gradient production, chemistry or turbulent*

398   *transport). In turn, in this observational research, this term represent a molecular diffusion*

399   *term and it is smaller compared to the other terms (see discussion at lines 23-25 at page*

400   *12935). Could the authors comment on this differences?*

401   We used the equation with molecular diffusion term D which is important at the

402   boundaries because our measurements were near boundaries (canopy, tower). They

403   disregard this term in the volume of the flow because there it is small compared to

404   others. Their term *D* in the LES studies is composed of the contributions of *subgrid*

405   *scale dissipation*, which is still turbulent dissipation below the spatial scale they

406   resolved (for example 1 – 10 m or larger).

407   For this spatial scale, *turbulent diffusivity* is comparable to values larger than about

408    $10^{-2} m^2 s^{-1}$ compared to $D \approx 10^{-5} m^2 s^{-1}$ for molecular diffusion in our Eq.5. Therefore

409   their Term *D* is of influence. This influence correctly increases with decreasing

410   distance to the boundary (as shear driven turbulence intensity increases).

411   **16.** *Section 5.2.2. In view of the completeness of the research and the temporal evolution of*

412   *the atmospheric stability, it is perhaps interesting to show a figure of Is as a function of a*

413   *stability parameter like z/L or the Richardson gradient number.*

414   We did a complete analysis on the behavior of cov(ISO, OH), I_s and other quantities

415   like variances, skewness and kurtosis but also mixed third moments as function of

416   stability parameter. The requirement (also by Reviewer #2) is that we remove

417   *unnecessary figures*. If we add this information $-I_s = f(z/L)$ or $-I_s = f(R_i)$ we will

418   therefore add this figure to the supplement where we also shortly discuss this result.

419   No clear dependence on z/L* for I_s is visible. This may be caused also by the finding

420   that the mixing processes above *tall* canopies in general do not scale with standard

421   surface layer scaling parameter schemes. In this layer phenomena as in a mixed layer

422   are observed and scaling might be better with mixing layer height and u* (e.g. Katul

423   et al., 1997; Katul et al., 1998: Journal Applied Meteorol., 37, 1533 – 1546).

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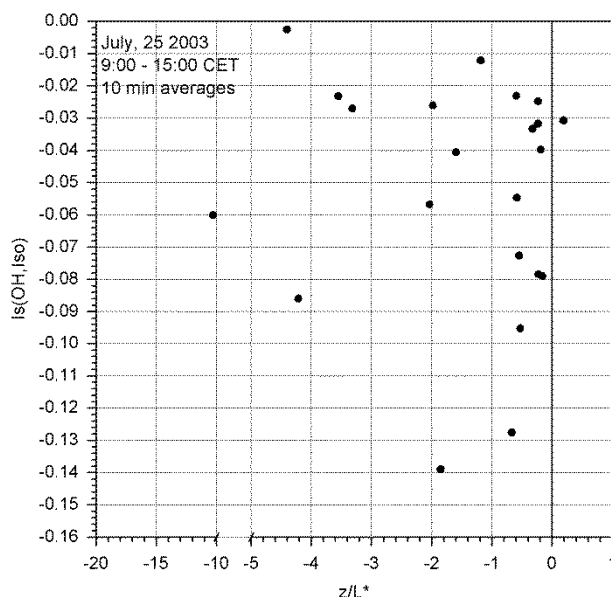
17. *General comment on figures and data treatment. In view of the uncertainties associated to the simultaneous measurements of turbulence and fast atmospheric compounds, ₁ will recommend the use of error bars in all the figures.*

We follow this recommendation and give the required information in the revised Table 3 and in Figures of the revised version.

18. *Figure 22 is a very good summary of the observational results of Is combined with the buoyancy surface forcing. In order to complete and integrate with the numerical studies, it is perhaps interesting to include some representative results reported by Patton et al. (2003) and additional point for Is under homogeneous surface conditions. The Is value from Ouwersloot et al. (2011) in Fig. 22 and line 28 of page 12947 is indeed for a numerical simulation with DeltaH_v = 0, but this experiment considers still differences in isoprene emissions (0.7 ppb m/s) and is therefore NOT representative for homogeneous surface conditions. To truly compare for homogeneous conditions, use their HOM experiment: Is = -0.070. As can be expected, this result also fits better with the other values in Fig. 22. It is possible to combine both values, explaining the difference.*

Yes, we will present now both values and explain the differences. But we will also point out here that the ECHO – site is not a homogeneous site! Therefore we used their I_s value for Delta H_v=0 instead of the value for HOM.
But in a revised version we will also add in the supplement additional information on the distribution of isoprene sources around the main tower.

19. *Appendix A: f is not the relative reaction rate for OH consumption by isoprene compared to total OH consumption, but compared to OH consumption by other compounds. However, it is stated (line 22 of p 12953) that f is an estimation to calculate the relative isoprene sink from the reaction with OH, so it would make more sense to calculate f as*

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450   *the relative reaction rate for OH consumption by isoprene compared to total OH*
451   *consumption. Why this discrepancy?*

452   The formulation in line 22 (page 12953) is misleading and should better read: "… *f* to
453   calculate the isoprene sink relative to the sink by other compounds for the reaction
454   with OH".

455   We have chosen this formulation of *f* because we found a better dependence of I_s on
456   OH_{mod} than on $OH_{measured}$ (Fig.6). In addition, I_S and the correlation coefficient better
457   follow the term ISO · OH_{mod} for all categories of *f* (see our Fig.24 and the 2 following
458   figures here). We will refer to these results in a supplement of the revised version.

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