



**Balances of mixing ratios and segregation intensity**

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# The balances of mixing ratios and segregation intensity: a case study from the field (ECHO 2003)

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## Abstract

An inhomogeneous mixing of reactants causes a reduction of their chemical removal compared to the homogeneously mixed case in turbulent atmospheric flows. This can be described by the intensity of segregation  $I_S$  being the covariance of the mixing ratios of two species divided by the product of their means. Both terms appear in the balance equation of the mixing ratio and are discussed for the reaction between isoprene and OH for data of the field study ECHO 2003 above a deciduous forest. For most of these data,  $I_S$  is negatively correlated with the fraction of mean OH mixing ratio reacting with isoprene.  $I_S$  is also negatively correlated with the isoprene standard deviation. Both findings agree with model results discussed by Patton et al. (2001) and others. The correlation coefficient between OH and isoprene, and, therefore,  $I_S$  increases with increasing mean reaction rate. In addition, the balance equation of the covariance between isoprene and OH is applied for the analysis of the same field data. The storage term is small, and, therefore, a diagnostic equation for this covariance can be derived. The chemical reaction term  $R_{ij}$  is dominated by the variance of isoprene times the quotient of mixing ratios of OH and isoprene. In addition a diagnostic equation for  $I_S$  is formulated. Comparing different terms of this equation,  $I_S$  and  $R_{ij}$  show a relation also to the normalized isoprene standard deviation. It is shown that not only chemistry, but also turbulent and convective mixing and advection – considered in a residual term – influence  $I_S$ . Despite this finding, a detection of the influence of coherent eddy transport above the forest according to Katul et al. (1997) on  $I_S$  fails, but a relation with the turbulent transport of isoprene variance is determined. In addition, largest values of  $I_S$  are found for most unstable conditions with increasing buoyancy. These results are compared to model results by Ouwersloot et al. (2011).

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## 1 Introduction

Mixing and simultaneous chemical reactions of trace gases in the atmospheric boundary layer (ABL) are shown to be influenced by the turbulent regimes of the fluid and convection as well as the oxidation potential of the atmosphere (e.g. Seinfeld and Pandis, 1997; Finlayson-Pitts and Pitts Jr., 1986; Lamb and Seinfeld, 1973; Donaldson, 1975). The early formulations of spatially resolved models to predict the development of photochemical air pollution considered therefore chemical reactions – mainly of first, second and third order – in a way that not only mean mixing ratios  $\overline{c_i}$  and their products (e.g.  $\overline{c_i} \cdot \overline{c_j}$  for a second order reaction) together with the rate constant  $k_{ij}$  appear in the rate equations, as determined from laboratory experiments (e.g. Finlayson-Pitts and Pitts Jr., 1986), but also additional terms, considering the deviation  $c'_i$  from means  $\overline{c_i}$ , like variances and covariances  $\overline{c'_i \cdot c'_j}$ , have to be considered (e.g. O'Brien, 1971; Lamb and Seinfeld, 1973; Shu, 1976; Mc Rae et al., 1982; Donaldson and Hilst, 1972; Donaldson, 1975; Lamb and Shu, 1978). If for a second order reaction the product of the mean mixing ratios fulfills the relation  $\overline{c_i} \cdot \overline{c_j} \gg \overline{c'_i c'_j}$ , the influence of turbulent fluctuating terms in the reaction rate equation  $k_{ij}(\overline{c_i} \cdot \overline{c_j} + \overline{c'_i c'_j})$  can be neglected for the prediction of either mean value  $\overline{c_i}$  or  $\overline{c_j}$  (e.g. Shu, 1976). The same conditions are valid if the balances of higher order moments (e.g. variances and covariances) are considered (e.g. Donaldson, 1975; Mc Rae et al., 1982). If this inequality is not valid, higher order moments have to be determined. The quotient of the covariance term and the product of the means is often called the intensity of segregation  $I_S$  and is applied to describe the degree of inhomogeneous mixing. As a consequence of this Reynolds type ensemble averaging of properties of a fluid, one concept to describe the influence of fluctuations on chemical reactions is to introduce additional differential equations to determine higher order moments (e.g. Donaldson and Hilst, 1972; Donaldson, 1973, 1975; Shu, 1976). Another is to find the exact properties of the probability density

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functions (pdfs) of turbulent quantities for each reactant (e.g., O'Brien, 1971; Bencula and Seinfeld, 1976; Lamb and Shu, 1978).

The balance equation approach was applied for the analysis of field studies of the  $\text{NO}_2\text{--NO--O}_3$  system (e.g. Lenschow, 1982; Vilà-Gureau de Arellano and Duynkerke, 1992; Vila-Guerau de Arellano et al., 1993; Kramm and Meixner, 2000) as well as modelling of the same system but for more complex atmospheric mixtures (e.g. Mc Rae et al., 1982; Verver et al., 2000; Krol et al., 2000; Ebel et al., 2007). In addition, also fundamental studies were performed with LES models on the general behaviour of slow, fast and very fast reacting compounds in the ABL mainly under the influence of free convective mixing conditions (e.g. Schumann, 1989; Verver et al., 1997; Vinuesa and Vila-Guerau de Arellano, 2005; Ouwersloot et al., 2011). Comparing their results, the inhomogeneously mixed reactants – especially in the case of bimolecular reactions – can have reaction rates significantly different from the well – mixed case.

It is suggested by different authors (e.g. Krol et al., 2000; Pugh et al., 2011; Ouwersloot et al., 2011) that also the spatial distribution of emission sources directly influences the segregation intensity  $I_S$ .

Most of these studies also applied the Damköhler number  $\text{Da}_c$ , the quotient ( $\tau_t/\tau_c$ ) between the characteristic mixing time scales of turbulent or convective processes  $\tau_t$  and the specific chemical reaction  $\tau_c$ , for a classification of  $I_S$  as function of nearly inert ( $\text{Da}_c \ll 1$ ), slow ( $0.05 \lesssim \text{Da}_c \lesssim 0.5$ ), fast ( $0.5 \lesssim \text{Da}_c \lesssim 5$ ) and very fast ( $\text{Da}_c > 5$ ) bimolecular reactions.

In addition, an extended scaling uses the turbulent flux of a species ( $\overline{w'c'_i}$ ) to find a description for reaction and inhomogeneous mixing (e.g. Schumann, 1989; Verver et al., 2000) and adds a second Damköhler number  $\text{Da}_f$  for the specific flux to this ranking concept. It seems that for many trace substances turbulent mixing ( $0.01 < \text{Da}_c < 50$ ) significantly influences volume mean reaction rates, and, therefore, also the budgets of trace gases (e.g. Verver et al., 2000; Ebel et al., 2007; Stockwell, 1995).

One should be aware that depending on the concentration scales and the concepts applied for the calculation of  $\tau_t$  the numerical  $\text{Da}_c$  values may differ from each other

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(e.g. Schumann, 1989; Sykes et al., 1994; Verver et al., 1997, 2000). But despite such differences the ranking of reactions being most influenced by inhomogeneous mixing is consistent within each scaling concept.

5 One of the chemical components studied beside the system  $\text{NO}_2\text{--NO--O}_3$  is the biogenic compound isoprene and the reaction with OH. After emission isoprene is mixed by turbulence and convection while transported by the wind field. This compound reacts with OH (e.g. Finlayson-Pitts and Pitts Jr., 1986) which itself, as a fast reacting compound with  $\tau_c < 1\text{ s}$ , has only local sources and sinks. Therefore isoprene (with  $\tau_c > 600\text{ s}$ ) is transported through a locally variable field of OH which is influenced by  
10 the solar actinic flux and additional reactants like  $\text{NO}_2$ , NO, CO,  $\text{CH}_4$  and various VOCs.

Such atmospheric chemical systems were analyzed by model studies of Verver et al. (2000) for isoprene in a complex chemical mixture and its behaviour in the complete ABL and by Patton et al. (2001) for isoprene in a mixture with CO but analyzing the influences of emission, mixing and reaction on the intensity of segregation  $I_S$  within and  
15 directly above an idealised deciduous forest. Both analysis found  $I_S < 0$  near the bottom of their model areas indicating that the reaction (isoprene + OH) imposes a negative correlation between both compounds. Patton et al. (2001) applied LES and specified terms in the balance equation for isoprene with largest influence on fluxes and  $I_S$ .

20 Recently Ouwersloot et al. (2011) discussed how convection and turbulence above a differentially heated land surface representing alternating forest and savanna areas influence  $I_S$  for the isoprene and OH reaction. In this study, buoyant production and their differences between both surface types cause changes in  $I_S$ . As in the study by Patton et al. (2001), the modeled chemical reactions are for low  $\text{NO}_x$  conditions where the major sink for OH is isoprene. Their chosen relations of friction velocity  
25  $u_*$  to convective scale velocity  $w_*$  with  $u_* < w_*$  or  $u_* \ll w_*$  represent free convective conditions (Stull, 1988).

Also recently Pugh et al. (2011) applied results from the field study ECHO 2003 (Dlugi et al., 2010) to estimate a potential influence of segregation for this reaction on results of an other field study above a tropical rain forest area. In addition, Butler et al.

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(2008) estimated that they need values of  $-0.6 \leq I_S \leq -0.3$  to interpret their chemical measurements with an aircraft in the ABL during the GABRIEL field campaign also above comparable vegetation types, but after an extended error analysis estimated  $I_S \approx -0.13$ .

As discussed by Dlugi et al. (2010), results from the experiment ECHO 2003 can be used to directly determine the possible influences of inhomogeneous mixing on chemical reactions with the balance equations for the mixing ratio of isoprene. They obtained  $-0.15 < I_S < 0$  for this reaction from a direct analysis of field data above a deciduous mixed forest. Their data are mostly for  $u_* \gtrsim w_*$ , variable  $\text{NO}_x$  with  $\text{NO}_x > 3\text{--}4$  ppb in the morning and significantly decreasing values around 10:00 CET and later on, but highly variable photolysis rates. In general an upward directed isoprene flux was determined. But occasionally, downdrafts with negative vertical mean velocity  $\bar{w}$  and negative turbulent isoprene fluxes were observed. In addition, some time intervals of this field study were also characterized by  $u_* < w_*$ , which allows a comparison with modeled results.

The analysis presented in the following focuses also on the same reaction between isoprene and OH and the influence of different processes on the reaction rate. The results in Sects. 2 and 3 show that findings from the ECHO study agree qualitatively with results of the modeling study by Patton et al. (2001) with respect to a relationship between  $I_S$  and OH-reactivity in a chemical system composed of isoprene, but also of  $\text{NO}_2$ , NO, CO,  $\text{CH}_4$  and various VOCs. It can be shown that the absolute value of the segregation intensity  $|I_S|$  increases with increasing variance (or standard deviation) of isoprene, although additional factors are of influence during the field experiment.

We also discuss the empirical relations found for a correlation coefficient  $r_{ij}$  between isoprene and OH and some parameter like the mean reaction rate  $k_{ij} \cdot \bar{c}_i \cdot \bar{c}_j$ .

In addition a diagnostic equation for the covariance of chemical compounds  $\overline{c'_i c'_j}$  between isoprene (index  $i$ ) and OH (index  $j$ ) is formulated in Sect. 4. The analysis of terms of the balance of the covariance  $\overline{c'_i c'_j}$ , which significantly influences sign and magnitude of  $I_S$ , is presented. A diagnostic equation for  $I_S$  is formulated and its application

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for the analysis of ECHO 2003 data from 25 July 2003 (Dlugi et al., 2010) is discussed. In the last chapters we focus on the different terms of the balance equation influencing the covariance between isoprene and OH as well as  $I_S$  and compare the results from the field with findings from model predictions especially by Patton et al. (2001) and

5 Ouwersloot et al. (2011).

## 2 Balance of the mixing ratio

### 2.1 Balance equation

The balance equation (Eq. 1) for the mixing ratios of trace gases is widely used to discuss the role of chemical reactions on fluxes of reactive compounds (e.g. Lenschow, 1982; Vila-Guerau de Arellano et al., 1995; Kramm et al., 1995; Dlugi et al., 2010). This equation has two terms (the covariance and the product of mean mixing ratio) which

10 compose  $I_S$ .  
The basic concept and formulation of Eq. (1) is discussed by Kramm and Meixner (2000) and Dlugi et al. (2010). As air temperature (see Fig. 6b in Dlugi et al., 2010) and pressure show only small variations during the measuring time on day 206 of year 2003 from 9:00 to 15:00 CET of the ECHO study, the variation of mixing ratios with time is almost comparable to the variation of partial densities or concentrations. In a simplified

15 version, neglecting advection, this Eq. (1) reads

$$\frac{\partial \overline{c_i}}{\partial t} = -\frac{\partial}{\partial z} \overline{w'c'_i} - k_{ij} \left( \overline{c_i} \cdot \overline{c_j} + \overline{c'_i c'_j} \right) \quad (1)$$

with

index  $i$  = here representing isoprene

index  $j$  = here representing OH

$\overline{c_i}, \overline{c_j}$  = mean values of mixing ratios of reactive components  $i, j$

$w'c'_i$  = vertical turbulent flux (here of isoprene)

$k_{ij}$  = reaction rate constant

$\overline{c'_i c'_j}$  = covariance between reactants caused by  
turbulent fluctuations of both compounds.

The time derivative on the left side of Eq. (1) is called “storage term” (e.g. Stull, 1988), the first term on the right side is the “flux divergence” of the isoprene flux which can be itself either negative or positive. The second term on the right side is the chemical reaction term composed of the product  $k_{ij}$  with the product of mean mixing ratios as well as the covariance. In this analysis OH is considered as the only reactant of isoprene. As explained in Appendix A of Dlugi et al. (2010), any emission flux of trace gases is introduced into this differential equation by boundary conditions when integrating over the vertical  $z$ -coordinate. Rearranging the terms in Eq. (1) for  $c_i$  = isoprene allows to estimate the vertical divergence of the turbulent flux as a residuum caused by the influences of the chemical reaction term and the storage term. For ECHO 2003, this can be calculated for the reaction of isoprene with OH (Dlugi et al., 2010) with

$$k_{ij} = \frac{170}{T} e^{\frac{409}{T}} \quad [\text{ppb}^{-1} \text{s}^{-1}] \quad (2)$$

and  $T$  in K. Equation (1) is applied for  $R$  = isoprene + OH and day 206 (25 July 2003) of ECHO 2003 at height  $z = 37$  m for the main tower for the data set as described in Dlugi et al. (2010) and presented there in Figs. 5a and 6a–c. The temperature for the time period from 09:00 to 15:00 CET (see Fig. 6b in Dlugi et al., 2010) varied



between 292 K and 298 K, which causes a variation of only 4.7 % in  $k_{ij}$  (e.g. from  $2.36 \text{ ppb}^{-1} \text{ s}^{-1}$  to  $2.25 \text{ ppb}^{-1} \text{ s}^{-1}$ ). Therefore, a mean value  $k_{ij} = 2.3 \text{ ppb}^{-1} \text{ s}^{-1}$  is used for further analysis.

## 2.2 Results for the balance of mixing ratio

5 For the analysis of the isoprene mixing ratio balance the mean values and covariances calculated from ten minute time intervals as in Dlugi et al. (2010) are considered. The terms of Eq. (1) can be calculated in three different ways replacing the differential in the storage term by a time difference  $\Delta t$  and taking (1) the lefthand value ( $t_k$ ), (2) the righthand value ( $t_{k+1}$ ) and (3) the arithmetic mean of quantities at time steps  $t_k$  and  
 10  $t_{k+1}$ . The results are not significantly different, and, therefore, data taking the lefthand value (at  $t_k$ ) are shown in the following (method 1).

The chemical reaction term splits into two parts with the first, positive part being larger than the negative covariance term by about an order of magnitude (Fig. 1). Note that the corresponding time series of OH and isoprene (see Figs. 5a and 6c in Dlugi  
 15 et al., 2010) show gaps when the calibration procedures were applied. These gaps appear even more pronounced in the time series of 10 min averages (Fig. 1).

The first term – the storage term – varies between about  $\pm 10^{-3} \text{ ppbs}^{-1}$  and zero. The resulting flux divergence is dominated by this term and the first term of the chemical reaction term with smaller contributions of the covariance term by up to an order of  
 20 magnitude. A residual positive isoprene flux divergence is partly related to the loss by reaction with OH during vertical transport. Note that the flux divergence itself is negative but the residuum in general becomes positive by the negative sign in Eq. (1).

The covariance term in the reaction term is negative and reduces the contribution of the reaction term to the flux balance but the absolute magnitude is significantly smaller  
 25 than the product of the mean values. The neglect of advection may not be strictly valid. Therefore the determination of the flux divergence – in the mathematical sense as a residuum – summarizes also unknown contributions of advection. The relation of

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the “flux divergence” and the product of the mean values of isoprene and OH times  $k_{ij}$  (the mean reaction rate) is linear with a correlation coefficient  $r = 0.81$  (Fig. 2). This shows that the mean contribution of advection is not significant in our case.

The relation between the flux divergence and the covariance of the reactants (not given) shows some more scatter ( $r = 0.60$ ) with increasing values for more negative covariances. Negative values of the “flux divergence” are caused by the storage term because both reaction terms are always smaller. Note that if the influences of changing photolysis frequency and inhomogeneous mixing for the covariance at 11:50 CET are separated from each other, the data point at  $\text{cov}(\text{Iso}, \text{OH}) \simeq 0$  and flux divergence  $6.8 \times 10^{-4} \text{ ppbs}^{-1}$  is shifted to a covariance of  $-1.8 \times 10^{-5} \text{ ppb}^2$  respectively a value of  $2.3 \times (-1.8 \times 10^{-5}) \text{ ppbs}^{-1} = -4.14 \times 10^{-5} \text{ ppbs}^{-1}$  in Fig. 1 (see Sect. 4.3.4). The relation between the two parts of the reaction term is the intensity of segregation and is discussed in the following.

### 3 Segregation intensity

#### 3.1 Introduction

The segregation intensity  $I_S$  (Eq. 3) for bimolecular reactions is defined as the covariance  $\overline{c'_i c'_j}$  of reactants mixing ratios  $c_i$  and  $c_j$  divided by their mean values  $\overline{c_i}$  and  $\overline{c_j}$  (e.g. Danckwerts, 1952; Damköhler, 1957; Vilà Guerau de Arellano and Lelieveld, 1998) and is given for the system of  $c_i$  = isoprene and  $c_j$  = OH by

$$I_S = \frac{\overline{c'_i \cdot c'_j}}{\overline{c_i} \cdot \overline{c_j}} \quad (3)$$

Any covariance can be also presented by the product of the standard deviations  $\sigma_i$ ,  $\sigma_j$  times the specific correlation coefficient  $r_{ij}$  (Eq. 4).

$$\overline{c'_i \cdot c'_j} = r_{ij} \cdot \sigma_i \cdot \sigma_j \quad (4)$$

Therefore, if  $\overline{c'_i \cdot c'_j} \simeq 0$  in Fig. 1,  $r_{ij} \simeq 0$ , e.g. the correlation between the turbulent field quantities  $c'_i$  and  $c'_j$  vanishes because, in general,  $\sigma_i > 0$  and  $\sigma_j > 0$  is valid. Inserting Eq. (4) into Eq. (3) shows that the product of the normalized standard deviations of both reactants have to be multiplied by their correlation coefficient. These quantities are presented in Figs. 3 and 4 from time series shown by Dlugi et al. (2010) for ECHO 2003.

## 3.2 Results for the segregation intensity

### 3.2.1 Relation to mean OH mixing ratio

The measured OH and isoprene concentrations show on average an inverse relationship (Fig. 5), which is plausible since the reaction with isoprene is the dominant OH loss (Table 1, 2). This behavior is more evident for shorter averaging times. The superimposed scatter in the correlation plot (Fig. 5) has several reasons. It is partly due to instrumental noise in the measurement of OH and isoprene, partly due to additional OH loss by other compounds (e.g. NO<sub>2</sub>, NO, CO, CH<sub>4</sub>, VOCs) and variations in the chemical production of OH. The observed relationship is comparable to the prediction by Patton et al. (2001) and Pugh et al. (2011), who assumed an inverse dependence of OH on isoprene in a mainly isoprene-dominated atmosphere.

