

H.G. Ouwersloot^{1,3*}, J. Vilà-Guerau de Arellano¹, C.C. van Heerwaarden¹,
L.N. Ganzeveld², M.C. Krol¹ and J. Lelieveld³

1) Meteorology and Air Quality, Wageningen University, Wageningen, The Netherlands

2) Earth System Sciences - Climate Change, Wageningen University, Wageningen, The Netherlands

3) Atmospheric Chemistry, Max Planck Institute for chemistry, Mainz, Germany

1. INTRODUCTION

Tropical rain forest chemistry is driven by the exchange of biogenic compounds, dynamic processes like turbulent mixing, and the diurnal variability of the atmospheric boundary layer (ABL). The influence of ABL dynamics on chemistry is normally not accounted when experimental observations are analysed (Ganzeveld et al., 2008; Vilà-Guerau de Arellano et al., 2009), even though there are numerous effects. Examples of these influences are listed in Table 1.

One of these processes, the segregation of species due to inefficient turbulent mixing, was previously studied for idealized cases (Schumann, 1989; Vilà-Guerau de Arellano et al., 1993). In short, the inability of turbulence to uniformly mix the emitted and entrained species creates regions where the species are non-uniformly distributed in a correlated or anti-correlated way, therefore modifying the mean chemical production rate in the boundary layer. These seminal studies focused on the boundary layer dynamics and did not consider complex chemistry. Krol et al. (2000) conducted a study for more complex chemistry by means of LES and investigated the effect of heterogeneous surface emissions of biogenic compounds on the intensity of segregation. They found that introducing heterogeneous surface emissions can largely alter the intensity of segregation. A numerical study based on dynamics and chemistry for Amazonian conditions was performed by Verver et al. (2000) using a second-order closure model coupled to a mixed layer model. It is shown that the segregation effect on the chemical production rates is largest near the surface and the top of the boundary layer. To complete these studies and seek for a representation of the intensity of segregation for large-scale models, Vinuesa and Vilà-Guerau de Arellano (2003) derived a parametrisation for the intensity of segregation based on the budget equations for the co-variances and fluxes. Their results show the importance of the Damköhler number and concentration ratios for the intensity of segregation.

The acquired knowledge of these studies was not applied to chemistry models and measurements for some time, but recently the intensity of segregation has been recognized as a possible relevant process

to take into account in the observational analyses and models (Butler et al., 2008; Pugh et al., 2010a,b). Intensity of segregation is considered as a potential explanation of large discrepancies between observations and model results of reactive trace gas concentrations over the tropical forest, in particular for isoprene and the hydroxyl radical. However, in order to make observations comply with model results, chemists currently assume ad hoc values of the intensity of segregation that correspond to a substantial decrease in the isoprene-OH reaction rate without considering the physical and chemical processes that govern this effect (e.g., Butler et al., 2008).

This paper aims at answering the questions:

- Is the segregation of species important?
How does this depend on dynamical and chemical conditions?
- Is the species segregation influenced by heterogeneous surface forcings?

To investigate these questions, we need to calculate explicitly the intensity of segregation. It will be quantified for real Amazonian conditions, using a Large Eddy Simulation model. The Dutch Atmospheric Large Eddy Simulation model (Heus et al., 2010) is used. This model takes into account the effects of boundary layer dynamics (Vilà-Guerau de Arellano et al., 2005) and is expanded with a chemistry module. Compared to box models it directly simulates turbulent processes with a resolution of 100 m x 100 m x 20 m. Since turbulence quantities are explicitly resolved, the intensities of segregation of species can be calculated directly. The system of chemical reactions is representative for the area and both chemical and dynamical input data are inspired by measurements in the Amazonian rain forest. The influence of the turbulent Damköhler number, concentration ratios and heterogeneous surface emissions for these Amazonian conditions are systematically studied. Previous to these simulations, we will introduce the derivation of the intensity of segregation.

