Effect of mixing on the atmospheric NO–O$_3$ system

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Abstract

A new Lagrangian concept is presented for the calculation of reactive substance transport in the atmosphere, which treats arbitrary complicated chemical reactions. The essential difference to existing methods is the inclusion of the atmospheric turbulence in Lagrangian substance transport calculations. The realization of such simulations and the application to the calculation of a reactive plume are described. Apart from the solution of the chemistry problem, this approach offers also an accurate and efficient method to assess the influence of mixing effects on mean conversion rates of species. Such effects are often neglected in other methods due to conceptual and computational problems of their consideration, which may result in overestimates of mean conversion rates of orders of magnitude. This problem is described and the influence of such effects is demonstrated in respect to the reactive plume considered here.

1   Introduction

Three essential ingredients are required in order to assess the transport of reactive substances that are released into the atmosphere: first, the calculation of their dispersion through the turbulence field, second, the estimation of their mixing on a molecular scale with species that are distributed in the ambient flow, and third, the calculation of chemical transformations between species. The description of the dispersion of

substances requires first of all knowledge about the turbulence field, which can be obtained by standard methods. Chemical reactions between species can be handled by adopting conversion rates that are estimated in laboratory experiments, provided the species are well-premixed. However, this is not the case for substances that are released from sources into the atmosphere, so that the problem arises to assess the efficiency of chemical transformations between species in dependence on their mixing state, which is obviously non-trivial. Therefore, such mixing effects are often simply neglected, which is justified with reference to their unclear effect and the related additional computational costs, in particular, if complex chemical schemes have to be considered. Such an approach may lead to overestimates of mean chemical conversion rates of orders of magnitude, because species that are not premixed cannot react with each other.

The tackling of this question in the Eulerian framework is related to problems. This is mainly caused by the fact that chemical conversion cannot be described independently of mixing effects, as illustrated in section 2. This problem does not appear in Lagrangian methods, this means their application reduces the need to describe complex turbulence-chemistry interactions to the problem to describe the turbulent mixing of substances, see Heinz et al.[1] It is described in the sections 3 and 4, how such Lagrangian equations can be obtained and numerical simulations can be realized. In section 5, we compare calculations of a reactive plume with the results of wind tunnel experiments.

2 Eulerian concentration budget equations

Eulerian methods (see, e.g., Galmarini et al. and Georgopoulos and Seinfeld)[2,3] calculate the turbulent transport of reactive substances in the atmosphere by means of budget equations for Reynolds-averaged concentrations of species, which have the following structure:

$$\frac{\partial \overline{C}_A}{\partial t} + \overline{U}_i \frac{\partial \overline{C}_A}{\partial x_i} = -\frac{\partial \overline{u_i c_A}}{\partial x_i} - k \overline{C}_A \overline{C}_B \left\{ 1 + \frac{\overline{c_A c_B}}{\overline{C}_A \overline{C}_B} \right\}, \tag{1}$$

where $\overline{C}_A$, $\overline{C}_B$, $\overline{U}_i$, $\overline{u_i c_A}$ and $\overline{c_A c_B}$ are the averaged concentrations of substances A and B, the component i of the mean wind field and the variance fluxes and covariances, respectively. A second-order chemical reaction between A and B (which is described by a transport equation corresponding to (1)) is assumed with the reaction rate k, and t and x_i denote time and (3-dimensional) space coordinates.