The relation between  $I_S$  and the mean OH mixing ratio in Fig. 6 shows that part of the data follow a negative correlation of  $I_S$  with  $\overline{OH}$ , a result also expected by a modeling study by Patton et al. (2001) if their definition of Damköhler number  $D_c = \tau_t \cdot k_{ij} \cdot \overline{OH}$  (with the notation as in this paper) is applied. A comparable presentation is given for ECHO2003 in Fig. 6 with a linear fit through the origin with a variability of  $\pm 40\%$

marked by the dotted lines. In the left part of Fig. 6 some data points are outside in a separate cluster for a range of  $I_S < -0.025$  which corresponds to situations with only a small correlation coefficient between isoprene and OH being determined by Eq. (4) and shown in Fig. 3.

(Note also that one point at  $I_S \approx 0$  and  $\overline{\text{OH}} = 2.7 \times 10^{-4}$  ppb is shifted to  $I_S = -0.06$  by the same effect discussed for the covariance (see Sect. 4.3.4)).

These data points (in the circle) are from measuring periods with neutral to slightly unstable stratification and mixing ratios of  $\text{NO}_2$ , NO and also CO higher than at other times as given in Table 1. For these conditions additional chemical sinks act more effectively on mean OH, and, therefore, the relative amount of OH consumed by isoprene decreases. The data points within the dotted sector in Fig. 6 are for a reduced influence of other chemical sinks for OH.

The measured mean OH-mixing ratio is nearly constant between 09:50–12:10 CET and reaches a maximum around 12:30 CET with a small decrease below the morning values after 12:50 CET. The maximum is for a maximum in ozone photolysis frequency  $J(\text{O}^1\text{D})$  (see Figs. 5a and 1 in Dlugi et al., 2010) and the decline for a decrease of  $J(\text{O}^1\text{D})$  on average with some maxima in between. The contributions of isoprene and other compounds given in Table 1 to the loss of OH,  $L(\text{OH})$ , is estimated for four time periods (Table 2). A mean fraction  $f$  of isoprene contribution to  $L(\text{OH})$  is calculated (Table 2) according to the concept described in Appendix A.  $L(\text{OH})$  has a maximum in the first period, a secondary maximum in the third period where the contribution of ozone photolysis to the production term  $P(\text{OH})$  reach a maximum, and comparable values with  $L(\text{OH}) \approx P(\text{OH})$  above  $4 \text{ s}^{-1}$  otherwise. But the relative contribution of isoprene to  $L(\text{OH})$  increases significantly over the measuring period. Therefore in the presentation of the segregation intensity  $I_S$  versus  $\text{OH}(\text{mod}) = f \cdot \text{OH}(\text{measured})$  in the right part of Fig. 6 all data points residing originally in the blue circle move to the left. With the exception of two of them at 10:40 CET and 13:30 CET all values move to the area within the dotted lines. The largest effect (see also Fig. 24, Appendix A) is found for time periods before 10:30 CET with  $f \leq 0.6$ . Note that  $f$  vanishes in  $I_S$  because  $f$  contributes to

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both terms in Eq. (3). The same holds for  $r_{ij}$  but not for the mean reaction rate or the covariance itself. In addition comparing the results in Appendix A (Fig. 24) with Fig. 6, the factor  $f$  acts on the complete range of segregation intensity. This suggests that not only the “the chemical reactivity” of the system but also mixing conditions should influence the magnitude of  $I_S$ .

### 3.2.2 Deviation from quasi-linear relationship

In Fig. 6 two data points in the right part are still above the upper dotted line. The small value  $I_S = -0.002$  (10:40 CET) is for a situation when a downward advection with mean vertical wind  $\bar{w} \simeq -0.25 \text{ ms}^{-1}$  transports air from a layer above the forest with isoprene mixing ratios below 0.3 ppb to the measuring site. For this condition the correlation between locally produced OH and advected isoprene decreases ( $r_{\text{ISO,OH}} = -0.02$ ).

Also the normalized standard deviations  $\text{std}(\text{ISO})/\overline{\text{ISO}} = 0.51$  and  $\text{std}(\text{OH})/\overline{\text{OH}} = 0.26$  cause only a small contribution to  $I_S$  if Eqs. (3) and (4) are combined. Note that for all cases during ECHO 2003 with downward directed  $\bar{w}$  the normalized standard deviation of isoprene becomes small. A comparable behavior is observed also for temperature. Also the correlation between isoprene mixing ratio and temperature becomes small for such cases (see: Dlugi et al., 2010). It appears that temperature and isoprene are better correlated if a direct influence of the emission source  $E$  is detected, because  $E$  itself is dependent also on leaf surface temperature and its variance (Ciccioli et al., 1997). Therefore, these quantities are less correlated if upward transported isoprene comes down again from atmospheric layers up to some hundred meters above the surface with only smaller temperature variance (e.g. Stull, 1988).

The other point ( $I_S = -0.02$ ,  $\text{OH}_{\text{mod}} = -2.04 \times 10^{-4}$  ppb) at 13:30 CET is for a secondary maximum in  $J(\text{O}^1\text{D})$ , for  $\bar{w} \simeq 0 \text{ ms}^{-1}$  and upward directed turbulent fluxes of heat, moisture and isoprene. The correction factor  $f = 0.95$  is for  $\overline{L(\text{OH})} = 4.18 \text{ s}^{-1}$  (Table 2), but has only to be reduced by 20 % for a shift of this data point to the area within the dotted lines (Fig. 6). Even if the variability of  $\text{NO}_2$  around the hourly mean

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value in Table 1 is considered the lowest possible value is  $f = 0.9$  but not  $f \leq 0.79$  as required. This may be caused by a short time maximum in OH production  $P(\text{OH})$  by ozone photolysis (and photolysis of other compounds like HONO, Kleffmann et al., 2005) occurring around 13:30 CET (Fig. 1 in Dlugi et al., 2010) and causing an increase of measured  $\overline{\text{OH}}$  relative to the loss term  $L(\text{OH})$  being dominated by isoprene reaction at this time.

### 3.2.3 Covariance and mean reaction rates

The segregation intensity  $I_S$  is composed of the covariance divided by the product of the means (Eq. 3). But both terms are correlated to a certain extent, because the covariance term increases with increasing product  $[\text{ISO}][\text{OH}]$  (Fig. 7). This is a qualitative relationship also described by Verver et al. (1997) and Patton et al. (2001) in their model studies.

An upper limit of  $3.1 \times 10^{-4} \text{ ppb}^2$  is observed for  $[\text{ISO}][\text{OH}]$  which is also reflected in the data of Fig. 5. The line (a) is given for  $I_S = -1$ , the case with no reaction between isoprene and OH, while line (b) is for  $I_S = 0$ , e.g. when the covariance between isoprene and OH is zero. Curve (c) is a trend line through all data points without forcing this function to be zero for  $\overline{c_i} \cdot \overline{c_j} = 0$ . Therefore most data are in the range  $-0.1 \leq I_S < 0$  with the diagonal representing  $I_S = -0.1$ .

If a functional like  $y = \overline{c_i'c_j'} = -a \cdot \overline{\text{ISO}} \cdot \overline{\text{OH}}$  is chosen this suggests a dependence like  $y = -a \cdot x^2$ . Both quantities,  $\overline{\text{ISO}}$  as well as  $\overline{\text{OH}}$ , are limited by biochemical processes in plants and the chemical system in the surrounding air. For  $f > 0.9$  they should follow some anticorrelated behavior (e.g. Fig. 5). In nature both mixing ratios will approach maximum values, and therefore, both functional forms (curve c) as well as  $y = -a \cdot x^2$  will result in an upper limit for  $\overline{c_i'c_j'}$ . An extrapolation of the covariance to an upper limit of  $\overline{\text{ISO}} \cdot \overline{\text{OH}} \simeq -5 \times 10^{-4} \text{ ppb}^2$  by  $y = -a \cdot x^2$  yields a value in the range  $-12 \times 10^{-4} \text{ ppb}^2 \leq$

$\text{cov}(\text{ISO}, \text{OH}) \leq -8 \times 10^{-4} \text{ ppb}^2$  with  $I_S$  in the range  $-0.24 \leq I_S \leq -0.16$  which should be compared to the largest value  $I_S = -0.14$  from this field study (Fig. 6).

Summarizing these results, the intensity of segregation  $I_S$  for the reaction between isoprene and OH reaches maximum values if isoprene becomes the dominant sink for OH. Therefore, for  $\text{NO}_x$  rich conditions in the morning (Tables 1,2) the loss of OH by  $\text{NO}_2$  is important and  $I_S$  has minimum values for  $f < 0.4$  by the influence of other concurrent reactants. But  $I_S$  strongly varies for a fixed value of  $f$  (see Fig. 24). This hints towards additional influences of turbulent mixing in the atmospheric flow and emission source strength  $E$  (Ciccioli et al., 1997), both acting on  $\sigma(\text{ISO})$  and  $r_{ij}$  in Eq. (4) as discussed below and in Sect. 5.

### 3.2.4 Dependence on correlation coefficient and isoprene standard deviation

During situations with OH higher than  $(2-3) \times 10^{-4} \text{ ppb}$  and isoprene above  $0.8 \text{ ppb}$  largest values of  $I_S$  are found. The correlation coefficient (see Eq. 4) is in the range  $-0.56 \leq r_{\text{ISO OH}} \leq 0$  (Fig. 3) and the normalized standard deviations (Fig. 4) vary in the range  $0.38 \leq \sigma(\text{ISO})/\overline{\text{ISO}} \leq 1.2$  and  $0.23 \leq \sigma(\text{OH})/\overline{\text{OH}} \leq 0.44$ . The lowest possible value of the product of normalized standard deviations is 0.09, and therefore any  $|I_S| < 0.09$  must be caused by  $|r_{ij}| < 1$  (Fig. 3). In addition, for larger segregation intensities  $I_S < -0.08$  a limiting range  $-0.55 > r_{\text{OH ISO}}$  is calculated. Following the dependence of the covariance (Fig. 7) also the correlation coefficient increases with the increasing product of mean mixing ratios (Fig. 8) or the mean reaction rate. This result differs from those obtained from model calculations (e.g. Vinuesa and Vila-Guerau de Arellano, 2005; Ouwersloot et al., 2011), with  $r_{\text{ISO OH}} > -0.70$  for the comparable magnitude of  $I_S$ . Applying these values to the field data the resulting  $I_S$  would be larger up to about a factor of two with maxima in the range  $-0.3 \leq I_S \leq -0.2$ . By a comparable assumption on  $r_{ij}$ , Pugh et al. (2011) obtained  $I_S$  values larger than determined in our study (Figs. 3, 6).

We will shortly discuss one possibility for such differences. For this analysis the covariance in Eq. (3) may be replaced by Eq. (4) resulting in the product of  $r_{ij}$  with normalised standard deviations of isoprene and OH (Fig. 4). The standard deviations  $\sigma$  of both compounds increase with increasing mixing ratio nearly in a linear manner for this data set which causes the dependencies given in Fig. 4.

For both compounds the normalized standard deviation, also called the turbulence intensity  $\sigma/\bar{c}$ , approaches some limiting value for large mixing ratios with about  $\sigma_{\text{ISO}}/\overline{\text{ISO}} \approx 0.45 - 0.55$ , if also data of Spirig et al. (2005) are taken into account, and  $\sigma_{\text{OH}}/\overline{\text{OH}} \approx 0.25 - 0.3$  (Fig. 4).

Extrapolating to small mixing ratios (Fig. 4) yield limiting values for low isoprene mixing ratios of about 1.5 and for OH mixing ratios of about 0.5. Note that the detection limits ( $S/N = 2$ ) on 25 July 2003 were 41 ppt for isoprene and 0.1 ppt for OH (Dlugi et al., 2010). Therefore all 10 min mean values given in Fig. 5 are above that limits. But not all data points for OH in Fig. 5 are far above this detection limit of the LIF for highly time resolved measurements.

Uncorrelated noise on the OH time series has no influence on the covariance term, e.g. in Eq. (3), but may have enhanced  $\sigma_{\text{OH}}$  in Eq. (4) and  $\sigma_{\text{OH}}/\overline{\text{OH}}$ , because the data are not very far from detection limit DL. This differs for isoprene with DL = 41 ppt. Therefore, if standard deviations are used to calculate  $r_{ij}$  the corresponding variance of the measured OH,  $\sigma_{\text{OH}}^2 = \sigma_{\text{OH}}^2(\text{signal}) + \sigma_{\text{OH}}^2(\text{noise})$ , and so  $\sigma_{\text{OH}}(\text{signal})$  may be too high. If a large contribution of noise  $\sigma_{\text{OH}}^2(\text{signal})/\sigma_{\text{OH}}^2(\text{noise}) = 2$  is assumed,  $\sigma_{\text{OH}}$  is a factor of 1.23 to large. With mean values of  $\sigma_{\text{ISO}}/\overline{\text{ISO}} = 0.65$  and  $\sigma_{\text{OH}}/\overline{\text{OH}} = 0.3$  with a corrected term  $\frac{1}{1.23} \cdot \frac{\sigma_{\text{OH}}}{\overline{\text{OH}}}$  (Fig. 4) the derived correlation coefficient would be larger by about the same factor of 1.23 and the maxima would be shifted to about  $r_{ij}(\text{corrected}) \approx -0.67$ . But even  $r_{ij}(\text{corrected})$  is still below the assumption made for model calculations.

Note that a correlation coefficient  $|r_{ij}| < 1$  also describes the deviation of the probability distribution of  $c_i, c_j$  from a normal distribution (see: Dlugi et al., 2010). Therefore

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the distribution of the mixing ratios of isoprene and OH during this field study seem to be different from the normal distribution as often assumed for model studies.

Combining the results from the ECHO field study a relation between  $I_S$  and the standard deviation  $\sigma_{ISO}$  of isoprene is found (Fig. 9) (Here again the data point  $I_S \simeq 0$ ,  $\sigma_{ISO} = 0.67$  ppb is shifted to  $I_S = -0.06$  and  $\sigma_{ISO} = 0.67$  ppb as discussed in Sect. 4.3.4). Another point ( $I_S = -0.002$ ;  $\sigma_{ISO} = 0.18$ ) is for a small covariance of  $-2 \times 10^{-7}$  ppb<sup>2</sup> but agrees with an increase of  $I_S$  with increasing  $\sigma_{ISO}$ . Note that this data point is for the conditions at 10:40 CET with a significant vertical advection as discussed in Sect. 3.2.2. Therefore, for the same range of  $\sigma_{ISO}$  the intensity of segregation  $I_S$  varies by a factor of about four in the data set.  $|I_S|$  increases with increasing  $\sigma(ISO)$ , but two branches are obtained with different proportionality between both quantities. This behavior changes if  $I_S$  is presented as function of normalized variance of isoprene  $nvar(ISO)$  on the right side of Fig. 9 with exception of two data points at 10:00 CET and 11:30 CET. For those points  $nvar(ISO)$  is large while  $r_{ij}$  and  $nvar(OH)$  are small. Therefore also  $I_S = r_{ij}(\sigma_{ISO}/\overline{ISO})(\sigma_{OH}/\overline{OH})$  becomes significantly smaller than for other conditions of comparable  $nvar(ISO)$ .

In Sects. 4.3 and 5 we further discuss the relevance of  $\sigma_{ISO}$  and normalized variances for the behavior of  $I_S$  as an influence of chemical reactions on the balance of covariance between isoprene and OH. Although further reactions have influenced the OH budget in our case (see Sect. 3.2.1 and Appendix A) and transport and mixing conditions change during the 6 h of the experiment on July, 25, 2003 (day 206), the general behavior of the absolute value of  $I_S$  – an increase with increasing  $\sigma_{ISO}$  in Fig. 9 – remains.

The error bars in Fig. 9 are given by the uncertainty of the covariance between isoprene and OH if the time delay between both time series is varied by up to  $\pm 0.2$  s. This is due to the fact that the wind vector varies inside the sampling volume of separated gas inlets and the METEK anemometer (Dlugi et al., 2010) during each 10 min interval. The “high frequency loss” of covariance as discussed by Spirig et al. (2005) is not added because the spectral behavior of both time series is not known above 0.2 Hz.

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## 4 Balance equations for the covariance between isoprene and OH and the segregation intensity $I_S$

### 4.1 The equations

The balance equation for the covariance of two reacting compounds (Eq. 5) was used by Verver et al. (2000) and Patton et al. (2001) obviously in a simplified version (a) neglecting advective terms (A) and (b) neglecting horizontal turbulent diffusion.

The analysis of the data from the experiment ECHO 2003 allows for some hours of day 206 (09:00–15:00 CET) to calculate a number of terms of Eq. (5), and to estimate their possible maximum and minimum contributions to the balance of  $\overline{c'_i c'_j}$  for the isoprene concentration  $c_i$  and the OH concentration  $c_j$ .

In the complete form the balance equation for  $\overline{c'_i c'_j}$  reads (e.g. Sorbjan, 1989; Stull, 1988; Schumann, 1989; Verver et al., 1997):

$$\underbrace{\frac{\partial \overline{c'_i c'_j}}{\partial t}}_S = - \underbrace{\overline{u'_k c'_i} \frac{\partial \overline{c'_j}}{\partial x_k}}_{TPI_k} - \underbrace{\overline{u'_k c'_j} \frac{\partial \overline{c'_i}}{\partial x_k}}_{TPOH_k} - \underbrace{\overline{c'_i c'_j} \frac{\partial \overline{u_k}}{\partial x_k}}_{A_{1k}} - \underbrace{\overline{u_k} \frac{\partial \overline{c'_i c'_j}}{\partial x_k}}_{A_{2k}} - \underbrace{\frac{\partial \overline{u'_k c'_i c'_j}}{\partial x_k}}_{TT_k} - \underbrace{(\nu_i + \nu_j) \left( \frac{\partial \overline{c'_i}}{\partial x_k} \right) \left( \frac{\partial \overline{c'_j}}{\partial x_k} \right)}_D + \underbrace{R_{ij}}_{R_{ij}} \quad (5)$$

with index  $k = 1$  (coordinate  $x$  and wind coordinate  $u$ );  $k = 2$  for  $y$ ,  $\nu$ ;  $k = 3$  for  $z$ ,  $w$  and  $S$  = storage term,  $TPI_k$  = turbulent production by a turbulent flux of isoprene in a spatially inhomogeneous field of OH,  $TPOH_k$  = turbulent production by a turbulent flux of OH in a spatially inhomogeneous field of isoprene,  $A_{1k}$  = advection of covariance by the influence of the divergence of the flow field,  $A_{2k}$  = advection of covariance with

the mean flow,  $TT_k$  = turbulent transport of covariance,  $D$  = molecular diffusion term,  $R_{ij}$  = chemical reaction term.