2. FORMULATION OF THE SEGREGATION

For the sake of simplicity we introduce the concept of the intensity of segregation for a chemical in the atmosphere that is produced by the second-order chemical reaction



*Corresponding author address: H.G. Ouwersloot, Wageningen University, Meteorology and Air Quality, P.O. Box 47, 6700 AA Wageningen, Netherlands (Huug.Ouwersloot@wur.nl)

Table 1: ABL dynamic processes influencing the atmospheric chemistry

Dynamic process	Effect on chemistry
Boundary layer growth	Lowering concentrations by diluting
Turbulence	Entraining air from the free troposphere
Clouds	Influencing segregation by mixing air which changes the reactivity Changing the photolysis rate by scattering and absorbing radiation
Temperature	Creating segregation by enhancement of coherent structures, thus changing the reactivity
Moisture	Changing the reactivity
Vegetation-atmosphere interaction	Changing reactivities by being a catalyst or being present in some reactions of the O ₃ -NO _x -VOC-HO _x system
Surface heterogeneity	Emission and deposition of chemical compounds (isoprene, ozone) depending on the atmospheric temperature, radiation and moisture Changing the reactivity by enhancement of segregation due to induced mesoscale horizontal flows

For a 3-dimensional field of data, as obtained from Large Eddy Simulations, it satisfies the conservation equation

$$\frac{\partial c_C}{\partial t} + \frac{\partial u_i c_C}{\partial x_i} = R \quad (2)$$

with

$$R = k \cdot c_A \cdot c_B. \quad (3)$$

A , B and C are indicators for chemical compounds, u_i and x_i are respectively the wind velocity and the coordinate in the i -direction, k is the reaction constant, R is the chemical production rate and c_A , c_B and c_C are the concentrations of respectively the chemicals A , B and C . In this research, the focus is placed on the chemical production part.

Equations (1), (2) and (3) describe processes for a 3D field. However, numerical calculations are often performed using spatially averaged values. Every arbitrary variable, ϕ , can be expressed as

$$\phi = [\phi] + \phi', \quad (4)$$

in which the rectangular brackets correspond to a spatial average and the prime corresponds to a deviation from the spatial average. The spatial average is calculated over a horizontal plane or over a volume. In order to compare box models with measurements, the averages for the 3D field should be calculated over the complete mixing volume. If the reaction constant is considered to be equal throughout the boundary layer, the spatial average of the production rate is equal to

$$[R] = k \cdot [c_A \cdot c_B]. \quad (5)$$

By applying a Reynolds decomposition (equation (4)) with its properties, equation (5) becomes

$$[R] = k \cdot ([c_A] \cdot [c_B] + [c'_A \cdot c'_B]). \quad (6)$$

The physical interpretation of the intensity of segregation is the relative deviation of the total chemical production rate from the production rate due to the mean concentrations, R_{mean} .

$$R_{mean} = k \cdot [c_A] \cdot [c_B] \quad (7)$$

This is expressed as

$$I_S = \frac{[R] - R_{mean}}{R_{mean}}. \quad (8)$$

I_S is the intensity of segregation. Substituting equations (6) and (7) in equation (8) yields

$$I_S = \frac{[c'_A \cdot c'_B]}{[c_A] \cdot [c_B]} \quad (9)$$

and finally the average chemical production rate reads:

$$[R] = k \cdot (1 + I_S) \cdot [c_A] \cdot [c_B]. \quad (10)$$

To better understand the physical meaning of the intensity of segregation, we discuss further its dependence on the physical and chemical processes. For instance, for a perfectly mixed situation I_S is equal to 0, but its value can range from -1 to infinity. More insight on the sign of the intensity of segregation can be obtained by analysing it as a function of the correlation and the concentration variances. The intensity of segregation for 2 species reacting together is related with the correlation factor, r , where

$$r = \frac{[c'_A \cdot c'_B]}{\sigma_A \cdot \sigma_B} \quad (11)$$

The standard deviations of the concentrations of compounds A and B are expressed by σ_A and σ_B respectively. The variance of c_A is defined as $\sigma_A^2 = [c'_A \cdot c'_A]$. Equations (9) and (11) show that

$$I_S = r \cdot \frac{\sigma_A \cdot \sigma_B}{[c_A] \cdot [c_B]} \quad (12)$$

Since concentrations and standard deviations are always positive if non-zero, the sign of I_S is equal to the sign of r . This correlation factor is controlled by transport and chemistry. First we will briefly address the influence of transport. Emission of two reacting compounds at the surface could lead to thermals in which the compounds are transported together upward. This would lead to a positive correlation, $r > 0$, since both compounds are transported in the same direction. If one compound is emitted from the surface and the other compound is entrained from the free troposphere, one would expect an anti-correlation, $r < 0$. Chemistry has impact on the correlation factor too. Since a high c_A would result in a large chemical destruction of c_B due to the combination of A and B to C , two compounds reacting together are expected to be anti-correlated, $r < 0$. For the chemical reactions under study the total intensity of segregation, and therefore also the total correlation factor, is negative.