The problem of Eulerian methods is related to the variance fluxes and covariances that appear as unclosed terms on the right-hand side of (1). Usually, (1) is applied to calculations of transport and reaction by adopting (gradient) closure assumptions for the variance fluxes that reflect the turbulent dispersion of A, whereas concentration covariances are neglected. This approach leads to significant errors in the assessment of chemical transformations in cases where A and B are not premixed on a molecular scale. This reveals the considering of the reaction term in (1), which arises from averaging the instantaneous reaction rate $k\,C_A\,C_B$, i.e.,

$$k\overline{C_A C_B} = k\overline{C}_A\,\overline{C}_B\left\{1 + \frac{\overline{c_A c_B}}{\overline{C}_A \overline{C}_B}\right\} = k\overline{C}_A\,\overline{C}_B\left\{1 + I_S\right\}, \tag{2}$$

where the intensity of segregation I_S is introduced for the concentration covariance term normalized to the mean concentrations. The Reynolds average of $C_A\,C_B$ is zero for A and B that are not premixed on a molecular scale, since there is either A or B at a fixed point so that their correlation vanishes. Hence, the neglect of I_S may lead to overestimates of chemical transformations of orders of magnitude.

The consideration of the variation of I_S in the range $-1 \le I_S \le 0$ is not a trivial question. As shown below, I_S depends not only on the mixing of substances but also on their amount and reaction rates. Calculations of I_S can be performed within the Eulerian framework, but this leads to different problems: First, additional closure assumptions are needed to close the covariance equations. Second, such calculations become very expensive, when more complex chemistry has to be assessed. On the other hand, the Lagrangian approach provides very different features to solve this question as illustrated now.

3   Lagrangian turbulence models

Figure 1 illustrates a (stack) plume that disperses in the atmosphere and reacts with substances that are distributed in the surrounding flow. Turbulence and substance transport are considered within the Lagrangian picture to be the result of turbulent motions of fluid particles, which are fluid volume elements that are much larger than the molecular but much smaller than the considered spatial scale. The particles have properties as velocity, temperature and composition, and the question to be solved is to find suited equations for their motion and the change of their properties.
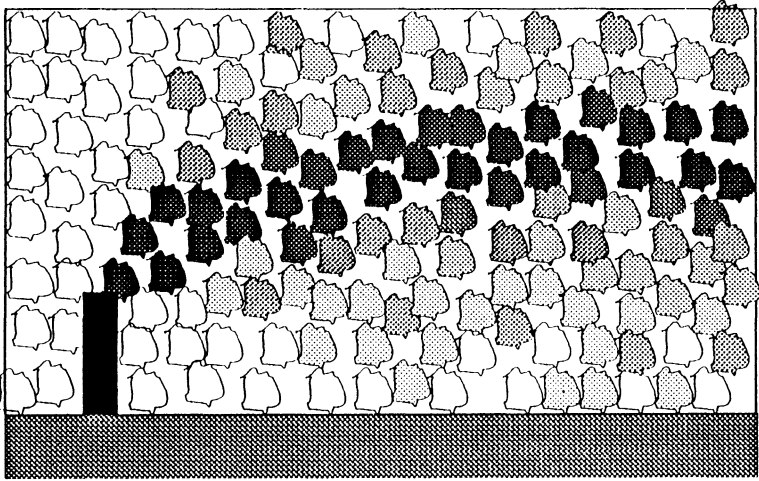
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Figure 1: Reactive (stack) plume considered in the Lagrangian frame-
          work. 🐾 is a fluid particle with temperature and composition.

    One approach to solve this problem successfully in respect to the
description of turbulence is to ensure that the particles move according to
usual budget equations. Such Lagrangian equations for particle positions
x_i^* and velocities U_i^* may be written for high-Reynolds number flows

$$\frac{d}{dt} x_i^*(t) = U_i^*, \tag{3a}$$

$$\frac{d}{dt} U_i^*(t) = a_i + G_{ij}\left(U_j^* - \langle U_j \rangle\right) + b^{ij} \frac{dW_j}{dt}, \tag{3b}$$

where the coefficients a_i, G_{ij} and b_{ij} are specified through the consistency
constraint with Eulerian transport equations. In equation (3b), dW_j / dt is a
Gaussian process with vanishing mean values, $\langle dW_j / dt \rangle = 0$, and
uncorrelated values at different times, $\langle dW_i / dt \,(t) \cdot dW_j / dt' \,(t') \rangle = \delta_{ij}$
$\delta(t - t')$, where δ_{ij} is the Kronecker delta and $\delta(t - t')$ the delta function.
$\langle U_j \rangle$ denotes the ensemble average of the jth-component of the Eulerian
mean velocity, which is evaluated at the actual particle position. For
simplicity, these equations are written without temperature effects. More
details to the derivation of such equations can be found elsewhere, see
Heinz[4, 5].