The chemical reaction term (Eq. 6) is formulated according to Donaldson and Hilst (1972); Vila-Guerau de Arellano et al. (1995) and Vilà Guerau de Arellano and Lelieveld (1998) for atmospheric conditions and was also applied by Verver et al. (1997, 2000) and Patton et al. (2001) for a bimolecular reaction in the following form:

$$R_{ij} = -k_{ij} \left[ (\overline{c'_i c'_j})(\overline{c_i} + \overline{c_j}) + \overline{c_i} \overline{c_j'^2} + \overline{c_j} \overline{c_i'^2} + \overline{c'_i c'_i c'_j} + \overline{c'_j c'_j c'_i} \right] \quad (6)$$

The data analysis in Sect. 4.3 (Fig. 10) proves that Eq. (5) with the data set of the ECHO 2003 study fulfills the criterium of stationarity. For these conditions Eq. (5) may be simplified:

$$S \equiv 0 = -TPI_k - TPOH_k - A_{1k} - A_{2k} - TT_k - D + R_{ij} \quad (7)$$

This allows us to find an expression for  $\overline{c'_i c'_j}$  in terms of all other quantities in Eq. (7) because this covariance also explicitly appears in the first term of  $R_{ij}$  (Eq. 6). The resulting diagnostic equation (Eq. 8) – see Appendix B – reads

$$\overline{c'_i c'_j} = -\frac{1}{k_{ij}(\overline{c_i} + \overline{c_j})} \left[ (TPI_k + TPOH_k + A_{1k} + A_{2k} + TT_k + D) - k_{ij} \left( \overline{c_i} \overline{c_j'^2} + \overline{c_j} \overline{c_i'^2} + \overline{c'_i c'_i c'_j} + \overline{c'_j c'_j c'_i} \right) \right] \quad (8)$$

In a further discussion in Sect. 4.2 and Appendix B we simplify Eq. (8) applying also some order of magnitude estimations for some terms. The fast measurements of fluctuations of mixing ratios of isoprene and OH in a small volume of air on 25 July 2003 were performed only at one point (7 m above canopy height,  $h_c = 30$  m) at the ECHO main tower (Dlugi et al., 2010). Therefore, spatial derivations of mixing ratios of these

compounds and their fluxes are not available. But all terms which describe turbulent production and transport as well as advection may be summarised in a residual term RES – in the mathematical sense – as

$$\text{RES} = \text{TPI}_K + \text{TPOH}_K + A_{1K} + A_{2K} + \text{TT}_K + D \quad (9)$$

- 5 This enables us to estimate the resulting influences of these processes on the covariance and  $I_S$ , although these detailed complex measurements were done only at one measuring height  $z_R = 37$  m (Dlugi et al., 2010).

- Also the chemistry term in Eq. (8) may be written in the following manner to separate the term with the variance of isoprene which shows a direct relation to  $I_S$  (Fig. 9) (e.g. Patton et al., 2001; Verver et al., 1997) from all other terms:

$$R_{ij,\text{res}} = -k_{ij} \left( \bar{c}_j \overline{c_i'^2} + C_{ij} \right) \quad (10)$$

Here  $C_{ij}$  is the sum of term two, four and five on the right side of Eq. (6).

For isoprene ( $i$ ) and OH ( $j$ ) with  $\bar{c}_i \gg \bar{c}_j$  (e.g. Dlugi et al., 2010) the prefactor in Eq. (8) can be simplified, and therefore, Eq. (8) finally reads

$$\begin{aligned} -\overline{c_i' c_j'} &= \frac{1}{k_{ij} \bar{c}_i} (\text{RES}) + \frac{k_{ij}}{\bar{c}_i k_{ij}} C_{ij} - \frac{\bar{c}_j}{\bar{c}_i} \overline{c_i'^2} \\ &= \frac{1}{k_{ij} \bar{c}_i} [\text{RES} + k_{ij} C_{ij}] - \frac{\bar{c}_j}{\bar{c}_i} \overline{c_i'^2} \\ &= \text{RE} + \frac{C_{ij}}{\bar{c}_i} - \frac{\bar{c}_j}{\bar{c}_i} \overline{c_i'^2} \end{aligned} \quad (11)$$

Therefore, for the reaction of isoprene with OH the covariance controlling the segregation intensity is determined by the product between the quotient of the mixing ratios of OH (index  $j$ ) and isoprene (index  $i$ ) times the variance of isoprene (notation:

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$\text{var}(\text{ISO}) = \overline{c_i'^2} = \sigma_{\text{ISO}}^2$ ) and two other terms. These terms describe the interactions of turbulent mixing and chemistry (RE) (see Eq. 9) and mainly third order chemical correlation terms ( $C_{ij}$ ) in the turbulent fields of reactants.

Dividing Eq. (11) by the product of the means, a diagnostic equation (Eq. 12) for  $I_S$  (see Eq. 3) can be formulated.

$$\begin{aligned} -I_S &= -\frac{\overline{c_i' c_j'}}{\overline{c_i} \cdot \overline{c_j}} \\ &= \frac{\text{RES}}{k_{ij} \cdot \overline{c_i} \cdot (\overline{c_i} \cdot \overline{c_j})} + \frac{C_{ij}}{\overline{c_i} (\overline{c_i} \cdot \overline{c_j})} - \frac{\overline{c_i'^2}}{\overline{c_i}^2} \\ &= \text{RE}_{iS} + \text{CH}_{iS} - \text{nvar}(\text{ISO})_{iS} \end{aligned} \quad (12)$$

The third term  $\text{nvar}(\text{ISO})_{iS}$  of Eq. (12) is the normalized variance with some proportionality versus  $\sigma_{\text{ISO}}$  itself and  $I_S$  (Fig. 9). The second term  $\text{CH}_{iS}$  summarizes all terms from  $C_{ij}$  but becomes also important by the inverse influence of  $\overline{c_j} < 10^{-3}$  ppb. The first term  $\text{RE}_{iS}$  is again determined as a residuum, as all other terms of Eq. (12) are directly calculated from measurements at height  $z_R = 37$  m at the ECHO main tower (Dlugi et al., 2010).

## 4.2 The terms of the balance equation of the covariance

In the following all different terms of the balance equation (Eq. 5) are estimated based on measured data from the field study ECHO 2003 and calculated quantities like first to fourth moments (Ammann et al., 2004; Dlugi et al., 2010; Kleffmann et al., 2005; Schaub, 2007; Spirig et al., 2005). This also helps to specify the impact of different processes on the residual terms RES respectively RE or  $\text{RE}_{iS}$ . Terms which cannot be determined this way, because the timely high resolved measurements were performed only at one measuring point, are estimated based on additional data from the ECHO

field study (Ammann et al., 2004; Bohn, 2006; Bohn and Rohrer, 2006; Kleffmann et al., 2005; Schaub, 2007; Spirig et al., 2005).

If advection with the mean flow is neglected and only the residual transport in the vertical direction is considered, Eq. (5) is simplified and is consistent with the equations as applied by Verver et al. (1997) and Patton et al. (2001) for their model studies, while Eq. (6) is identical with their formulations.

For the following estimation of the order of magnitude of all terms of Eq. (5),  $A_{1k}$  and  $A_{2k}$  are not neglected (see Appendix B) but for some terms only changes in  $z$ -direction are considered which simplifies the first and second term on the right side of Eq. (5). The storage term (Fig. 10) is always smaller than most other terms (Table 3) and can be neglected to formulate diagnostic equations for the covariance and  $I_S$  (Sect. 4.1). The first term on the right side is the product of the turbulent isoprene flux and the mean vertical gradient of OH mixing ratio, which can be estimated from measurements during ECHO 2003 (Dlugi et al., 2010). The isoprene flux varies in the range 0.02–0.2 ppb ms<sup>-1</sup> (see: Dlugi et al., 2010; Spirig et al., 2005) and the mean gradient of OH above canopy – from unpublished measurements – is about  $3 \times 10^{-5}$  ppb m<sup>-1</sup>. Thus the combined first term is  $6 \times 10^{-7}$  to  $6 \times 10^{-6}$  ppb<sup>2</sup> s<sup>-1</sup> (Table 3). The second term is obtained if isoprene and OH are replaced. The vertical gradient of isoprene (see: Schaub, 2007; Ammann et al., 2004) varies in the range  $\pm 0.14$  ppb m<sup>-1</sup> to  $\pm 0.01$  ppb m<sup>-1</sup> and the OH-flux between zero and  $-4 \times 10^{-5}$  ppb ms<sup>-1</sup> (Dlugi et al., 2010). Note that the vertical turbulent flux of OH is caused by transport of compounds like isoprene and others (e.g. Table 1) to the measuring volume where they locally react with OH. The product is of the same order of magnitude as the first term  $TPI_k$ . Depending on the sign of  $TPI_k$  and  $TPOH_k$ , in an order of magnitude estimation, both terms may cancel out each other or may add up to about  $1.2 \times 10^{-5}$  ppb<sup>2</sup> s<sup>-1</sup> (Table 3).

The following two terms  $A_{1k}$  and  $A_{2k}$  describe the influence of advective transport of covariance. As discussed in Appendix B, the term  $A_{1k}$  depends on the divergence of the wind field (Sun, 2007). Even for a large local divergence of 10<sup>-1</sup> s<sup>-1</sup> on a length scale of about 10 m with a strong change of a wind component by 1 ms<sup>-1</sup> this term

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is always below  $10^{-6} \text{ ppb}^2 \text{ s}^{-1}$  because the covariance is smaller than  $3 \times 10^{-5} \text{ ppb}^2$ . Therefore a maximum value  $A_{1k}$  is of the order of  $\text{TPI}_k$  and  $\text{TPOH}_k$  but becomes neglectable if the divergence of the wind field is less than  $10^{-2} \text{ s}^{-1}$ , which is a common value estimated for small mesoscale flow (e.g. Stull, 1988). Term  $A_{2k}$  is composed of the spatial gradient of the covariance multiplied by the corresponding mean velocity component. According to the ergodic theorem (Lippmann, 1952) we may assume that this spatial gradient is comparable to the time derivative  $S$ . As shown in Table 3 and in Fig. 10  $S$  is small. Even for a high horizontal wind velocity component  $\overline{u_x} = 3 \text{ m s}^{-1}$ ,  $A_{2k}$  is smaller than the other terms (Table 3), also because most values of  $\overline{u_x}$  are only up to  $1 \text{ m s}^{-1}$  for the considered time during ECHO 2003 (see Fig. 3 in Dlugi et al., 2010). But if we assume that the covariance is expressed by Eq. (4) this term can be significantly larger as discussed below and shown in Table 3 in parenthesis. Compared to other terms which compose RES or  $\text{RE}_{is}$  (Eq. 12),  $A_{1k}$  can be neglected if the divergence of the wind field is below  $10^{-2} \text{ s}^{-1}$ .

The term  $\text{TT}_k$  is given by the divergence of the turbulent transport of the numerator of segregation intensity. The turbulent transport is also one term in the chemical part of the flux balance (e.g. Patton et al., 2001) and is calculated directly from measured quantities at  $z_R = 37 \text{ m}$ . This term is generally below  $\pm 10^{-5} \text{ ppb m s}^{-1}$  with one exception around 12:00 CET with a value of  $3.7 \times 10^{-5} \text{ ppb m s}^{-1}$ . The vertical divergence of third order moments (e.g. of  $\overline{w'\theta'q'}$ ) is at least smaller by an order of magnitude than the moment itself, e.g. smaller than  $4 \times 10^{-6} \text{ ppb}^2 \text{ s}^{-1}$  (Table 3). Therefore also this term may be of same order of magnitude as the terms  $\text{TPI}_k$  and  $\text{TPOH}_k$ .

The molecular diffusion term  $D$  is composed of the product of vertical gradients of fluctuations of isoprene (about  $10^{-2} \text{ ppb m}^{-1}$ ) and OH (about  $10^{-5} \text{ ppb m}^{-1}$ ) based on the data presented by Dlugi et al. (2010) times the sum of the molecular kinematic diffusivities of order  $10^{-5} \text{ m}^2 \text{ s}^{-1}$ . Therefore this term  $D$  is smaller than  $10^{-10} \text{ ppb}^2 \text{ s}^{-1}$  and can be neglected in the following.

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In this order of magnitude estimation the maximum of the terms which compose RES is about  $1.6 \times 10^{-5} \text{ ppb}^2 \text{ s}^{-1}$  while  $R_{ij}$  is below  $4 \times 10^{-4} \text{ ppb}^2 \text{ s}^{-1}$  (Table 3), and  $\text{RES} \simeq R_{ij}$  (Eq. 7) is not fulfilled. Therefore, not only the vertical but also the horizontal derivatives should significantly contribute to all terms without  $D$  in Eq. (5). Based on the available data the horizontal contributions to  $\text{TPI}_k$  and  $\text{TPOH}_k$  may be estimated to be as large as the vertical contribution. The covariance is always determined locally by the transport of isoprene variance through a field of locally variable ( $\sigma_{\text{OH}}^2$ ) OH-mixing ratio. Depending on  $r_{ij}$ , the horizontal contributions of  $A_{2k}$  may therefore also approach values in the range of  $5 - 10 \times 10^{-5} \text{ ppb}^2 \text{ s}^{-1}$ , and, therefore significantly contribute to RES.

The chemical reaction rate  $R_{ij}$  (Eq. 6) consists of 5 terms which can be estimated from results given by Dlugi et al. (2010) and is discussed in more detail in Sect. 4.3.2 (e.g. Fig. 11, Table 4). The third term  $-k_{ij} \cdot \bar{c}_j \overline{c_i'^2}$  (term III3 in Fig. 11) is proportional to the variance of the isoprene mixing ratio and becomes dominant for most 10 min intervals sometimes together with the first term  $-k_{ij} \cdot \overline{c_i' c_j'} (\bar{c}_i + \bar{c}_j)$ , which should be positive (see term I3 in Fig. 11) by the influence of the covariance, which itself has only negative values. The terms II3 and V3 are small and may be neglected. The magnitude of term IV3 is of order of term I3 but with positive as well as negative values. This points towards the results obtained in Sect. 3.2.4 that the standard deviation (Fig. 9) of isoprene mixing ratio – or normalized variance as in Eq. (12) – controls segregation intensity  $I_S$  if isoprene is the dominant hydrocarbon in the gas mixture with respect to the reaction with OH. As discussed in Sect. 3.2.1, an extended analysis is necessary because concurrent reactants like CO,  $\text{NO}_2$  and NO with mixing ratios higher by a factor of two respectively four in the morning hours (09:00–10:40, 11:10–11:30 CET) than during other time intervals of day 206 (25 July 2003) are observed (Table 1). This aspect and its influence on  $R_{ij}$  is further discussed in the following Sects. 4.3.2 and 5.1.



## 4.3 Results for the balances of covariance and segregation intensity

### 4.3.1 The storage term

As mentioned before the storage term in Eq. (5) is small and can be neglected compared to other terms (Fig. 10) because of its magnitude of  $\pm 10^{-8} \text{ ppb}^2 \text{ s}^{-1}$ . This empirical behaviour allows to simplify Eq. (5) and to derive Eq. (7), the diagnostic form Eq. (8), and, finally, Eqs. (11) and (12) for conditions of 25 July 2003 during ECHO. But this may not reflect the general behaviour of the chemical system at other field sites. For completeness, the storage term of the balance of isoprene mixing ratio is shown, which – in general – is not small compared to other terms as discussed in Sect. 2.

### 4.3.2 The chemical reaction term

The analysis on the relation between mixing ratios and the covariance between isoprene and OH suggests that the variations of  $\overline{c'_i c'_j}$  and  $I_S$  are better described by the normalized variance of isoprene  $\sigma_{\text{ISO}}^2 / \overline{\text{ISO}}^2$  as given on the right side of Fig. 9 for the dependency of  $I_S$  on the isoprene standard deviation  $\sigma_{\text{ISO}}$ . This behavior is also reflected by the third term  $\text{nvar}(\text{ISO})_{iS} = \overline{c'^2_i} / \overline{c_i^2}$  on the right side of the diagnostic equation for  $I_S$  Eq. (12), and, therefore is consistent with the theoretical concept, which is applied to the data analysis.

The numerical results for  $R_{ij}$  (Eq. 6) support the estimation in Sect. 4.2 (Table 4) but show more details (Fig. 11). All terms in brackets (I3 – V3) are third order by dimensions and are given from left (below) to right (fifth term, V3) like in Table 4 with the sum of all terms  $R_{ij}$  at top. Term III3 is proportional to the variance of isoprene mixing ratio, and, therefore is dominant while term I3 is negative by the influence of the covariance but changes sign like term III3, because all terms in  $R_{ij}$  are multiplied by  $(-1)$  in Eq. (6). In general I3 has a tendency to reduce the influence of term III3 on  $R_{ij}$ . The chemical

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reaction term  $R_{ij}$  enters into Eq. (8) with a negative sign to compensate for positive contributions from terms in RES (see also Eq. 9).

Comparing the storage terms from the balance equations with  $I_S$  (Fig. 10) shows that many features of  $I_S$  can also be seen in the storage term of the balance for the covariance (Eq. 11) between isoprene and OH but also in  $R_{ij}$  and term III3 until about 12:30 CET (Fig. 11).

This dominant term III3 is composed of the quotient  $\overline{OH}/(\overline{Iso} + \overline{OH}) \simeq \overline{OH}/\overline{ISO}$  and the variance of isoprene, and, therefore, this influence can also be seen in a comparison of  $I_S$  to  $R_{ij\text{mod}}$  (Fig. 12). Two branches appear in the left part of Fig. 12 with a different dependence of  $I_S$  on  $R_{ij}$ . This behaviour is comparable to the dependence of  $I_S$  on standard deviation and normalized variance of isoprene as shown in Fig. 9.

The error bars for  $I_S$  are discussed in Sect. 3.2. The error for  $R_{ij}$  is mainly caused by the uncertainty in the covariance in term I3 and the triple moment in term IV3 when the same calculation as for  $I_S$  (e.g. for the covariance) is performed (Sect. 3.2). Therefore the same possible source of uncertainty influences both quantities.

If only the relative loss of OH caused by isoprene is considered all terms in  $R_{ij}$  become smaller by the correction  $f$  described in Sect. 3.2.1 (Table 2) and in Appendix A. Note that all terms in  $R_{ij}$  are affected by this procedure if the mixing ration of OH is replaced by  $OH_{\text{mod}} = f \cdot OH$ , but  $I_S$  remains unchanged.

The modification is largest for the first and second period and almost negligible for the last period. But some data points are still outside the new relation between  $I_S$  and  $R_{ij\text{mod}}$  on the right side of Fig. 12. After 14:00 CET the influence of the maximum value of isoprene mixing ratio and isoprene variance cause maxima in both terms I3 and III3. Therefore also  $R_{ij\text{mod}}$  has a maximum significantly different from the expected range of the relation to  $-I_S$  if smaller and larger values of  $|I_S|$  are considered. At least three other data points at 11:50 CET ( $I_S = -0.06$ ), 12:50 CET ( $I_S = -0.055$ ) and 13:30 CET ( $I_S = -0.024$ ) with different factors  $f$  (Table 2) are shifted still to the right only by the influence of term III3. The variance of isoprene is in the range  $0.3 < \sigma_{\text{ISO}}^2 < 0.46$  and the mixing ratio of  $\overline{OH}_{\text{mod}}$  is still above  $2 \times 10^{-4}$  ppb, and, therefore, their product times

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$k_{ij} = 2.3 \text{ ppb}^{-1} \text{ s}^{-1}$  is larger than for other data points with comparable  $I_S$ , but lower OH and  $\text{OH}_{\text{mod}}$  (Fig. 12).

At 12:50 CET,  $I_S = -0.055$  is for a situation with a dominating downdraft instead a convective updraft also with a negative net isoprene flux (see: Dlugi et al., 2010). The magnitude of  $I_S = -0.06$  (at 11:50 CET) is a result of a combined influence of a change in OH-production  $P(\text{OH})$  (Appendix A) and isoprene emission source as discussed in Sect. 4.3.4. The third data point at 13:30 CET is from the period when stable conditions developed above canopy (Dlugi et al., 2010). Therefore these conditions are different compared to all other time intervals with more “common conditions” like (a) an upward directed isoprene flux, (b) nearly constant relation  $P(\text{OH})/L(\text{OH})$  (see Appendix A) and (c) unstable or neutral stratification above canopy during daytime.