3. RESULTS

Our numerical experiments are constrained by typical dynamic and chemistry conditions in the Amazonian rain forest. These conditions are obtained from measurements during the TROFFEE campaign (Karl et al., 2007; Vilà-Guerau de Arellano et al., 2010). A noon situation without diurnal variability is considered. The model is run for 4 hours of which the first hour is the spin up phase.

A Governing dimensionless numbers

To introduce the subject, we first identify the main processes that control the species segregation. In this study this dependence of the intensity of segregation is examined for the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ in a similar way as the evaluation described by Schumann (1989). In a second-order reaction (e.g. isoprene with hydroxyl radicals, nitric oxide with ozone) the intensity of segregation is governed by the turbulent Damköhler number and the ratio between the concentrations (Vinueza and Vilà-Guerau de Arellano, 2003). The turbulent Damköhler number is defined as the ratio of the turbulence timescale over the chemistry timescale, so for NO

$$Da_{\text{NO}} = \frac{\tau_{\text{turbulence}}}{\tau_{\text{chemistry}}} \quad (13)$$

$$\tau_{\text{turbulence}} = \frac{z_i}{w_*} \quad (14)$$

$$\tau_{\text{chemistry}} = \frac{1}{k \cdot c_{\text{O}_3}} \quad (15)$$

In these equations, z_i is the boundary layer height, w_* is the convective velocity, k is the reaction constant and c_{O_3} is the concentration of ozone. The dependence of the intensity of segregation on concentration ratios and the Damköhler number is investigated by altering the ozone concentrations and the reaction

constants for different DALES numerical simulations. Our results are shown in Figure 1. For a higher Damköhler number, the intensity of segregation becomes more negative. The largest dependence, however, is on the concentration ratio. A higher ozone over NO ratio causes a much less negative intensity of segregation. This finding already indicates the influence of segregation is less than 10 % in a typical situation for the Amazonian rain forest characterized by uniform emission conditions ($c_{\text{O}_3} \gg c_{\text{NO}}$). Figure 1 shows that the intensity of segregation is not only dependent on the reaction itself, but also on the dynamics. The figure complies with previous work of Schumann (1989), validating our model results, but gives a more complete overview of the dependences.

B Quantifying the intensity of segregation

The intensities of segregation are investigated for a more comprehensive chemical scheme too. This scheme contains the 19 essential reactions of the O_3 - NO_x -VOC- HO_x system during daytime in the Amazonian rain forest (Vilà-Guerau de Arellano et al., 2010). The two main objectives are, first, to quantify the intensity of segregation of species and, second, to investigate the influence of heterogeneous surface forcings on the intensity of segregation.

The focus lies upon the chemical reaction $\text{ISO} + \text{OH} \rightarrow \text{RO}_2$. Even though the research on the effects of surface heterogeneity is work in progress, preliminary results are shown and discussed. For the heterogeneous numerical experiment a savannah patch and a forested patch are considered, similar to the configuration of van Heerwaarden and Vilà-Guerau de Arellano (2008). Both patches have a length scale in the order of a few kilometres. Over the relatively cold and wet forested patch the sensible heat flux is smaller than over the relatively warm and dry savannah patch, but the latent heat flux is higher. The sum of the latent heat flux and the sensible heat flux is equal for both patches. The forested patch is characterized by high isoprene emissions, whereas the savannah patch is characterized by low isoprene emissions. The heterogeneous surface heat fluxes induce a mesoscale circulation characterized by a warm moist plume rising over the warm dry savannah patch. This mesoscale circulation affects the distribution of the chemical compounds.

For both the homogeneous case as well as the heterogeneous case, the intensities of segregations are calculated and visualized for all 19 chemical reactions. In Figure 2 these plots are shown for the reaction in which isoprene and the hydroxyl radical combine. The intensity of segregation decreases to about twice its value by implementing the heterogeneous surface properties. However, the value remains less in magnitude than -0.15, indicating that the chemical production rates are altered by less than 15 % due to the segregation of species. For the other 18 reactions this value is even closer to 0. Our results show