Before mixing: After mixing:

Figure 2: Illustration of the treatment of mixing processes.

Mixing and chemical reactions of substances proceeds in two steps: First, the particle mass fraction $\Phi_\alpha{}^*$ of a substance α (e.g., nitric monoxide) changes its value in response to the mass fractions of this substance that have the particles of the surrounding fluid, see Figure 2 for an illustration. Second, reaction takes places within the particles, where the instantaneous reaction rates are applied. By simulating the mixing by the simple IEM model, this scheme can be expressed mathematically by

$$\frac{d}{dt}\Phi_\alpha{}^*(t) = -\frac{C_\varphi}{2\tau}\left(\Phi_\alpha{}^* - \langle\Phi_\alpha\rangle\right) - k\Phi_\alpha{}^*\Phi_\beta{}^*, \qquad (3c)$$

where C_φ is a constant that is usually taken equal to 2.0, and τ is the dissipation time scale of turbulence.

The most important difference between Eulerian and Lagrangian methods is related to the treatment of chemical reactions. In Lagrangian methods, the instantaneous reaction rates of arbitrary complicated transformations can be applied directly, as can be seen in (3c). However, this concept requires in contrast to previously applied Lagrangian models the consideration of all the fluid particles of the flow. This means, e.g., in respect to reactive plumes (see Figure 1) that not only the plume particles have to be considered but additionally those of the surrounding flow.

4 Numerical realization of simulations

The numerical realization of simulations is illustrated in Figure 3. Initially, particles are stochastically distributed over a two-dimensional computational area. The particles have initial velocities and composition variables that are chosen in accord with vertical profiles of the means and variances of these quantities which have to be provided at the west boundary. The particle properties are advanced then according to the
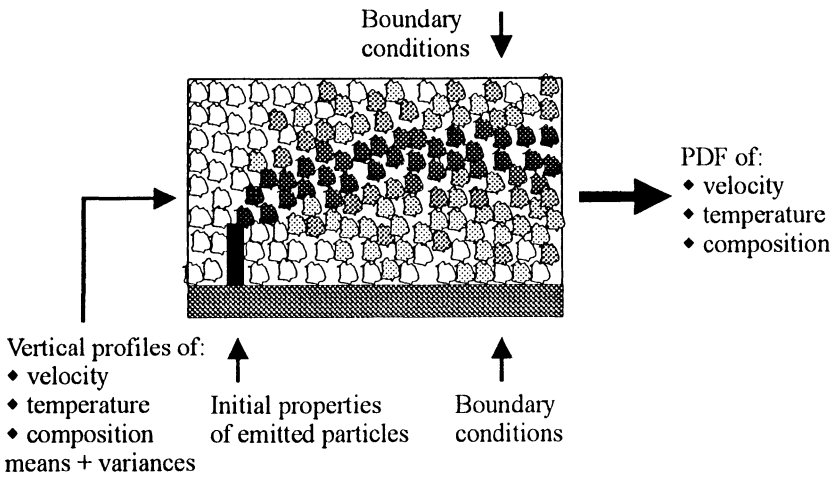
Figure 3: Model input and output quantities.

stochastic differential equations described above. In that way, the particles move from west to east. Their properties change according to boundary conditions that have also to be provided, when they arrive at the north or south boundaries. Particles that flow out at the east boundary are replaced by new particles at the west boundary. The advance of particle properties requires the mean velocity and composition values at the particle location, see equations (3b-c). These quantities are obtained by taking in grid cells the sum over particles properties which will be interpolated then to the particle location. The calculation proceeds until a stationary state is reached. This provides the joint probability density function (PDF) of velocity and composition, from which mean quantities can be calculated by integration.