In general, both parameters,  $\sigma^2(\text{ISO})$  and  $\text{OH}$  respectively  $\text{OH}_{\text{mod}}$  influence  $R_{ij}$  ( $R_{ij_{\text{mod}}}$ ) for these data during unstable stratification above canopy. At 14:10 CET,  $R_{ij}$  ( $R_{ij_{\text{mod}}}$ ) is mainly determined by the large variance  $\sigma^2(\text{ISO}) = 0.78 \text{ ppb}^2$  during a short interval with unstable stratification and a sensible heat flux  $H \approx 0.1 \text{ K m s}^{-1}$  within a period with otherwise slightly stable conditions after 13:20 CET. In addition, all other data points for the relation between  $-I_S$  and  $R_{ij_{\text{mod}}}$  are as well influenced by the relative contribution of isoprene to the reaction with OH (Tables 1, 2) as the change of stratification above canopy which is unstable until 13:20 CET (Dlugi et al., 2010).

Therefore, although isoprene becomes more dominant in OH removal after 13:00 CET the changing mixing conditions tend to reduce this influence on  $I_S$ . This aspect of influences of turbulence and convection on mixing processes and segregation is further discussed in Sect. 5. In the periods, when the atmosphere above canopy partly becomes stable, maximum values of  $I_S$  are in between  $I_S = -0.07$  (13:40 CET) and  $I_S = -0.095$  (14:20 CET), although isoprene is the dominant sink for OH (Tables 1, 2).

This hints again towards a combined influence of chemical reactions ( $R_{ij}$ ) and turbulent respectively convective mixing and advection ( $\text{RES}$ ,  $\text{RE}_{I_S}$ ) as given in Eqs. (11) and (12).

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### 4.3.3 Covariance and segregation intensity

The covariance  $\overline{c'_i c'_j}$  and  $I_S$  are influenced by chemical reactions as well as transport and mixing processes. The latter can only be determined as a mathematical residuum as RE in Eq. (11) or  $RE_{is}$  in Eq. (12).

5 Solving Eq. (11) for RE gives the results in Fig. 13. Note that the covariance itself is negative, so the result becomes positive by the minus sign in Eq. (11). This term is determined from measured data in the order of  $10^{-5}$  ppb<sup>2</sup>. Also  $-C_{ij}/ISO$  and  $\overline{OH}/ISO \cdot \text{var}(ISO)$  are determined from measured data. The latter term is larger than an order of magnitude than both other terms. Therefore RE is largely compensated by  $\overline{OH}/ISO \cdot \text{var}(ISO)$  because the storage term  $S$  in Eq. (5) (Fig. 10) is negligible. A comparable result is obtained if Eq. (12) is solved for  $RE_{is}$  with  $RE_{is} \approx n\text{var}(ISO)_{is}$  (Fig. 14) because the normalization does not change the relative magnitudes of the different terms.  $CH_{is}$  is dominated by the forth term in Eq. (6) and is only about 15 % or less of the magnitude of  $n\text{var}(ISO)_{is}$ . Therefore the covariance and  $I_S$  are controlled by the difference of two terms being larger by about one order of magnitude than the two other terms (Figs. 13, 14). The magnitude of RE and  $RE_{is}$  support the conclusion in Sect. 4.2 (Table 3) that the magnitude of horizontal derivatives in term  $A_{2k}$  should be of the same order as  $R_{ij}$  to fulfill the findings  $S \approx 0$  respectively  $R_{ij} \approx RES$  in Sect. 4.1.

### 4.3.4 Sources of isoprene and OH and mixing

20 As mentioned in Sects. 3 and 4.3.2 one point around  $I_S \approx 0$  with  $\sigma_{ISO} = 0.67$  (Fig. 9) and  $R_{ij} = 2.78 \times 10^{-4}$  ppb<sup>2</sup> s<sup>-1</sup> (Fig. 12) does not follow the general behavior namely that  $-I_S$  increases with increasing  $\sigma_{ISO}$  and  $R_{ij}$ . The reason for this can be found if the spectral distribution of the covariance  $\overline{OH' Iso'}$ , the ogive (Oncley, 1989; Beier and Weber, 1992), is considered (Fig. 15) for this 10 min time interval at 11:50 CET and compared – for example – to the time interval at 12:30 CET with the maximum value of  $I_S = -0.14$ . At 11:50 CET the influences of changing OH production rate by photolysis

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as well as isoprene emission cause a positive correlation between OH and isoprene in the low frequency part of the time window of 10 min between  $1.6 \times 10^{-3}$  Hz and 0.2 Hz. The isoprene source strength  $E$  (e.g. Guenther et al., 1995, 2006) is significantly influenced by solar radiation and leaf surface (volume) temperature on time scales larger than about 30–60 s. Ciccioli et al. (1997) described the oscillation of leaf surface temperature – caused by strongly variable solar radiation flux as also found on day 206 for ECHO 2003 (Dlugi et al., 2010) – and its influence on the variability of  $E$ . Also the influence of variation of  $J(\text{O}^1\text{D})$  photolysis frequency can be directly found for time intervals larger about one minute (Dlugi et al., 2010). Both processes are related to each other by fluctuations of radiation quantities and are partly correlated. Therefore the covariance between OH and isoprene for time periods larger than about 60 s appears as a positive contribution to the ogive in the lower part of Fig. 15. In addition, for higher frequencies mixing of both compounds is not complete as observed also for other time periods e.g. at 12:30 CET (Fig. 15). If integrated over the whole spectrum to calculate the covariance, the remaining negative contribution to  $I_S$  above  $1.5 \times 10^{-2}$  Hz from inhomogeneous mixing is compensated by the other part which leads to  $I_S \approx 0$ .

If only the process of inhomogeneous mixing is considered, this type of ogive is given in the upper part of Fig. 15 for the maximum case but being in principle valid for all other data points except at 11:50 CET. The change of the ogive for inhomogeneous mixing is most significant below about  $5 \times 10^{-2}$  Hz suggesting also that the detection limit of both measuring devices (PTR-MS, LIF), causing a loss of high frequency contributions as discussed by Dlugi et al. (2010), has no significant influence on these results. If one considers only the contribution from the negative part of the ogive at 11:50 CET, the corresponding data point moves to  $I_S \approx -0.06$  for  $R_{ij} = 2.78 \times 10^{-4}$  ppb<sup>2</sup> s<sup>-1</sup> in Fig. 12 and for  $\sigma_{\text{ISO}} = 0.67$  in Fig. 9.

If the negative part of the ogive is extrapolated to the lowest frequency,  $I_S$  becomes larger within the range  $-0.095 \leq I_S < -0.13$  depending on the spectral dependence below  $1.5 \times 10^{-2}$  Hz as illustrated in Fig. 15. As this spectral behavior needs some assumptions, only the value  $I_S \approx -0.06$  is given.

The ogive (upper part of Fig. 15) shows that an estimate for the covariance and  $I_S$  may be achieved even if the instruments have a time resolution of only about 0.06–0.2 Hz.

#### 4.4 Empirical relations

5 The analysis of data from ECHO 2003 shows that the intensity of segregation  $I_S$  for the reaction between isoprene and OH negatively increases with increasing  $\text{OH}_{\text{mod}}$  (Fig. 6). For an estimation of  $I_S$  a linear approximation yields  $I_S = -320[\text{ppb}^{-1}] \cdot \text{OH}_{\text{mod}}[\text{ppb}]$ . Therefore, doubling the mixing ratio  $\text{OH}_{\text{mod}}$  (Appendix A) also doubles  $I_S$  in the range  $4 \times 10^{-5} \leq \text{OH}_{\text{mod}} \leq 4 \times 10^{-4}$  ppb.

10 Often measurements are performed which cannot be used to estimate the influence of other chemical compounds than isoprene on OH removal.

Then  $f$  (Appendix A) cannot be estimated and  $\text{OH}_{\text{mod}}$  is unknown. But with measured OH,  $|R_{ij}|$  may be estimated in the linear relation to  $\text{OH} \cdot \text{var}(\text{ISO})$  (Fig. 16).  $|R_{ij}|$  also shows a high correlation, but larger scatter, with  $\sigma_{\text{ISO}}$  (Fig. 17).

15 If only data points for “common conditions” (Sect. 4.3.2) are considered on the right side of Fig. 12 on can estimate  $I_S$  for a more completely characterized system by  $I_S \approx 1100|R_{ij_{\text{mod}}}|$  even if  $|R_{ij_{\text{mod}}}|$  is replaced by  $R_{ij} \approx 2 \cdot \text{OH} \cdot \text{var}(\text{ISO})$  as shown in Fig. 16. Based on this data set the magnitude of  $I_S$  does not “vary simply much like the magnitude of the isoprene variance but with opposite sign” (Davis, 1992), as cited also by Patton et al. (2001) and applied by their “simple formulation” for their model study. The relation is modified by  $\text{nvar}(\text{ISO})_{I_S}$  and is not the only factor of influence as given by Eq. (12), which will be further discussed in the following.

20 This finding from Fig. 16 also agrees qualitatively with the basic assumptions made to calculate segregation intensity by LES by Patton et al. (2001). They found  $I_S$  (and  $R_{ij}$ ) being proportional to  $\sigma_{\text{ISO}}$ , but, contrary to the analysis of field data from ECHO 2003,  $-r_{\text{ISO-OH}} > 0.8$  was established while experimental data from ECHO 2003 point

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towards  $-r_{\text{ISO.OH}} < 0.55$  but may be too low as discussed in Sect. 3.2.4. The magnitude of the correlation coefficient increases with increasing mean reaction rate.

Note, a correlation coefficient  $-r_{\text{ISO.OH}} > 0.8$  would shift  $I_S$  towards the maximum values around  $I_S \approx -0.2$  to  $-0.25$  as applied by Pugh et al. (2011) in their analysis.

## 5 Reaction and transport

### 5.1 Comparison of reaction terms and the sum of transport terms

The storage term in the balance of the covariance (Eq. (8), Fig. 10) is shown to be small compared to terms which compose  $R_{ij}$ . Therefore Eq. (11) can be formulated as a diagnostic equation for the covariance to analyze the contributions of term three on the right side being the variance of isoprene times the quotient of mean mixing ratios of OH and isoprene for each 10 min interval. The other chemical term  $k_{ij} \cdot C_{ij}$  (divided by the sum of OH and isoprene mixing ratios times  $k_{ij}$ ) reduces this contribution to the covariance by about 15 % or less. The residuum RES summarises the net effect of turbulent interaction and advection (Eq. 9) and must be also divided by the same factor as  $k_{ij} \cdot C_{ij}$ . This term is called RE in Eq. (11).

The different contributions of terms of Eq. (11) in Fig. 13 show that  $\overline{\text{OH}}/\overline{\text{ISO}} \cdot \text{var}(\text{Iso})$  largely dominates the behavior of the covariance, because RE is a residuum and mathematically serves to close the balance of covariance. Both terms,  $\overline{\text{OH}}/\overline{\text{ISO}} \cdot \text{var}(\text{ISO})$  and RE, are larger by about one order of magnitude than the other two terms. A relation between  $k_{ij} \cdot \overline{\text{OH}}/\overline{\text{ISO}} \cdot \text{var}(\text{Iso})$  and RES can also be found, because  $S = 0$ , and, therefore,  $\text{RES} = R_{ij}$  in Eq. (7) (Fig. 18). The three marked points belong to the results obtained at 11:50 CET ( $\text{RES} = -2.73 \times 10^{-4} \text{ ppb}^2 \text{ s}^{-1}$ ), 12:00 CET ( $\text{RES} = -1.78 \times 10^{-4} \text{ ppb}^2 \text{ s}^{-1}$ ) and 14:20 CET ( $\text{RES} = -2.4 \times 10^{-4} \text{ ppb}^2 \text{ s}^{-1}$ ) with dynamic and turbulent conditions different from other time intervals. As discussed in Sect. 4.3.4, the apparent intensity of segregation is  $I_S \approx 0$  at 11:50 CET, but with the correction



discussed,  $I_S \geq -0.06$  is most reliable.  $I_S$  increases to about  $-0.13$  at 12:00 CET and  $I_S = -0.097$  at 14:20 CET with both ogives completely valid for the case of inhomogeneous mixing as for 12:30 CET (Fig. 15).

As mentioned above, the maxima of  $I_S$  are found when  $\text{NO}_x$  and CO-mixing ratios (Table 1) decrease and unstable conditions develop above canopy after 11:30 CET until about 13:00 CET and again around 14:10 CET. The period around 12:00 CET is characterized by a vertical downdraft with  $-0.06 \leq \bar{w} \leq -0.14 \text{ ms}^{-1}$  and a mean Monin–Obukhov length  $L_* = -55 \text{ m}$ . Therefore mean reaction conditions are influenced by the chemical mixture (Table 1, 2) and by advective and convective transport rather than only by locally produced turbulence. The data point for 14:10 CET is for unstable conditions with  $u_* = 0.45 \text{ ms}^{-1}$  and  $L_* = -70 \text{ m}$  within a period with neutral to stable stratification before and after that time interval as given also in Sect. 4.3.3. In all cases with  $I_S > -0.04$  turbulent kinetic energy (TKE) as well as buoyant production (BP) (Stull, 1988) becomes larger showing again that non-local transport (convection) and mixing may have influenced segregation intensity as discussed in Sect. 5.2.

A tendency is observed that for increasing  $k_{ij} \cdot \overline{\text{OH}} / \overline{\text{ISO}} \cdot \text{var}(\text{ISO})$  the term RES seems to be limited by a maximum of about 67 % for line (a) and 85 % for the mean (line b) (Fig. 18). Another approximation is obtained with  $\text{RES} = |R_{ij}| = -a \cdot k_{ij} \cdot \overline{\text{OH}} / \overline{\text{ISO}} \cdot \text{var}(\text{ISO})$ . The normalization does not modify this relation, and, therefore, this behaviour is even more obvious (Fig. 19) if both sides of Eq. (11) are divided by the product of the mean mixing ratios of isoprene and OH to obtain the diagnostic equation for the intensity of segregation  $I_S$ , Eq. (12). The two terms are  $\text{RE}_{IS}$  and  $\text{nvar}(\text{ISO})_{IS}$ . Their difference determines  $I_S$  because the remaining chemical terms  $\text{CH}_{IS}$  and  $I_S$  in Eq. (12) are smaller (Fig. 13) but causes the scatter around the mean of the curve in (Fig. 19). Therefore in the time behavior an increase of  $\text{nvar}(\text{ISO})_{IS} - \text{RE}_{IS}$  is always related to a decrease of  $I_S$  and vice versa (Fig. 14).

Note, the three critical points discussed before (Fig. 18) are not outside all other data points in Fig. 19. As before, the red circle is for the corrected value of  $I_S$  (see Sect. 4.3.4) and the other circles are for time intervals at 12:00 CET and 14:10 CET.

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The intensity of segregation increases with increasing difference of both terms, but the increase of  $RE_{IS}$ , as it is for RES (Fig. 18), is limited. Also the normalized variance of isoprene and the standard deviation  $\sigma_{Iso}$  (Fig. 9) have an upper bound. If – in addition – data from the ECHO field study also by Spirig et al. (2005) are considered – at least at this site – the difference term in Fig. 19 should not exceed a value of 0.3. This agrees with an upper most value of about  $I_S \lesssim -0.20$  from the data of this field study if the correlation coefficient would approach values  $r_{OH,Iso} \gtrsim -0.7$ . From Fig. 19 one may also conclude that the net effect of all terms in  $RE_{IS}$  is to reduce the correlation between  $I_S$  and  $nvar(Iso)_{IS}$  or with  $\sigma_{Iso}$  and  $R_{ij}$  (Figs. 9, 17).

A linear regression between  $I_S$  and the difference of both terms leads to

$$I_S = -0.67(nvar(Iso)_{IS} - RE_{IS}) - 0.0023$$

with a correlation coefficient of  $R = -0.92$ . This linear anticorrelation is also reflected in the time behavior of these quantities in Fig. 14 because transport and mixing processes as well as the chemical system itself (Table 2) influence  $I_S$ .

The chemical term  $var(Iso)$  (or  $nvar(Iso)_{IS}$ ) is also directly modified by the reaction conditions at the main tower which are given by the quotient between the mean mixing ratios  $\overline{OH}/(\overline{Iso} + \overline{OH}) \simeq \overline{OH}/\overline{Iso}$  in Eq. (11). This quotient increases with increasing variance  $var(Iso)$ , but should be limited as measured field data show  $OH/Iso < 5 \times 10^{-4}$  (Fig. 5) with modifications according to Table 2.

Without direct measurements of these quantities composing the terms in Eqs. (11, 12) and the direct determination of  $I_S$  (and  $C_{ij}$ ) it is only possible to roughly estimate (see Sect. 4.4) the potential magnitude of  $I_S$  but not to understand the variability of segregation in this complex chemical system.

## 5.2 Potential influences of mixing processes

### 5.2.1 Eddy motion near canopy top

The relations between the covariance or  $l_s$  and different terms of their balance equations point towards the combined influences of chemical conditions as well as of turbulent transport and mixing processes near canopy top or even on a horizontally larger scale e.g. by the influence of convection or small mesoscale circulation. On the smaller scale Katul et al. (1997) discussed the role of eddy motion near the forest-atmosphere interface. Also Patton et al. (2001) showed that coherent eddy motion and related mixing processes (with  $r_{OH,Iso} \geq -0.8$ ) should influence the intensity of segregation  $l_s$ . In this paper such effects are related to terms like  $RE_{is}$  and  $nvar(Iso)_{is}$ . This is done without further specification of processes behind the nature of terms RES or  $RE_{is}$  in Eqs. (11, 12). For this purpose we calculated all terms of the Katul et al. (1997) version of third order cumulant expansion method (CEM) to find out if the relative contribution of sweeps or ejections to the flux of isoprene can be related to the terms  $nvar(ISO)_{is}$  or  $RE_{is}$ . A measure for this effect is the “stress function”  $\Delta S_0$  for the isoprene flux. This may be expressed in a simplified formulation derived from complete CEM (Katul et al., 1997; Cava et al., 2006) as

$$\Delta S_0 \approx \frac{1}{\sqrt{2\pi}R_{wc}}[M_{21} - M_{12}] \quad (13)$$

with

$$M_{ji} = \left( \overline{c^i j w^i} \right) / \left( \sigma_c^i \sigma_w^i \right) \quad (14)$$

and  $R_{wc}$  the correlation coefficient between the vertical velocity and isoprene mixing ratio in this case.  $M_{21}$  is a generalised correlation coefficient for the turbulent transport of isoprene variance and  $M_{12}$  the corresponding correlation coefficient for the turbulent flux of isoprene.

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Neither the “stress function”  $\Delta S_0$  from the complete CEM nor from the simplified parameterisation Eq. (13) shows a significant correlation with  $I_S$  or terms of the balance Eq. (12).  $M_{21}$ , as the measure for turbulent transport of isoprene variance, shows some relation to  $RE_{IS}$  and  $nvar(Iso)_{IS}$  as presented in Fig. 20. Here a simple relation to  $M_{12}$  cannot be established. The smaller values of  $nvar(Iso)_{IS}$  correspond to small values of  $I_S$  (Fig. 9) and belong to smaller negative or positive  $M_{21}$  (Fig. 20). Therefore isoprene variance is transported by turbulence in both directions but only upwards for larger values of  $nvar(Iso)_{IS}$ . This agrees with the finding that an upward directed flux is related also to higher isoprene variance and downdrafts are characterized by smaller values of  $\sigma_{ISO}$  or  $nvar(ISO)_{IS}$ . A typical sweep ejection cycle, as often discussed in literature (see discussion in: Katul et al., 1997) cannot be simply established for this data set. The behavior for  $RE_{IS}$  is comparable as both terms are dominant, and therefore, are correlated.

### 5.2.2 Forced and free convective mixing

During the measuring period of 25 July 2003 (day 206) of ECHO 2003 the stratification varied between slightly stable to unstable conditions with a change from mechanically induced turbulence to nearly free convective conditions. This allows to compare the results from this field study to model results.