Volume segregation of reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$

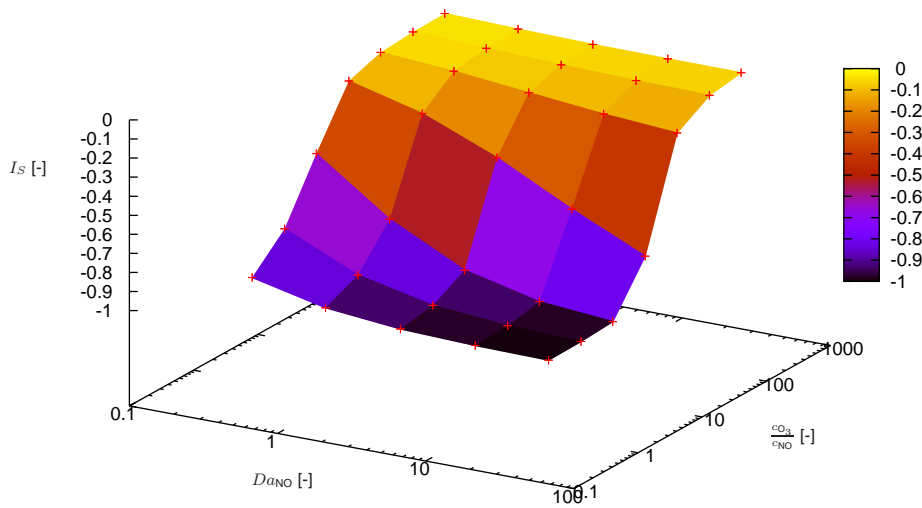


FIG. 1: Intensity of segregation for the reaction of NO and O₃ as function of the turbulent Damköhler number ($D_{A\text{NO}}$) and concentration ratio ($\frac{c_{\text{O}_3}}{c_{\text{NO}}}$). For typical Amazonian conditions the Damköhler number would be near the middle of the shown regime and the concentration ratio of O₃ over NO would be higher than shown here. These conditions correspond to a low intensity of segregation.

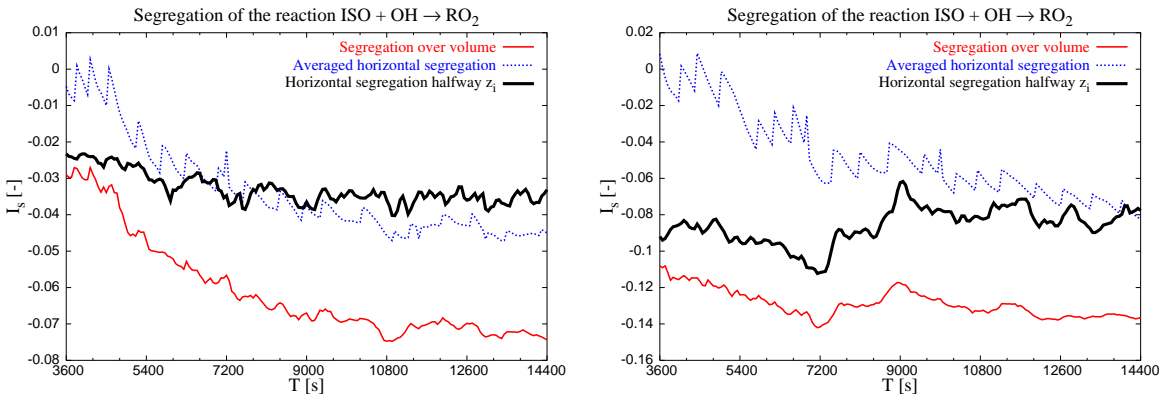


FIG. 2: Intensities of segregation as function of time for the chemical reaction of isoprene with the hydroxyl radical. The left graph represents the intensity of segregation for the homogeneous case and the right graph represents the heterogeneous case. The red line shows the total segregation. The black and blue lines are representations of the horizontal segregation, halfway the boundary layer and averaged over the boundary layer, respectively. The differences between the red and the blue lines are caused by vertical segregation. These figures show that the intensity of segregation for the heterogeneous case is about twice the intensity of segregation for the homogeneous case.

that the effect of segregation for the chemical production rates in Amazonian conditions is present, but relatively low.

4. OUTLOOK

Further research will be conducted on the interaction between boundary layer dynamics and atmospheric chemistry. One area of interest is more detailed information about the effects of the heterogeneous surface conditions. Examples of this are the effects of the length scale of heterogeneity and the influence of heterogeneity amplitudes, both for sensible heat flux and isoprene emissions. In future research the impact of the difference in roughness lengths between forest and savannah patches will be taken into account as well. Another future research topic will be the influence of diurnal variability.