Lagrangian codes are very well suited for the application of high-performance computing tools. The communication between processors is relatively small and accounts only a few percent of the simulation time, so that the time for computations scales nearly linearly over multiple processors, see Heinz et al.[1] The computations of a reactive plume presented in the next section had been performed with about 3 million particles at 8 processors, where 41 grid points were used in each direction. The stationary state is reached after 400 time steps, which requires about 2 hours CPU time.
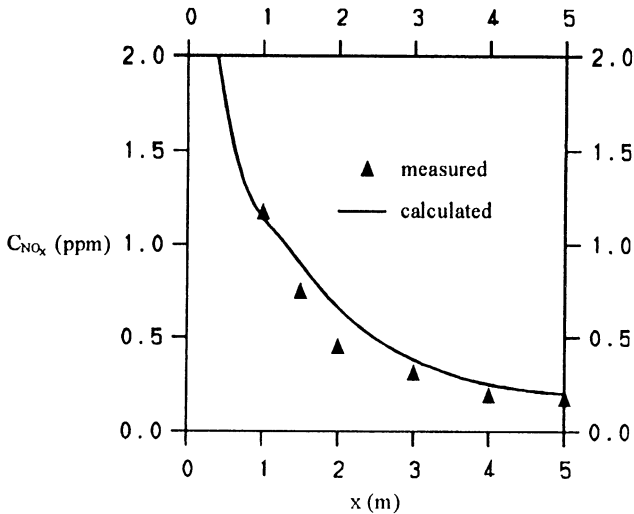
Figure 4: Concentration of the inert surrogate NO_x = NO + NO_2 of NO along the plume centerline and the measurements of Builtjes.[6, 7]

5   Reactive plume simulations

The reactive plume wind tunnel experiments of Builtjes[6, 7] were often applied to assess the performance of models that deal with calculations of reactive substance transport, as for instance second-order closure models or Lagrangian models.[2, 3, 8] These experiments were carried out in a wind tunnel of 10 m length that simulates a neutrally stratified atmospheric boundary layer with a thickness of 0.8 m. NO was supplied from a point-source 0.14 m above ground, which reacts in a second-order reaction with the rate k = 0.4 ppm^{-1} s^{-1} with O_3. The background concentration of ozone was maintained constant.

Figure 4 and 5 show calculations of NO_x and NO along the plume centerline, where NO_x = NO + NO_2 is an inert surrogate of NO, which contains NO and the reaction product NO_2. Hence, the decay of NO_x along the length x of the wind tunnel reveals the dispersion rate. Here, it is worth emphasizing that this rate was not provided in agreement to measurements as done by other methods, but it is calculated here. We see that there is a good agreement with the measured results, which have a reproducibility of 25% - 30%. Figure 5 reveals the effect of reaction between NO and O_3 on the decay of NO.
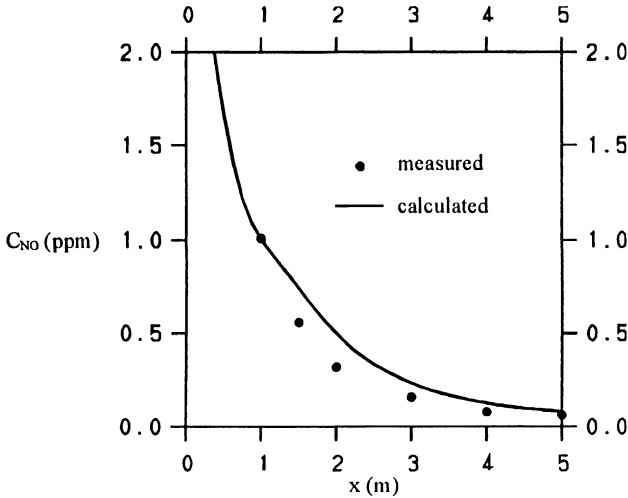
Figure 5: Concentration of NO along the plume centerline and the measurements of Builtjes.[6, 7]