Recently Ouwersloot et al. (2011) showed that in a region with an inhomogeneous distribution of surface sensible heat fluxes  $H$  and, therefore, surface buoyancy  $H_v$  and isoprene emission fluxes, the segregation intensity for the reaction between isoprene and OH can increase with increasing differences  $\Delta H_v$  between a cooler forest and a warmer savanna type area. This situation is qualitatively comparable to the Jülich site as the deciduous forest is surrounded by urbanized area with buildings of the research center and agricultural areas being dryer, and, therefore warmer than the forest canopy. Their results also point towards an increase in the turbulent kinetic energy TKE and also buoyant production BP – a term in the TKE balance – with increasing  $\Delta H_v$  but also  $H_v$  itself. In their Fig. 13 they show a case with  $I_S \approx -0.195$  for  $\Delta H_v = 0$  and

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obviously a mean surface kinematic heat flux of  $H = 0.15 \text{ K m s}^{-1}$ . Their finding suggests that one should observe  $I_S$  increasing with TKE and with BP respectively  $H$  or  $H_v$  itself. These relations between  $I_S$  and TKE respectively BP from the ECHO measuring period (25 July 2003, 09:00–15:00 CET) are presented in Fig. 21 and Fig. 22. Indeed, the largest values for  $I_S$  are found for largest values of TKE and BP, but – as discussed before (Sect. 4.3.2) – are for smaller values significantly modified by the influence of the chemical state of the reactants mixture. Therefore two data points with TKE  $> 0.85 \text{ m}^2 \text{ s}^{-2}$  have  $I_S < -0.03$  because they are for the morning hours with larger mixing ratios of  $\text{NO}_x$  (see Sect. 3.2.1) which are conditions with lower mean percentage of OH-reactivity related to isoprene as given in Fig. 6 and Tables 1, 2. These results also belong to the data points in the blue circle in Fig. 6 between  $I_S$  and mean OH-mixing ratio. Two other data points with  $I_S = -0.06$  and  $I_S = -0.057$  are for lowest  $\text{NO}_x$  mixing ratio and for TKE  $< 0.5 \text{ m}^2 \text{ s}^{-2}$ , reflecting the possible variability by influences of chemistry and turbulent transport and mixing. Note that for these two points the friction velocity  $u_*$  is significantly lower than the convective scale velocity  $w_*$ . This hints towards a significant contribution of convection to vertical transport for both cases as can be seen for the relation between  $I_S$  and  $H$  respectively BP in Fig. 22. If these aspects are considered,  $I_S$  increases on average with increasing TKE in the range where chemical isoprene removal is influenced by concurrent reactants (e.g.  $f < 0.9$ , Appendix A) up to about  $I_S \simeq -0.04$ . Larger values of  $I_S$  are in the range with  $f \geq 0.75$  where  $I_S$  becomes nearly independent of TKE.

As for TKE comparable findings are obtained for  $I_S$  as function of BP (Fig. 22). The data points for low  $\text{NO}_x$  mixing ratios – as also found for the TKE- $I_S$ -relation – are mainly in a range BP  $> 3 \times 10^{-3} \text{ m}^2 \text{ s}^{-2}$  and  $|I_S| > 0.04$ .

The behavior of  $-I_S$  as function of BP shows an increase of  $-I_S$  for BP  $> 3.0 \times 10^{-3} \text{ m}^2 \text{ s}^{-3}$ , if two data points with  $I_S = -0.078$  and BP  $= 1.1 \times 10^{-3} \text{ m}^2 \text{ s}^{-3}$  and  $I_S = -0.079$  and BP  $= 2.4 \times 10^{-3} \text{ m}^2 \text{ s}^{-3}$  are neglected for this consideration. This range for BP is equivalent to a sensible heat flux  $H > 0.08 \text{ K m s}^{-1}$ , defining the conditions for the onset of convection at canopy top ( $z_R/L_* > -1.0$ ) for which  $I_S > -0.04$  is valid. If  $H_v$  is

calculated instead of  $H$ ,  $H_v \approx 1.08 \cdot H$  for  $H > 0.06 \text{ K m s}^{-1}$  for this data set. An extrapolation of the data to  $H_v = 0.15 \text{ K m s}^{-1}$  yields  $I_S \gtrsim -0.2$ , and a qualitative agreement with the model calculations by Ouwersloot et al. (2011).

The dependence of the correlation coefficient  $r_{ij}$  as function of the mean reaction rate  $k_{ij} \cdot \overline{\text{ISO}} \cdot \overline{\text{OH}}$  given in Fig. 8 can be compared to results by Ouwersloot et al. (2011). They reported that the correlation coefficient increases with increasing reaction rate. The ECHO 2003 data have a maximum of  $k_{ij} \cdot \overline{\text{ISO}} \cdot \overline{\text{OH}} \approx 6.9 \times 10^{-4} \text{ ppb s}^{-1}$  (Fig. 8) which is somewhat larger than given by Ouwersloot et al. (2011) in their Fig. 4. Their corresponding correlation coefficient is significantly larger but for mean mixing ratios of OH about one third of the ECHO 2003 data and about a threefold mixing ratio of isoprene. Note that the chemical regime is different with  $\text{NO}_x < 1 \text{ ppb}$  for the model study and  $\text{NO}_x \geq 2-3 \text{ ppb}$  for the ECHO field study. The results of Fig. 13 of Ouwersloot et al. (2011) show that  $I_S$  is a function of  $\Delta H_v$ . A comparable spatial variability of  $H_v$  may be possible for ECHO 2003 which suggests that the result from Sect. 4.2 that the horizontal derivations of term  $A_{2k}$  should significantly modify RES respectively  $\text{RE}_{I_S}$  in Eqs. (11), (12) to achieve  $S \approx 0$ , may be caused by this influence of inhomogeneous distributed sources of heat and isoprene.

### 5.3 Damköhler number dependence

Some authors related the effective rates of second order chemical reactions and also the segregation intensity  $I_S$  to specific Damköhler numbers  $\text{Da}_c$  of specific compounds  $c_i$ . For the situation during ECHO 2003 the only available study at least for a qualitative comparison of the dependence of  $I_S$  on  $\text{Da}_c$  is from Patton et al. (2001). Their results from a LES-modeling study are for a forest with a comparable leaf area index and canopy height  $h_c = 20 \text{ m}$  (ECHO:  $h_c = 30 \text{ m}$ ). For the model study  $\text{Da}_c$  is defined by  $\text{Da}_c = \frac{\tau_t}{\tau_c} = \frac{h_c}{u_*} \cdot k_{ij} \cdot \overline{\text{OH}}$  (see also Sect. 3.2.1). While  $u_* = 0.28 \text{ m s}^{-1}$  in this model study the friction velocity from the field experiment during the considered time period is in

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the range  $0.12 \leq u_* \leq 0.71 \text{ ms}^{-1}$  with a mean value  $\overline{u_*} = 0.39 \text{ ms}^{-1}$  (see Fig. 3 in Dlugi et al., 2010). Therefore, in the field  $\tau_t$  varied by a factor of about six by the influence of  $u_*$ , and  $\text{Da}_c$  is not only modified by  $\text{OH}$  like in the model study by Patton et al. (2001). A comparison with this model study can only be performed if  $\text{OH}_{\text{mod}}$  is applied in the definition of  $\text{Da}_c$  because this quantity is comparable to the  $\text{NO}_x$ -free system as used in their model.  $\text{OH}$  and  $\text{OH}_{\text{mod}}$  are comparable with  $\text{OH}$  mixing ratios in the model studies, e.g. about  $1.2 \times 10^{-4}$  ppb for the volume average  $\overline{\text{OH}}_v$  for  $\text{Da}_c = 0.02$  compared to the data presented in Fig. 6. For the model study  $\text{Da}_c$  increases linearly with  $\overline{\text{OH}}_v$ , and, therefore, for  $\text{Da}_c = 0.1$  a significantly higher mixing ratio of  $\overline{\text{OH}}_v = 6 \times 10^{-4}$  ppb is calculated than obtained in the field. Not only the chemical system is different. The model describes free convective conditions with the kinematic sensible flux of  $0.35 \text{ Kms}^{-1}$ , also significantly larger than measured in the field (Fig. 22).

The calculated Damköhler numbers  $\text{Da}_c$  for the chemical removal of isoprene by  $\text{OH}$  during ECHO 2003 are given in Fig. 23. A chemical plausible result is obtained only on the right part for the dependence of  $I_S$  on  $\text{Da}_{c,\text{mod}}$  with  $\overline{\text{OH}}$  substituted by  $\overline{\text{OH}}_{\text{mod}}$  (Appendix A). Here  $I_S$  increases on average with increasing mixing ratio  $\overline{\text{OH}}_{\text{mod}}$  for the effective chemical sink for isoprene with the exception of two data points. The relation  $I_S \sim f(\text{Da}_c)$  seems to be different for  $I_S < -0.04$  and  $I_S > -0.04$ . Such a behavior is also suggested by the results given in Fig. 4 of Patton et al. (2001). For a linear interpolation through zero, on average, the ECHO data yield  $I_S \approx -2.7 \cdot \text{Da}_{c,\text{mod}}$  for an atmosphere which is influenced by shear driven and convective driven turbulence roughly separated by the line through  $H = 0.085 \text{ Kms}^{-1}$  in Fig. 22, while all data presented by Patton et al. (2001) are given for  $H = 0.34 \text{ Kms}^{-1}$  in the free convection range. Patton et al. (2001) obtained  $I_S \approx -0.175$  for  $\text{Da}_c = 0.17$  while a comparable linear extrapolation through zero from the ECHO data set yields a similar value  $I_S \approx -0.175$  for  $\text{Da}_c \approx 0.065$ . The effective turbulent exchange process during free convective conditions is rather different compared to shear driven turbulence (Stull, 1988). Also the application of the applied definition of  $\text{Da}_c \sim u_*^{-1}$  can only be an estimate for convective conditions.

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Therefore the experimental and model results only quantitatively agree with respect to the increase of  $I_S$  with increasing  $Da_c$ .

## 6 Summary

The terms of the balances of mixing ratio of isoprene, the covariance  $\overline{ISO' OH'}$  and the segregation intensity  $I_S$  are compared to each other. For the mixing ratio the storage term is compensated by a residuum which is mainly composed by the divergence of the turbulent flux but also by (unknown) contributions from advection because both terms of the chemical sink are smaller. Within this chemical term the covariance between isoprene and OH is less than 15 % of the product of the means of the mixing ratios. The quotient of both terms, the intensity of segregation  $I_S$ , increases with mean OH-mixing ratio as well as standard deviation of isoprene  $\sigma_{ISO}$  and normalized variance. The further data analysis shows that both findings from the ECHO field study are at least partly and qualitatively comparable to model results by Patton et al. (2001). Therefore, for increasing  $\sigma_{ISO}$ ,  $I_S$  increases with the restriction that other chemical compounds reacting with OH at comparable reaction rates reduce the degree of inhomogeneous mixing for the isoprene-OH reaction. The estimation of the contribution of isoprene to  $\overline{OH}$  removal shows that the correlation between  $I_S$  and the modeled  $\overline{OH}_{mod}$  is significantly enhanced compared to measured  $\overline{OH}_{meas}$ .

In the following step the balance equation for the covariance between OH and isoprene,  $\overline{c'_i c'_j}$ , was applied for the analysis of field data from ECHO 2003. The storage term is found to be small compared to other terms of the balance. This allows to formulate a diagnostic version of the balance equation also to relate turbulent and advective transport and mixing terms (RES respectively  $RE_{I_S}$ ) and influences of chemical reactions ( $R_{ij}$ ) to the intensity of segregation  $I_S$ . The following analysis shows that the reaction rate  $R_{ij}$  is largely dominated by the variance of isoprene  $\text{var}(Iso)_{I_S}$  times the quotient  $(\overline{OH}/\overline{ISO}) \cdot k_{ij}$  which supports the findings discussed above. This is the reason

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why  $I_S$  and  $R_{ij}$  show a relation also to the normalized variance. The results prove that the chemical term as well as the transport and mixing term are of nearly equal influence on the covariance, and therefore,  $I_S$ . Some data points show deviations from simple relations. This is caused by dynamics different from the general picture that isoprene is emitted at the surface, mixed upward and react with locally produced OH.

The detailed spectral analysis of the ogive of  $\overline{c'_i c'_j}$  shows that a case with an apparent value  $I_S \approx 0$  is obtained at 11:50 CET by a counteracting influence of the time dependent positively correlated change of OH-production and isoprene emission for lower frequencies together with inhomogeneous mixing for higher frequencies. If only the process of inhomogeneous mixing is considered, a value  $I_S \approx -0.06$  is calculated which corrects results earlier published by Dlugi et al. (2010). But in general for this field study  $I_S$  can be related to the dominant term in the chemical reaction term – the normalized variance of isoprene – and to the action of the residual term RES respectively  $RE_{iS}$ . If their difference increases,  $-I_S$  increases as well. This points towards a decreasing influence of concurrent chemical reaction cycles on  $I_S$  (Table 2) and a smaller relative contribution of advection within terms RES and  $RE_{iS}$  for larger values of  $-I_S$  for the conditions of this field study.

On the one hand for a negligible influence of RES or  $RE_{iS}$  one may simply estimate a maximum value of  $I_S$  by the variance term  $\text{nvar}(\text{Iso})_{iS}$  itself with consideration of the reactivity of the chemical system (Tables 1 and 2). On the other hand,  $I_S$  can approach small values, although reaction conditions suggest  $I_S > -0.04$ , only by the influence of  $RE_{iS}$ .

Within this framework the processes influencing the terms  $\text{nvar}(\text{ISO})_{iS}$  and  $RE_{iS}$  remain undefined. Therefore a different additional analysis to find out at least physical parameter controlling exchange and mixing and revealing some relation to  $I_S$  is performed.

An indicator  $\Delta S_0$  for the amount of appearance and influence of coherent eddies on the flux of isoprene shows no clear relation to  $I_S$  or other terms of its balance. But a relation between the correlation coefficient for the turbulent transport of isoprene



variance  $M_{21}$  is found with the normalized variance of isoprene  $\text{nvar}(\text{Iso})_{is}$  itself as well as the residuum  $\text{RE}_{is}$ . This hints towards the influence of turbulent transport of isoprene variance on the residual term  $\text{RE}_{is}$ .

In addition, the absolute value of  $I_S$  shows a tendency to increase with increasing TKE and BP if concurrent chemical reactions are of less influence.

These results qualitatively agree with findings by Ouwersloot et al. (2011) on an increase of  $-I_S$  with increasing influence of turbulent mixing and convection. This effect can only be evaluated from data for conditions when isoprene is the main sink for OH. Otherwise if the reaction rates of concurrent chemical reactions are dominant, the segregation intensity for the reaction isoprene + OH is found to be below  $I_S = -0.04$ .

If the Damköhler number  $\text{Da}_c$  is applied to describe the reaction by the influence of shear driven turbulence, an increase of  $|I_S|$  with increasing  $\text{Da}_{c,\text{mod}}$  is found. This finding only qualitatively agrees to model results by Patton et al. (2001) because mixing conditions and chemical conditions from the field are different.

In addition, if measurements were performed with a smaller time resolution, our analysis (Sect. 4.3.4) shows that estimates of  $I_S$  can still be achieved to compare to other results from the field and model studies.

## Appendix A

Following the concept (Eq. A1) that measured OH can be expressed by the influences of production  $P(\text{OH})$  and loss  $L(\text{OH})$  we formulate an equation (Eq. A4) to estimate a factor  $f$  to calculate the relative isoprene sink from the reaction with OH(measured). From measurements during ECHO 2003 the mixing ratios of NO, NO<sub>2</sub>, CH<sub>4</sub>, CO, sum of monoterpenes and also OH and isoprene are known. For stationary conditions Eq. (A1) is valid:

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$$\text{OH(measured)} = \frac{\text{production}}{\text{loss}} = \frac{P}{L} = \frac{P}{\sum_{l=1}^N k_{lj} \cdot \bar{c}_l} \quad (\text{A1})$$

Here index  $j$  is for OH while index  $l$  is for any chemical compound with an average concentration  $\bar{c}_l$  reacting with OH. Therefore one may formulate

$$L = k_{ij} \cdot \overline{\text{ISO}} + \sum_{l=0}^{N-1} k_{lj} \cdot \bar{c}_l \quad (\text{A2})$$

- 5 to separate the OH loss by isoprene (index  $i$ ) from those of other compounds. With Eq. (A1) and division by the sum term in Eq. (A2) we obtain:

$$\text{OH(measured)} \cdot \left( \frac{k_{ij} \cdot \overline{\text{ISO}}}{\sum_{l=1}^{N-1} k_{lj} \cdot \bar{c}_l} + 1 \right) = \frac{P}{\sum_{l=1}^{N-1} k_{lj} \cdot \bar{c}_l} = \frac{P}{L - k_{ij} \cdot \overline{\text{ISO}}} \quad (\text{A3})$$

Finally one obtains for a modeled OH-mixing ratio OH(mod):

$$\text{OH(mod)} = \text{OH(measured)} \cdot \left( \frac{k_{ij} \cdot \overline{\text{ISO}}}{\sum_{l=1}^{N-1} k_{lj} \cdot \bar{c}_l} \right) = \overline{\text{OH}} \cdot f = \frac{k_{ij} \cdot \overline{\text{ISO}}}{L - k_{ij} \cdot \overline{\text{ISO}}} \cdot \frac{P}{L} \quad (\text{A4})$$

- 10 The factor  $f$  is the relative reaction rate for OH consumption by isoprene compared to other compounds in the atmospheric mixture also called the fraction of isoprene reactivity to total reactivity.

The influence of different chemical compounds on  $f$  is given in Tables 1 and 2. Note that if all other compounds influencing  $L(\text{OH})$  would be considered one gets  $f > f(\text{all reactants})$ . Half-hourly and hourly values are available from vertical profile and concentration measurements for compounds  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{CO}$  and  $\text{CH}_4$  in Table 1 which limits the time resolution for the calculation of factor  $f$ .

The intensity of segregation  $I_S$  is affected by  $f$  over the whole range of its magnitude (Fig. 24).

## Appendix B

In the balance equation of the covariance between isoprene and OH the advection term is decomposed into terms  $A_{1k}$  and  $A_{2k}$  with

$$A_{1k} = \overline{c'^i c'^j} \frac{\partial \bar{u}_k}{\partial x_k} \quad (\text{B1})$$

and

$$A_{2k} = \bar{u}_k \frac{\partial}{\partial x_k} \overline{c'^i c'^j} \quad (\text{B2})$$

On a local scale the divergence of the wind field in  $A_{1k}$  – especially under the influence of tall vegetation and complex terrain (e.g. Sun, 2007; Stull, 1988) – can be as large as  $0.1 \text{ s}^{-1}$  but may decrease to  $10^{-3} - 10^{-2} \text{ s}^{-1}$  for small mesoscale circulation (e.g. Stull, 1988). With the covariance in the range of  $10^{-5}$  (Fig. 1) term  $A_{1k}$  becomes smaller than  $10^{-6} \text{ ppb}^2 \text{ s}^{-1}$  (Table 3).

As discussed in Sects. 4.1 and 4.2,  $A_{1k}$  is not added to the covariance on the left side of Eq. (8) because in general the wind field divergence is  $< 0.1 \text{ s}^{-1}$ , and, therefore, the covariance on the left side of Eq. (8) will only be influenced by less than 10%.

The other term  $A_{2k}$  is estimated to be below  $2 \times 10^{-7} \text{ ppb}^2 \text{ s}^{-1}$  if the spatial gradient of the covariance is proportional to the change with time.

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The spatial variability of  $\overline{c'_i c'_j}$  is caused by local variability of OH mixing ratio caused by photolysis and chemical reactions during advection of isoprene from emission sources to the site of measurements. As discussed in Sect. 4.3.4, OH production and isoprene emission are found to be locally positively correlated in a frequency range below about 0.02 Hz.