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REFERENCES

- T.M. Butler, D. Taraborrelli, C. Brühl, H. Fischer, H. Harder, M. Martinez, J. Williams, M.G. Lawrence, and J. Lelieveld. Improved simulation of isoprene oxidation chemistry with the echam5/messy chemistry-climate model: lessons from the gabriel airborne field campaign. *Atmos. Chem. Phys. Discuss.*, 8:6273–6312, 2008.
- L. Ganzeveld, G. Eerdekens, G. Feig, H. Fischer, H. Harder, R. Königstedt, D. Kubistin, M. Martinez, F.X. Meixner, H.A. Scheeren, V. Sinha, D. Taraborrelli, J. Williams, J. Vilà-Guerau de Arellano, and J. Lelieveld. Surface and boundary layer exchanges of volatile organic compounds, nitrogen oxides and ozone during the gabriel campaign. *Atmos. Chem. Phys.*, 8:6223–6243, 2008.
- T. Heus, C.C. van Heerwaarden, H.J.J. Jonker, A.P. Siebesma, S. Axelsen, K. van den Dries, O. Geofroy, A. Moene, D. Pino, S.R. de Roode, and J. Vilà-Guerau de Arellano. Formulation and numerical studies by the dutch atmospheric large-eddy simulation (dales). *Geosci. Model Dev.*, 3:99–180, 2010.
- T. Karl, A. Guenther, R.J. Yokelson, J. Greenberg, M. Potosnak, D.R. Blake, and P. Artaxo. The tropical forest and fire emissions experiment: Emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over amazonia. *J. Geophys. Res.*, 112:D18302, 2007.
- M.C. Krol, M.J. Molemaker, and J. Vilà-Guerau de Arellano. Effects of turbulence and heterogeneous emissions on photochemically active species in the convective boundary layer. *J. Geophys. Res.*, 105: 6871–6884, 2000.
- T.A.M. Pugh, A.R. MacKenzie, C.N. Hewitt, B. Langford, P.M. Edwards, K.L. Furneaux, D.E. Heard, J.R. Hopkins, C.E. Jones, A. Karunaharan, J. Lee, G. Mills, P. Misztal, S. Moller, P.S. Monks, and L.K. Whalley. Simulating atmospheric composition over a South-East Asian tropical rainforest: performance of a chemistry box model. *Atmos. Chem. Phys.*, 10: 279–298, 2010a.
- T.A.M. Pugh, A.R. MacKenzie, B. Langford, E. Nemitz, P.K. Misztal, and C.N. Hewitt. The influence of small-scale variations in isoprene concentrations on atmospheric chemistry over a tropical rainforest. *Atmos. Chem. Phys. Discuss.*, 10:18197–18234, 2010b.
- U. Schumann. Large-eddy simulation of turbulent diffusion with chemical reactions in the convective boundary layer. *Atmos. Environ.*, 23(8):1713–1727, 1989.
- C.C. van Heerwaarden and J. Vilà-Guerau de Arellano. Relative humidity as an indicator for cloud formation over heterogeneous land surfaces. *J. Atmos. Sci.*, 65:3263–3277, 2008.
- G.H.L. Verver, H. van Dop, and A.A.M. Holtslag. Turbulent mixing and the chemical breakdown of isoprene in the atmospheric boundary layer. *J. Geophys. Res.*, 105:3983–4002, 2000.
- J. Vilà-Guerau de Arellano, P.G. Duynkerke, P.J. Jonker, and P.J.H. Builtjes. An observational study on the effects of time and space averaging in photochemical models. *Atmos. Environ.*, 27A:353–362, 1993.
- J. Vilà-Guerau de Arellano, S.-W. Kim, M.C. Barth, and E.G. Patton. Transport and chemical transformations influenced by shallow cumulus over land. *Atmos. Chem. Phys.*, 5:3219–3231, 2005.
- J. Vilà-Guerau de Arellano, K. van den Dries, and D. Pino. On inferring isoprene emission surface flux from atmospheric boundary layer concentration measurements. *Atmos. Chem. Phys.*, 9:3629–3640, 2009.
- J. Vilà-Guerau de Arellano, E.G. Patton, T. Karl, K. van den Dries, M.C. Barth, and J.J. Orlando. Diurnal evolution of isoprene and the hydroxyl radical over tropical forests. *J. Geophys. Res.*, 2010. Under revision.
- J.-F. Vinuesa and J. Vilà-Guerau de Arellano. Fluxes and (co-)variances of reacting scalars in the convective boundary layer. *Tellus B*, 55(4):935–949, 2003.