The variation of the intensity of segregation I_S between -1 and 0 is shown in Figure 6. This figure demonstrates clearly that the reduction of the mean reaction rate (see equation (1) for the effect of I_S) due to mixing effects is significant. As a consequence, the effect of reaction on the decay of the NO concentration (see Figure 5) is much smaller than it would be predicted by methods that neglect the mixing effect. The curve obtained with $k = 0$ corresponds to the intensity of segregation between NO_x and O_3 and reveals the effect of the reaction rate on I_S, which would be found close to its initial value for an infinite high reaction rate. Figure 7 shows the effect of varying NO emission rates. We see, the higher the input of NO the larger the range of inhomogeneous mixing is found.

6 Conclusions

These are our conclusions:
1) The developed Lagrangian method represents a technique that can be applied in contrast to previously presented Eulerian and Lagrangian methods to calculations of reactive substance transport in the atmosphere under real conditions, where arbitrary complicated reactions are treated without additional assumptions and the important mixing effects on mean conversion rates are taken into account.
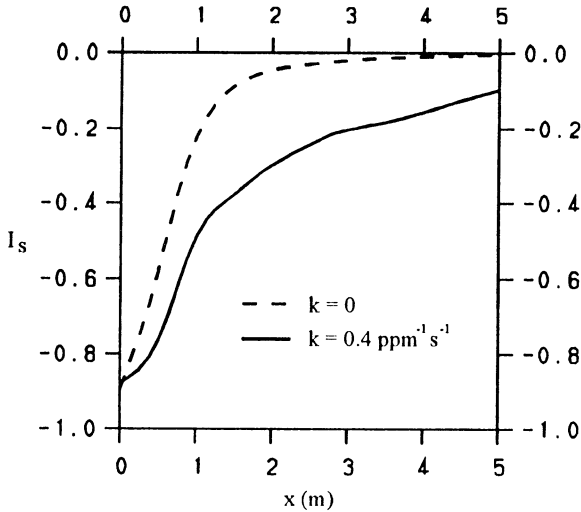
Figure 6: The intensity of segregation $I_S = \langle c_{NO} c_{O_3} \rangle / (\langle C_{NO} \rangle \langle C_{O_3} \rangle)$ (the solid line) along the plume centerline. The dashed line is obtained for $k = 0$ and corresponds to the intensity of segregation between the inert surrogate NO_x and O_3.

2) High-performance computing permits efficient calculations through the application of parallelization.
3) Our reactive plume calculations reveal the significant effect of mixing on mean conversion rates and permit the assessment of variations of these effects as for instance with the emission rate.

Acknowledgement

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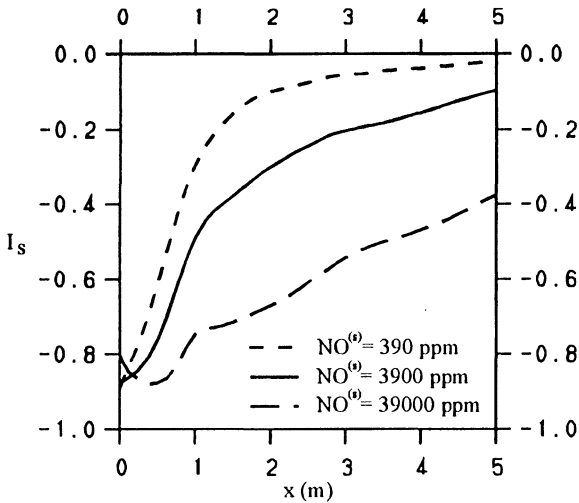
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Figure 7: I_s along the plume centerline for varying emissions. $NO^{(a)} = 3900$ ppm corresponds to the measurements of Builtjes.[6, 7]

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