The covariance for inhomogeneous mixing conditions describes a negative correlation between isoprene and OH (Fig. 7). Therefore, as mostly negative covariances are determined, the change from locally positive to negative correlation is caused by advective transport of isoprene and isoprene variance through the field of OH being variable in time and space. The influence of horizontal derivations in  $A_{2k}$  is discussed in Sect. 4.2.

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**Table 1.** Mean Mixing ratios on 25 July 2003 (day 206) at the ECHO site.

Time period	CET	09:00–10:30	10:30–11:30	11:30–13:00	13:00–15:00
NO <sub>2</sub>	ppb	> 2.5	2.0–2.5	1.8–2.1	1.1–1.8
NO	ppb	> 0.75	0.6–0.95	0.4–0.8	0.2–0.5
CO	ppb	> 150	> 140	> 140	> 140
CH <sub>4</sub>	ppb	≈ 1800	≈ 1800	≈ 1800	≈ 1800
Isoprene	ppb	0.5–0.7	0.3–0.7	0.3–1.13	0.45–1.58
∑ Monoterpenes	ppb	0.13–0.27	0.21–0.32	0.2–0.34	0.23–0.30
O <sub>3</sub>	ppb	19–25	25–30	30–35	35–39

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**Table 2.** Mean Reaction Rates [ $\text{s}^{-1}$ ] for different reactants, the total OH loss  $L(\text{OH})[\text{s}^{-1}]$  and the percentage of OH-reacting related to isoprene for 25 July 2003 at the ECHO site (see Appendix A).

Time (CET)	09:00–10:30	10:30–11:30	11:30–13:00	13:00–15:00
ISO	1.76–0.88	1.61	1.78	2
NO <sub>2</sub>	> 1	0.78	0.67	0.45
NO	0.07	0.06	0.03	0.02
CO	0.9	0.84	0.84	0.84
CH <sub>4</sub>	0.28	0.28	0.28	0.28
$\Sigma$ Monoterpenes	< 0.68	0.51	0.55	0.5
%	30–60	65	75	≈ 95
$L(\text{OH})$	4.69	4.08	4.15	4.09

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**Table 3.** Order of magnitude of terms of the balance equation of the covariance (Eq. 5) in  $\text{ppb}^2 \text{s}^{-1}$  as explained in Sects. 4.2 and 4.3 for  $x_k = z$  (vertical coordinate).

Term	Range
$S$	$< 6 \times 10^{-8}$
$\text{TPI}_k$	$6 \times 10^{-7}$ to $6 \times 10^{-6}$
$\text{TPOH}_k$	$6 \times 10^{-7}$ to $6 \times 10^{-6}$
$A_{1k}$	$< 10^{-6}$
$A_{2k}$	$< 2 \times 10^{-7}$ ( $\leq 10^{-4}$ )
$\text{TT}_k$	$< 4 \times 10^{-6}$
$D$	$< 10^{-10}$
$R_{ij}$	$< 4 \times 10^{-4}$

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**Table 4.** Order of magnitude of the five terms of  $R_{ij}$  [ppb<sup>2</sup> s<sup>-1</sup>] (Eq. 6) according to the analysis in Sect. 4.3.

Term	Range
$R_{ij_1}$	$7 \times 10^{-6}$ to $1.3 \times 10^{-4}$
$R_{ij_2}$	$10^{-7}$ to $10^{-8}$
$R_{ij_3}$	$\approx 10^{-4}$
$R_{ij_4}$	$< 3 \times 10^{-5}$
$R_{ij_5}$	$< 10^{-8}$

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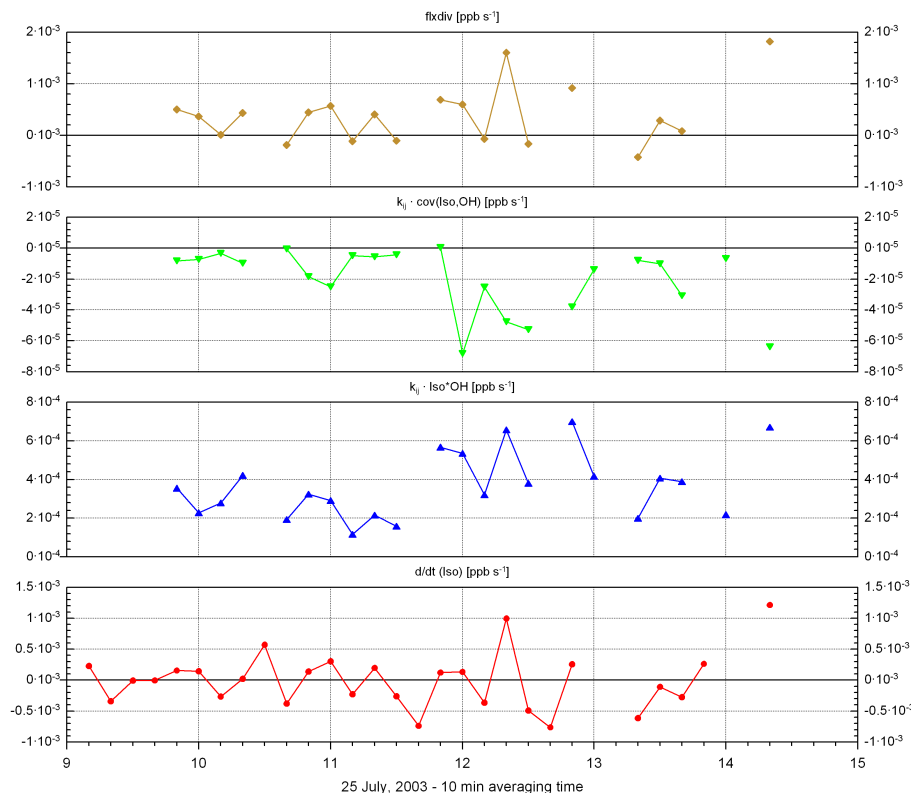
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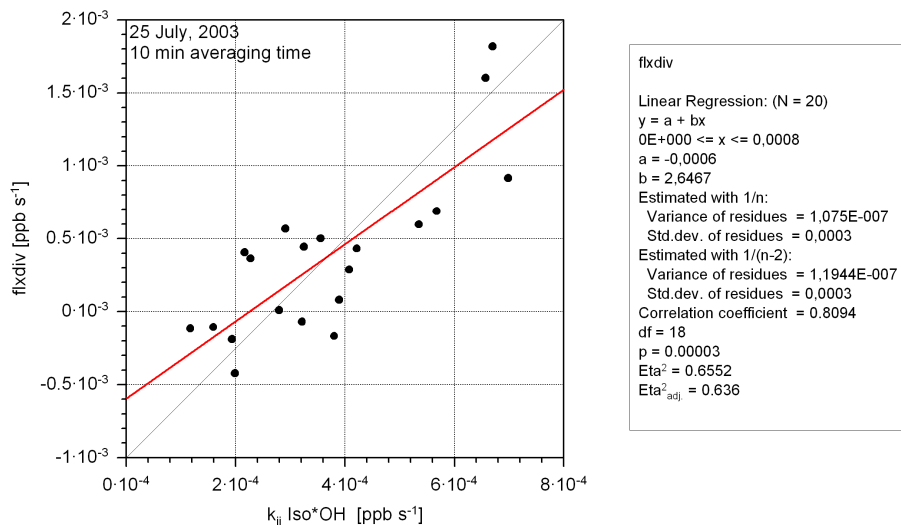
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**Fig. 1.** The four terms of the balance equation for the mixing ratio of isoprene (Eq. 1) calculated from lefthandvalues (method (1)) as described in the text).

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**Fig. 2.** The flux divergence from Eq. (1) as a function of the product of mean mixing ratios of both reactants with statistical parameter. (Remark:  $df$  = degrees of freedom,  $p$  = probability of error,  $\text{Eta}^2$  = square of correlation coefficient,  $\text{Eta}^2_{\text{adj}}$  = normalized variance of residues.)

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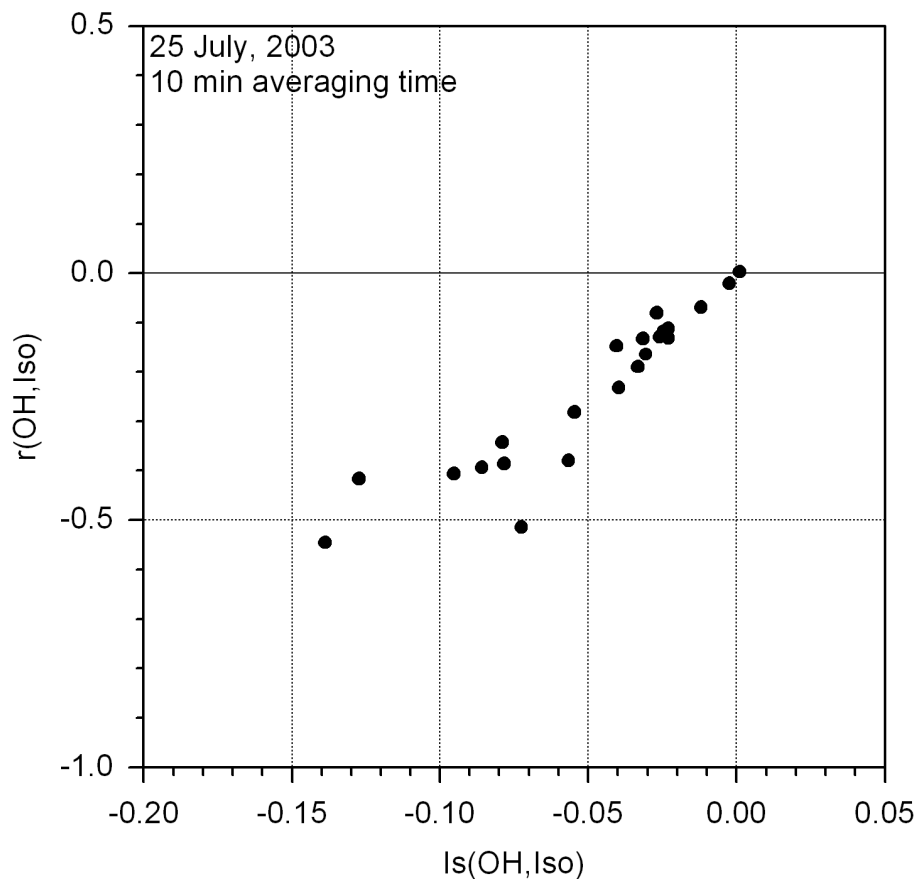
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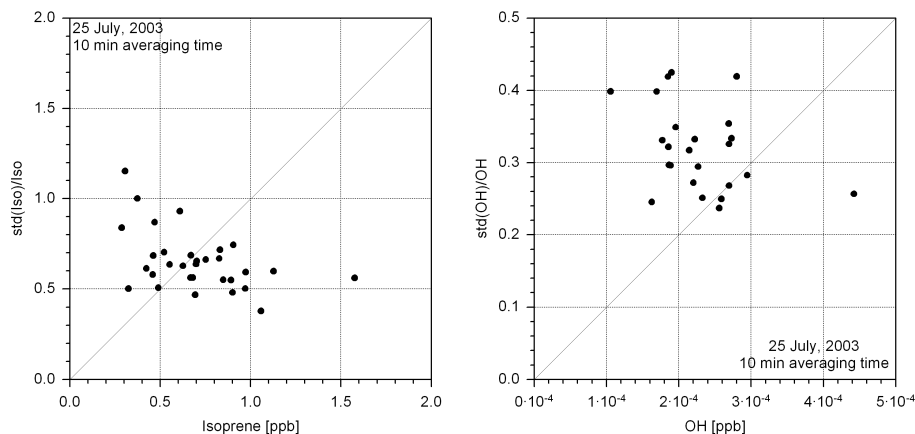


**Fig. 3.** The correlation coefficient between isoprene and OH as function of segregation intensity  $I_s$ .



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**Fig. 4.** The normalised standard deviations of isoprene and OH versus their mixing ratios.

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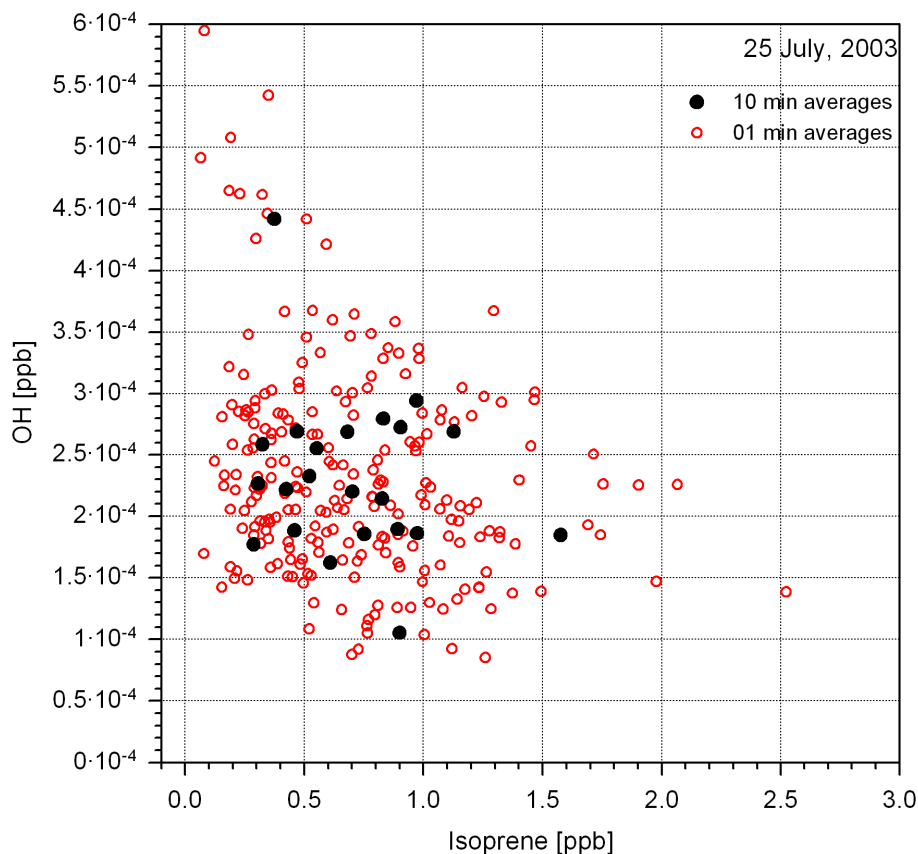
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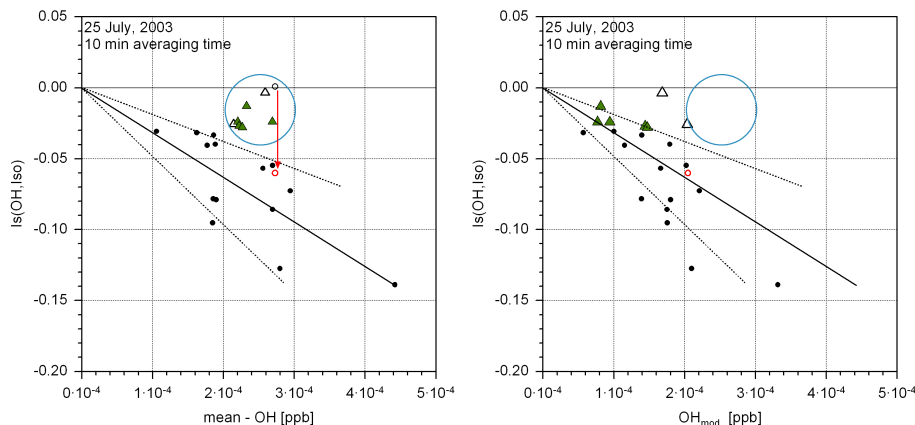




**Fig. 5.** The relation between mixing ratios of isoprene and OH (25 July 2003 09:00–15:00 CET). The detection limit ( $S/N = 2$ ) of the LIF instrument is 0.1 ppt for OH and of the PTR-MS 41 ppt for isoprene at a measuring frequency up to 0.2 Hz (Dlugi et al., 2010). The results for two time average intervals are given.

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**Fig. 6.** The intensity of segregation  $I_S$  as a function of the measured mean OH mixing ratio with a relation proposed according to model calculations of (Patton et al., 2001). Left part: data points outside this relation are within the blue circle. Right part:  $I_S$  as function of the modeled  $OH_{mod}$  according to Appendix A and OH – loss as given in Table 2 for mean mixing ratios of Table 1. The arrow gives the corrected value according to Sect. 4.3.4.

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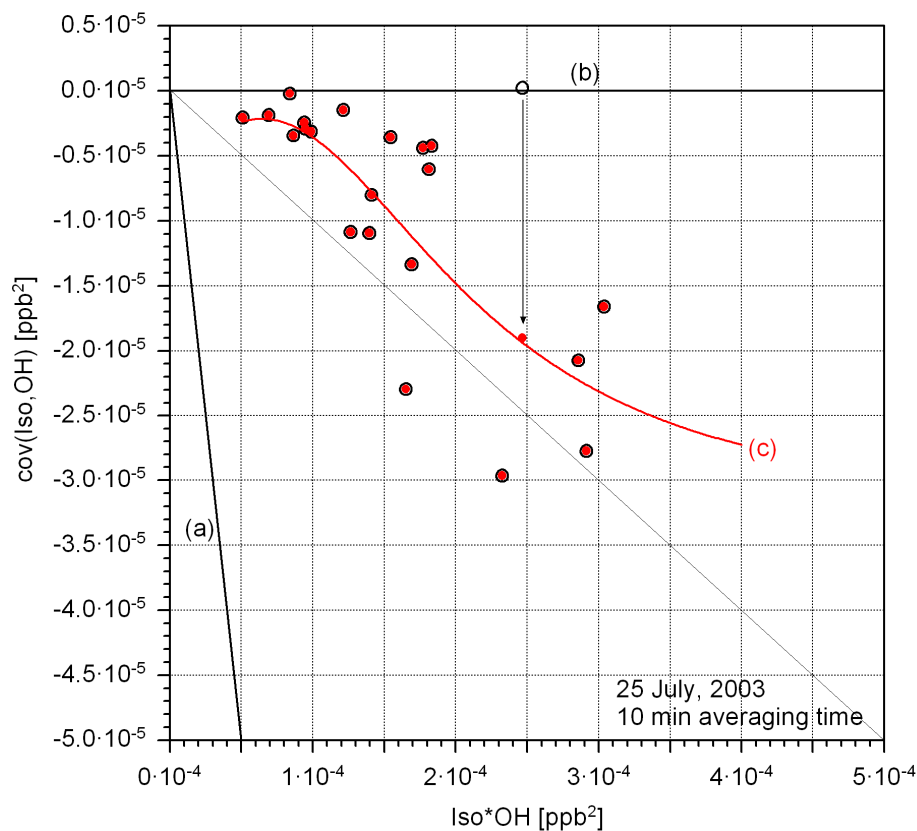
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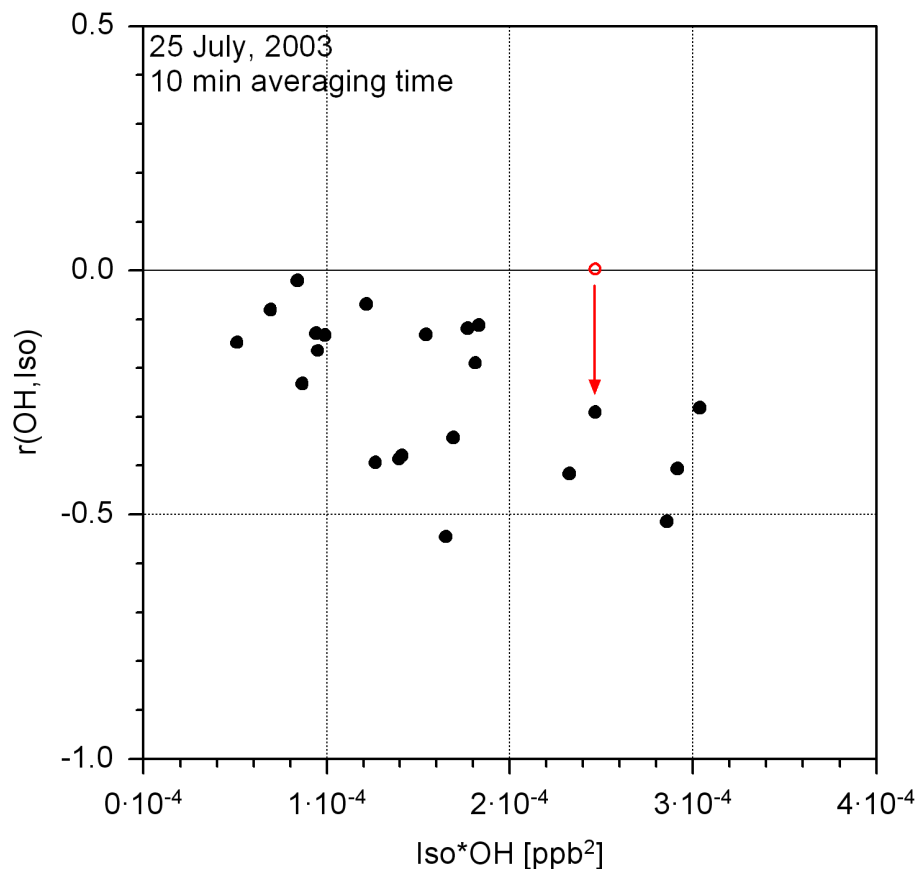
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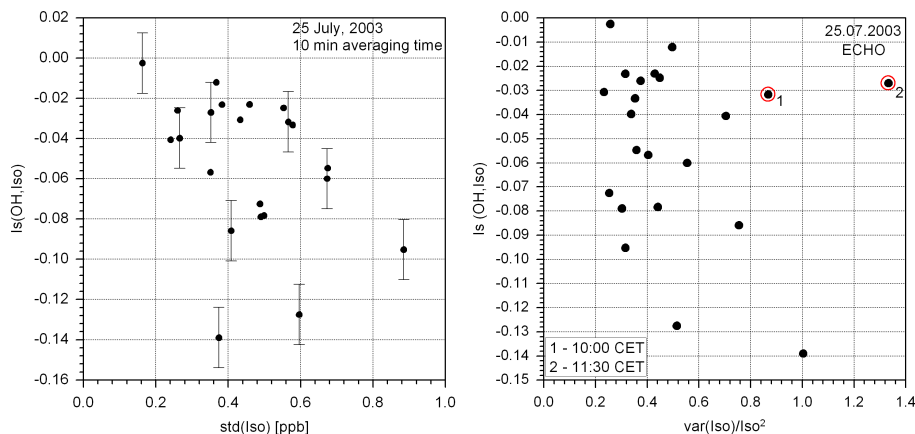
**Fig. 7.** The covariance between isoprene and OH calculated as explained in the text as function of product of means. The corrected value (indicated by the arrow) is explained in Sect. 4.3.4. The three lines (a–c) are explained in the text.



**Fig. 8.** The correlation coefficient between isoprene and OH as function of the product of mean mixing ratios with the corrected point as discussed in Sect. 4.3.4.

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**Fig. 9.** The dependence of the intensity of segregation on isoprene standard deviation (left) and normalized standard deviation (right). The specific conditions for the red marked points are described in Sect. 3.2.4.

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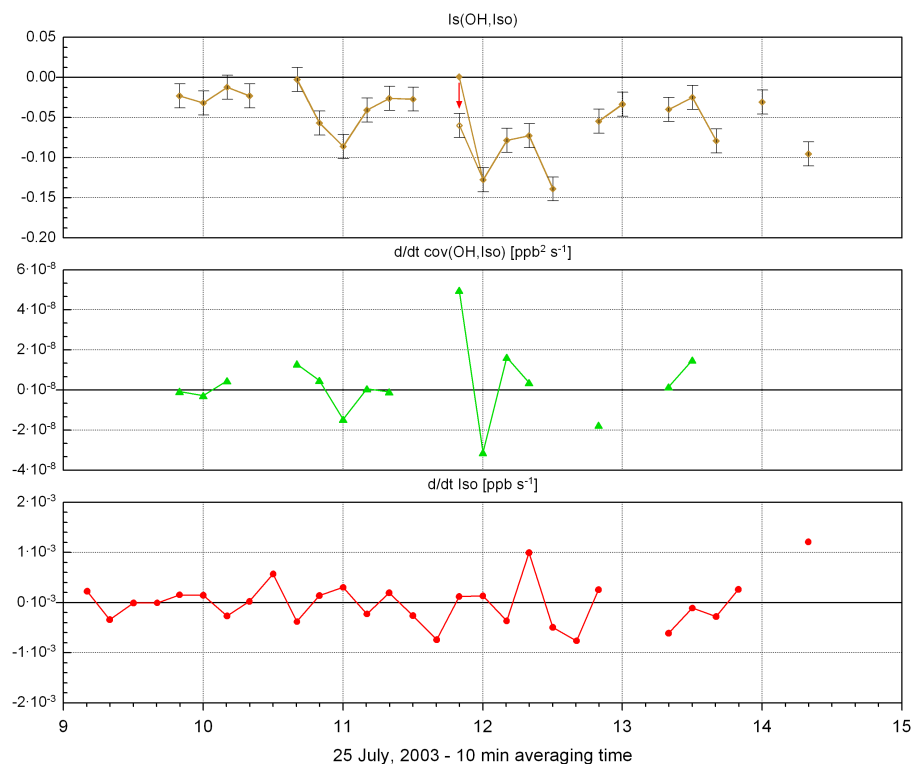
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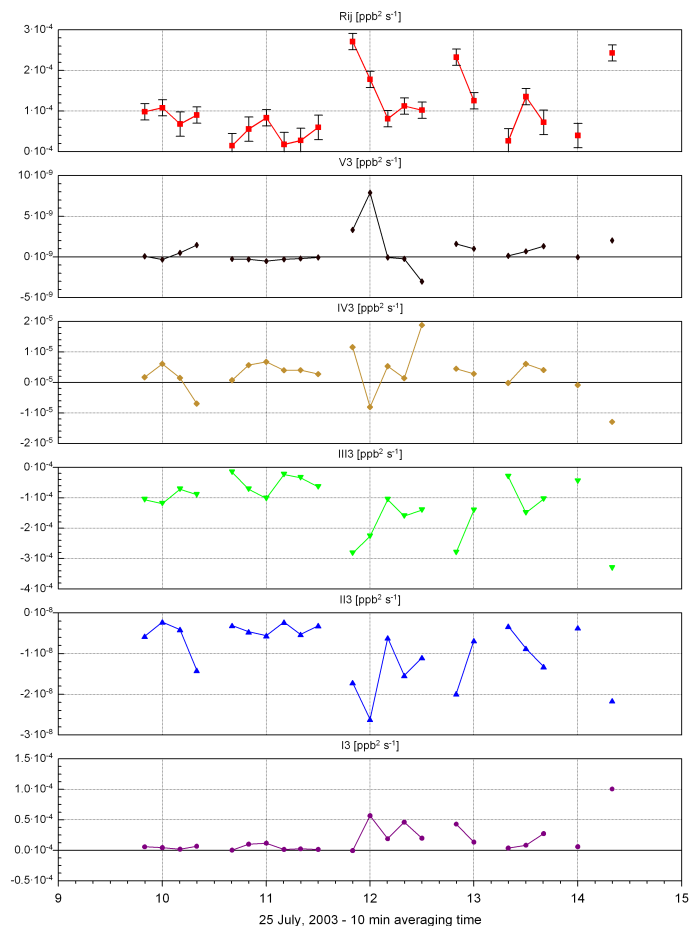
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**Fig. 10.** The storage term for the covariance between isoprene and OH from Eq. (5) compared to the storage terms of the balances of isoprene (Eq. 1) and the intensity of segregation  $I_S$  as given by Dlugi et al. (2010) with the corrected data point (Sect. 4.3.4).

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**Fig. 11.** The chemical reaction terms (I3–V3) and the sum  $R_{ij}$  of Eq. (6) for day 206 (25 July 2003) of ECHO 2003 at the maintower  $z_R = 37$  m.

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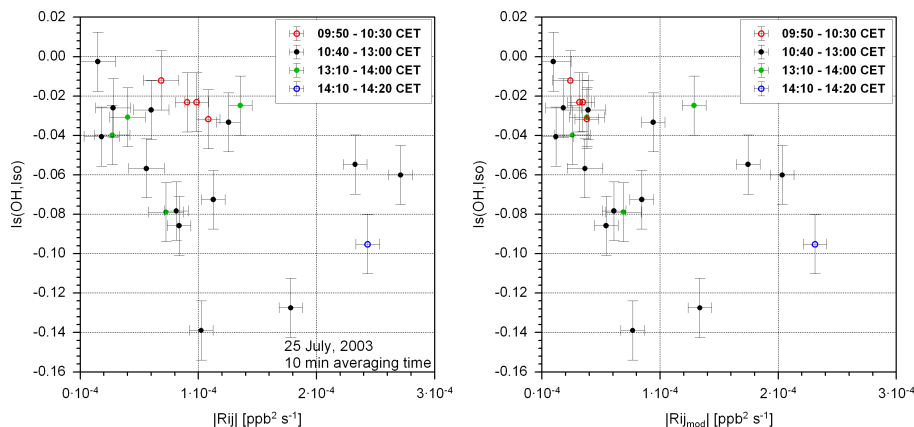
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**Fig. 12.** The intensity of segregation as function of  $R_{ij}$  with a data point corrected for the exceptional conditions (see text). The error bars are explained in the text.

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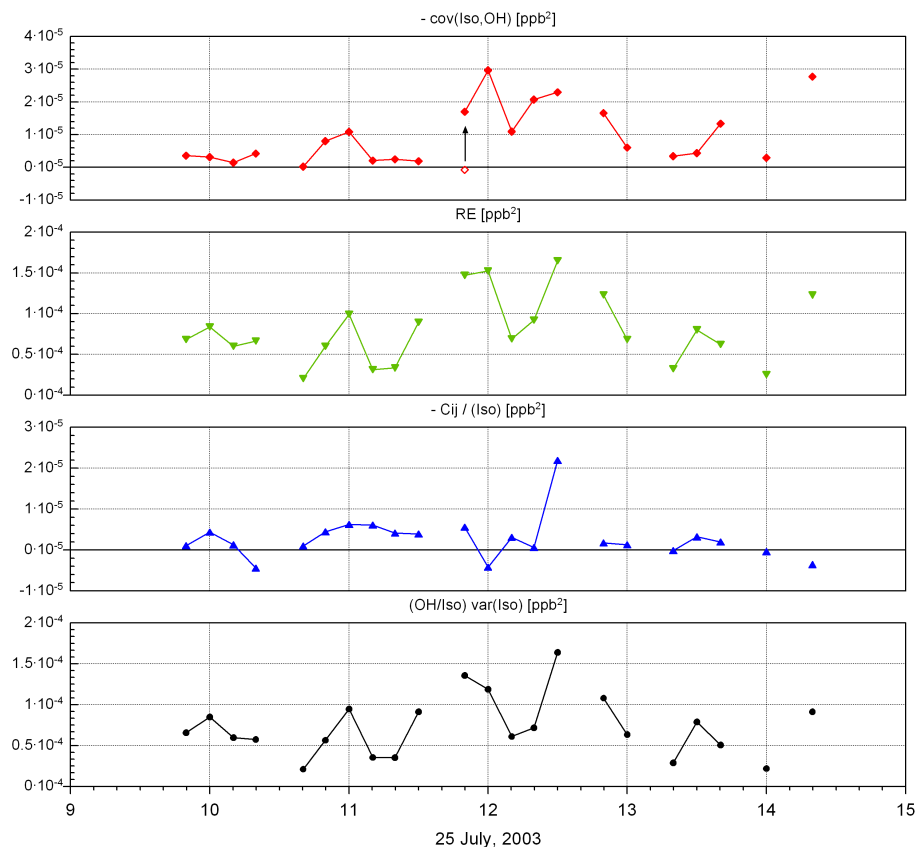
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**Fig. 13.** The four terms of Eq. (11) solved for RE as function of time.

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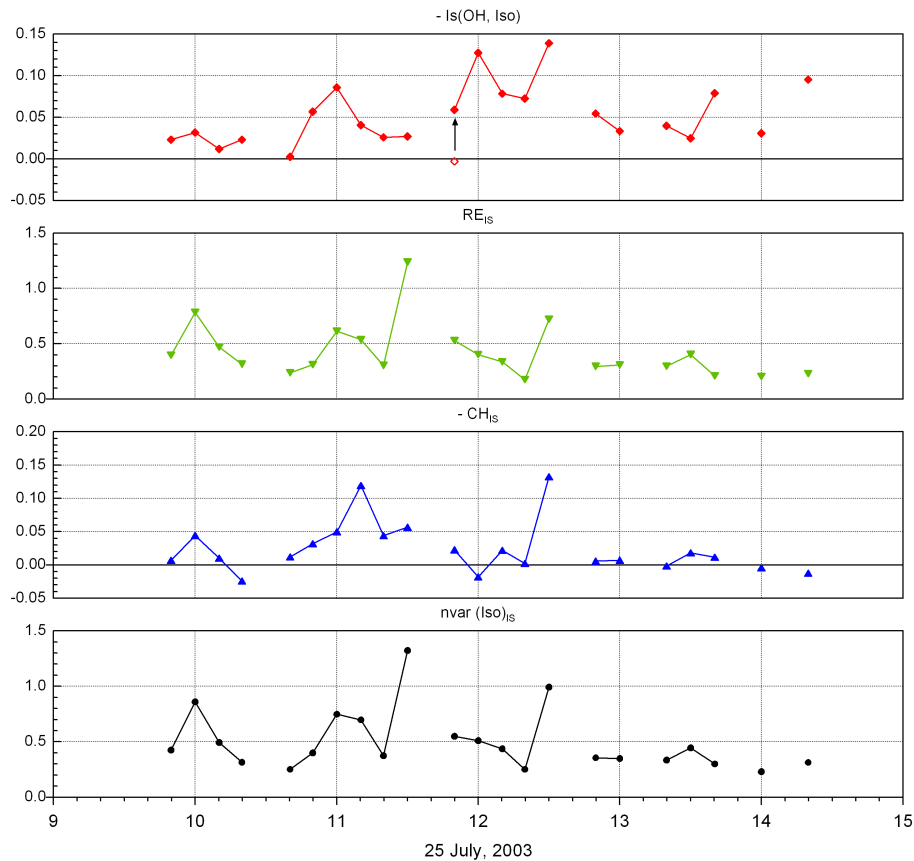
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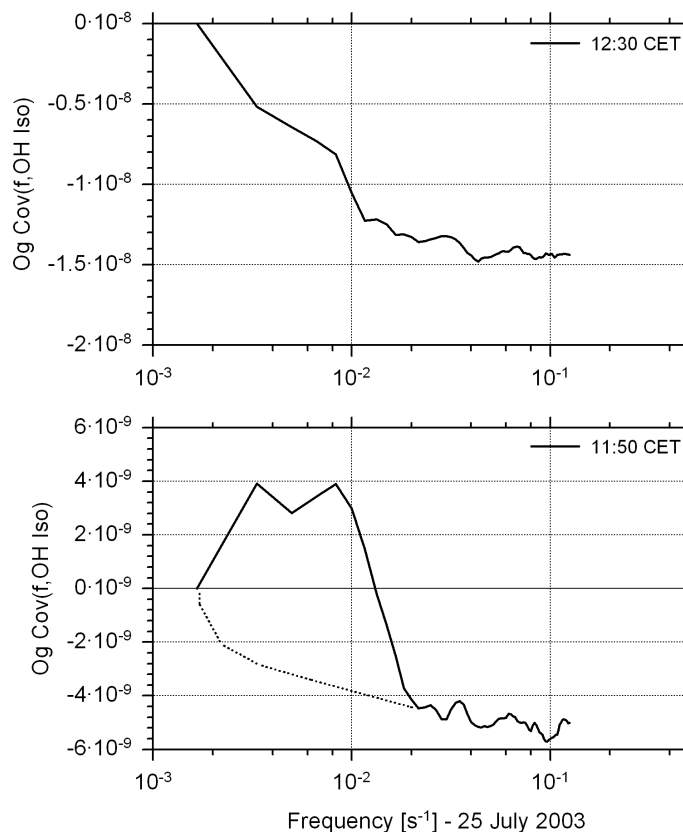
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**Fig. 14.** The four terms of Eq. (12) solved for  $RE_{is}$  as function of time.

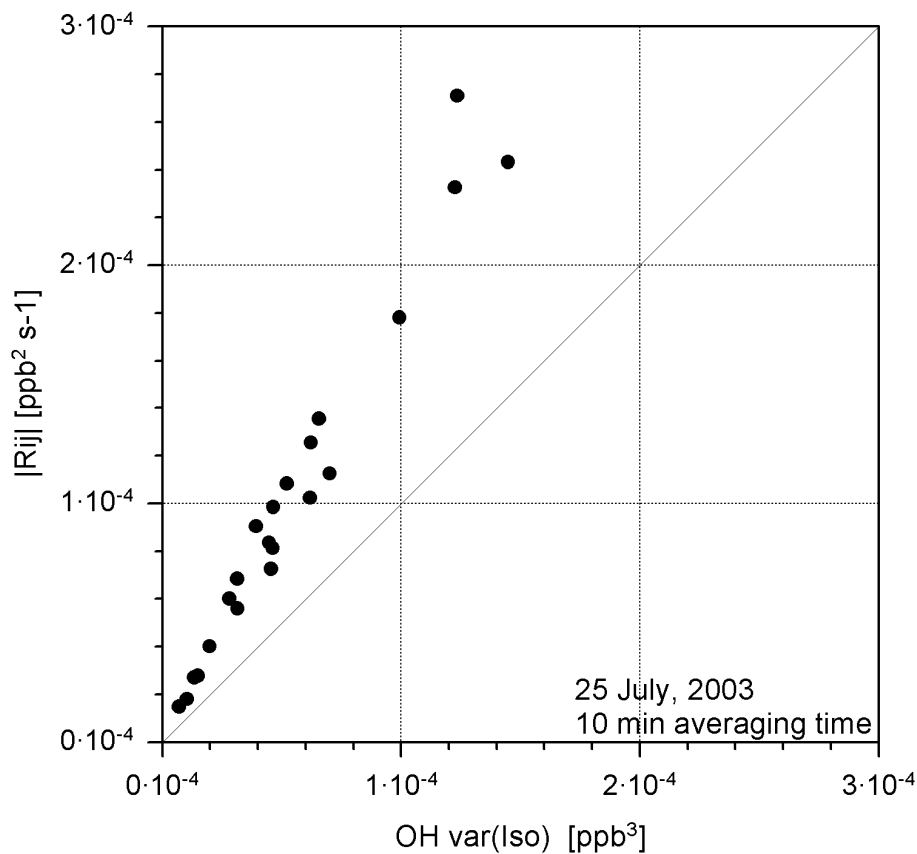
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**Fig. 15.** The spectral presentation of the ogives of the covariance of OH and isoprene for the maximum of  $I_S$  at 12:30 CET and the minimum of  $I_S$  at 11:50 CET when both parts compensate and apparently result in  $I_S \approx 0$  (see Sect. 4.3.4). The broken line for the results at 11:50 CET shows a possible behavior of the ogive if only inhomogeneous mixing occurs.

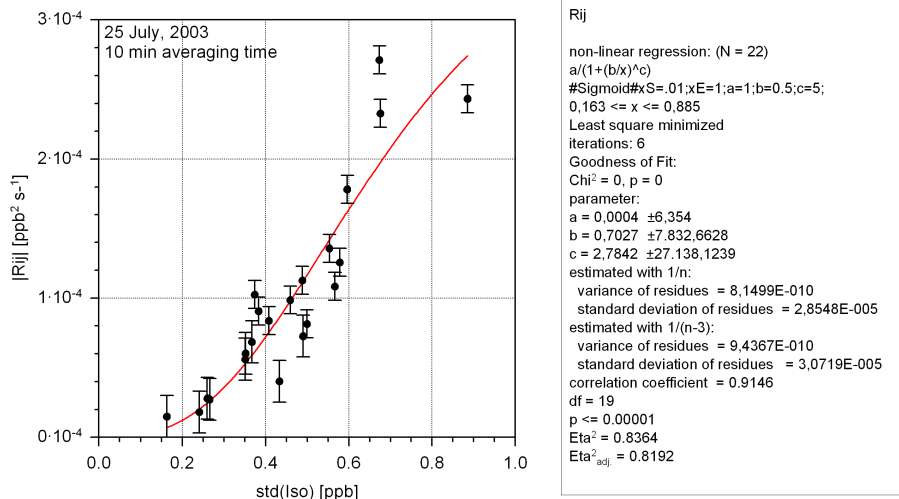
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**Fig. 16.** The magnitude of  $R_{ij}$  as function of the third term of Eq. (6).

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**Fig. 17.** Empirical relation between  $R_{ij}$  and  $\sigma(\text{ISO})$  with parameter for the trend line; see also description for Fig. 2.

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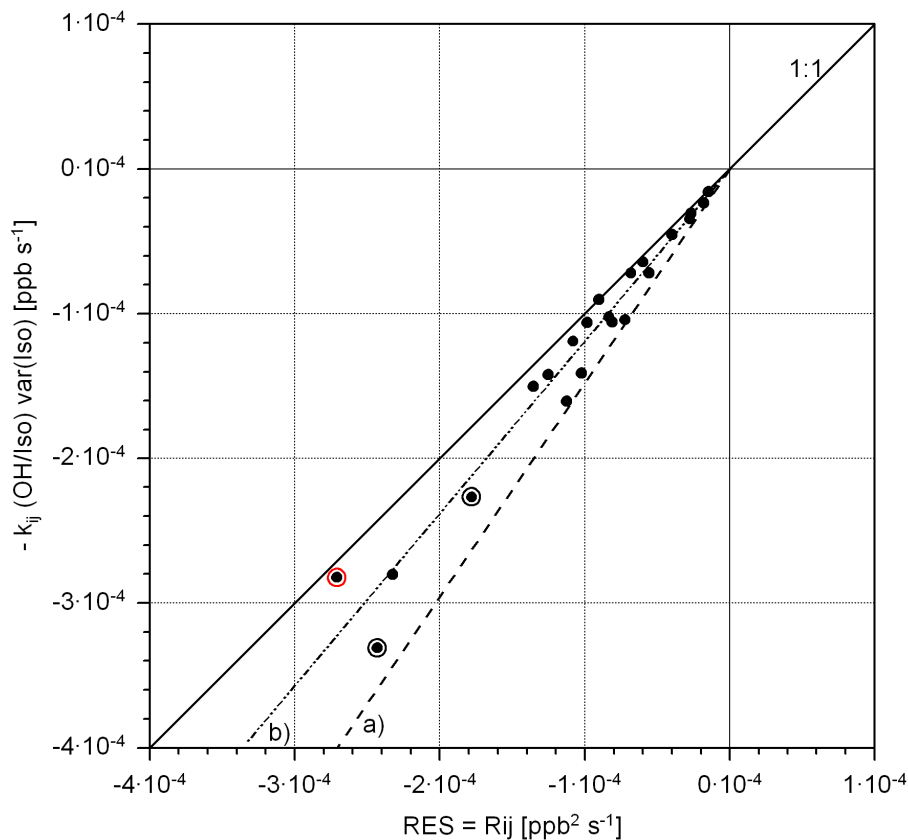
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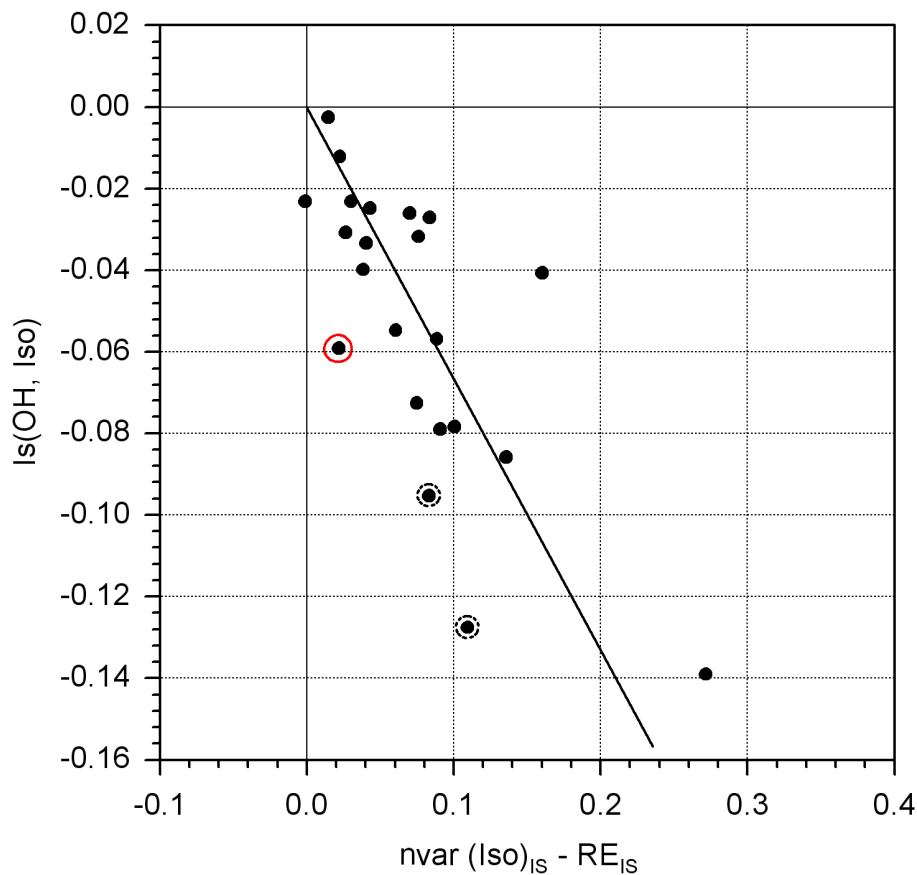
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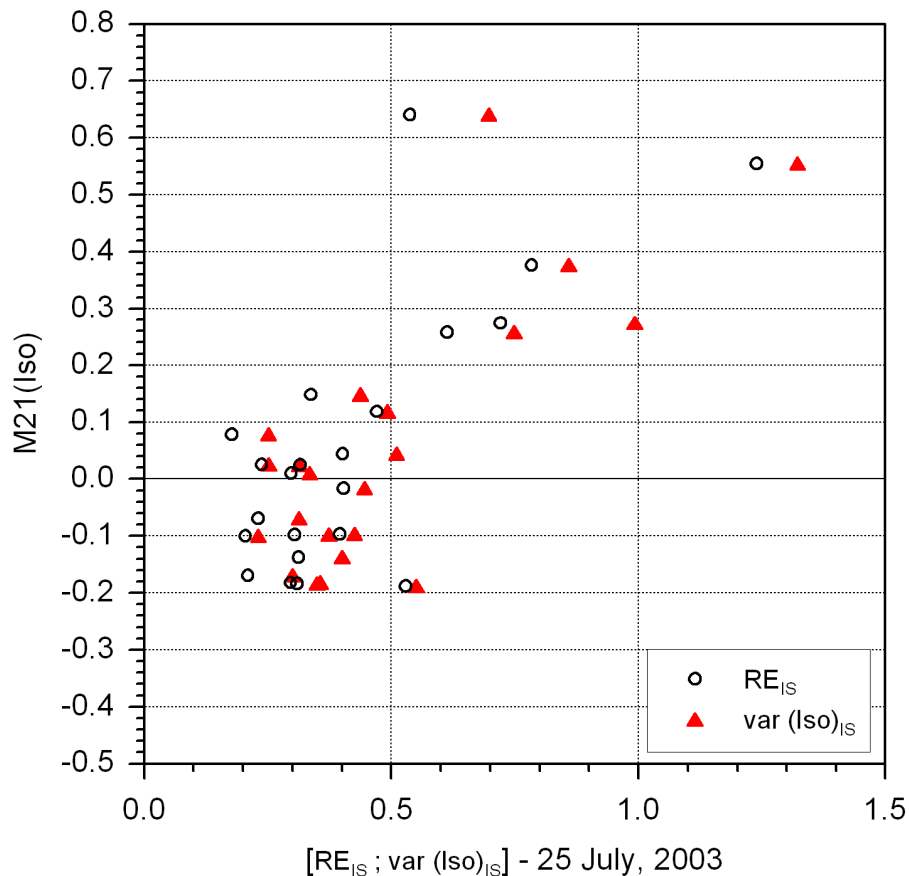


**Fig. 18.** The term  $k_{ij} \cdot \overline{(\text{OH}/\text{ISO})} \cdot \text{var}(\text{ISO})$  as function of term RES for 25 July 2003 (09:00–15:00 CET) The three marked points are discussed in the text.

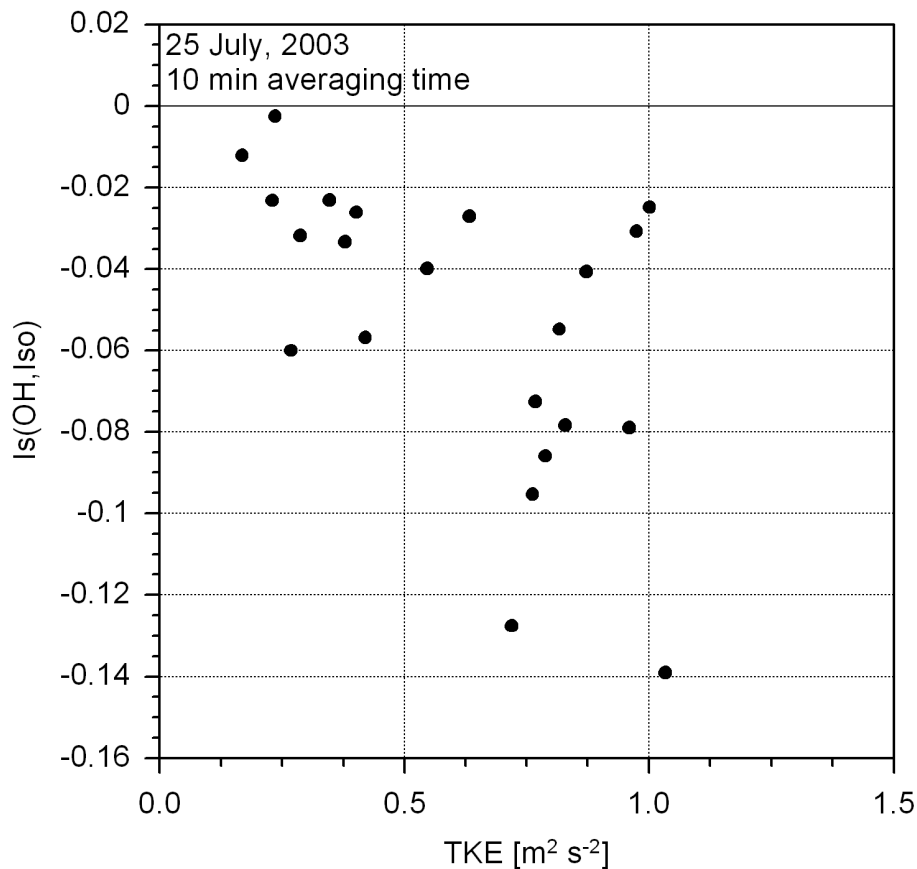


**Fig. 19.** The intensity of segregation as function of the difference  $nvar(Iso)_{IS} - RE_{IS}$  according Eq. (12) as explained in the text.

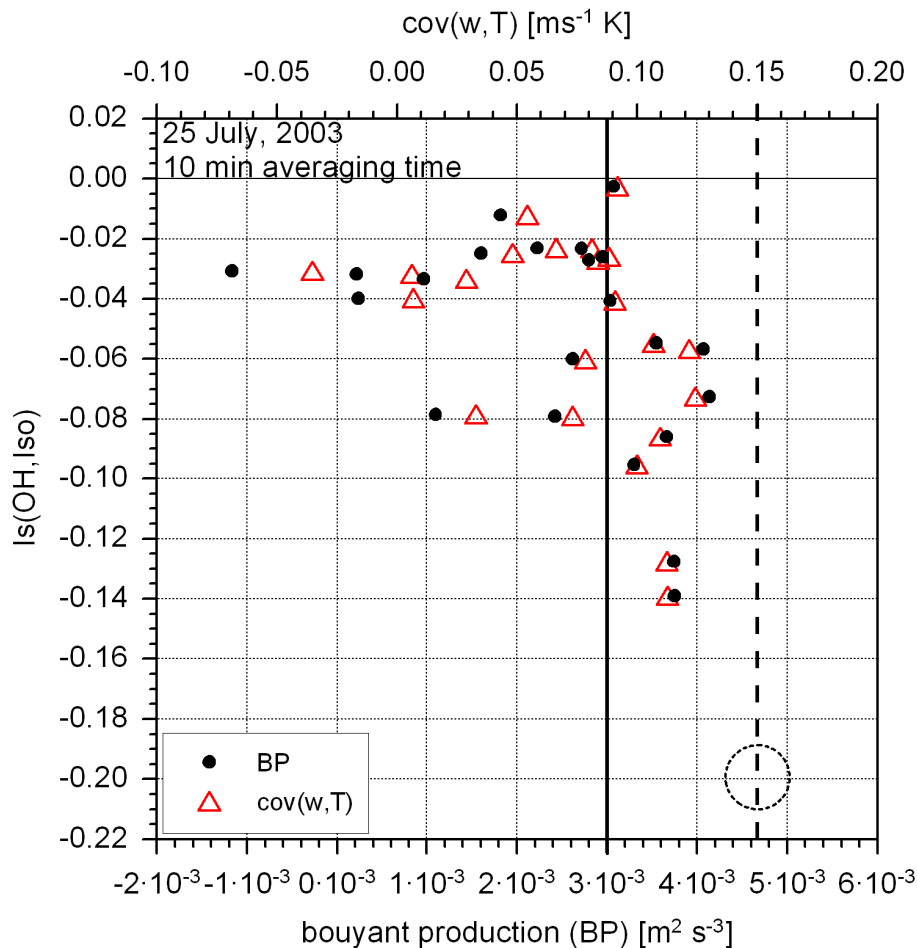




**Fig. 20.** The correlation coefficient  $M21$  (see Eq. 13) as function of the two dominant terms  $var(Iso)_{IS}$  and  $RE_{IS}$  in the diagnostic equation to determine  $I_S$  (Eq. 12).



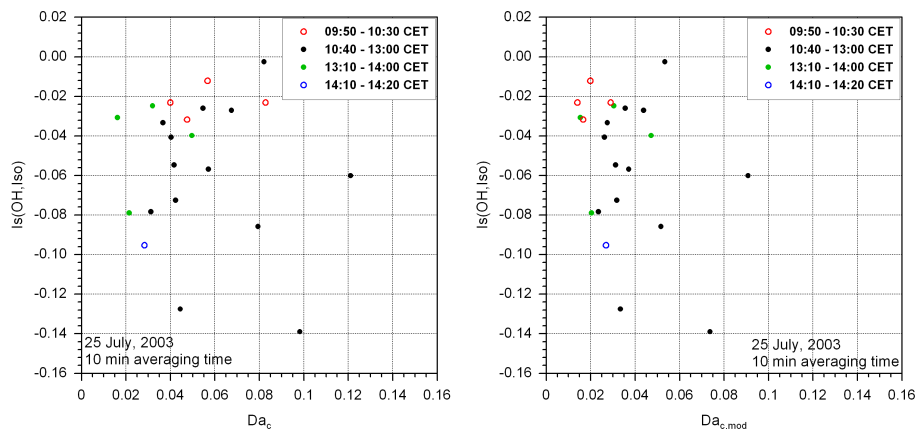
**Fig. 21.** The intensity of segregation as function of TKE.



**Fig. 22.** The intensity of segregation as function of buoyant production (BP) and sensible heat flux  $H$ . The circle indicates the range of results presented by Ouwersloot et al. (2011).

## Balances of mixing ratios and segregation intensity

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**Fig. 23.**  $I_s$  as function of Damköhler numbers  $Da_c$  (left) and  $Da_{c,\text{mod}}$  (right) for the time periods from Tables 1, 2 with OH substituted by modeled  $\text{OH}_{\text{mod}}$  (see Appendix A).

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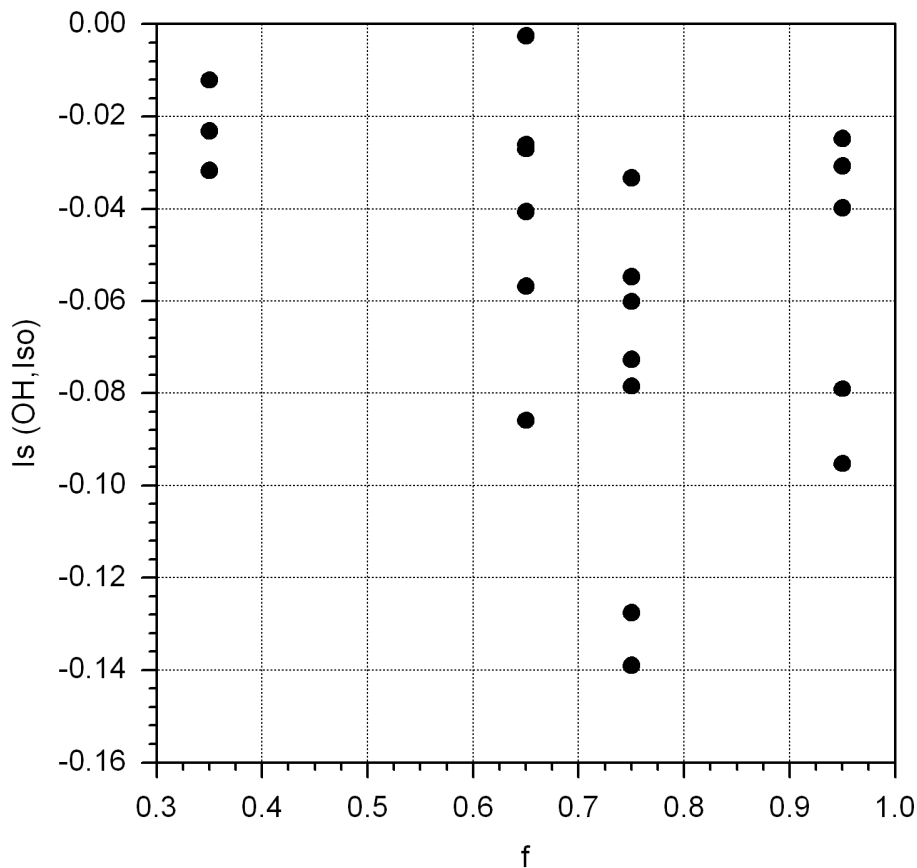
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Interactive Discussion





**Fig. 24.** The intensity of segregation  $I_S$  as function of factor  $f$  from Eq. (A1) with data from Tables 1, 2.