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MODELLING REACTIVE ATMOSPHERIC PLUMES USING CONDITIONAL MOMENT CLOSURE AND A SCALAR PROBABILITY DENSITY FUNCTION

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ABSTRACT

A chemically reactive atmospheric plume of NO undergoing a reaction with O_3 in the atmospheric boundary layer is considered. Predictions of reactive concentrations are made using a relatively new approach for modelling turbulent reacting flows, the conditional moment closure, combined with an assumed form for the probability density function (pdf) of a conserved scalar. Model inputs are the conditional scalar dissipation and the form of the pdf. Model predictions compare well with field data measured in a power station plume. Future research will focus on improvements to the model for the conditional scalar dissipation and the form of the pdf.

INTRODUCTION

Motivation for this work comes from the need to predict concentrations of reactive pollutants in the atmosphere. We consider the simplified situation of a continuous point release such as a power station plume. The only reaction considered is $NO+O_3 \rightarrow NO_2+O_2$ (ignoring the back reaction in the presence of sunlight). Levels of O_3 and NO_2 are of particular concern because of adverse health and environmental impacts.

The aim of this work is to obtain predictions of reactive atmospheric pollutants by combining the conditional moment closure (CMC) theory of Klimenko & Bilger (1998) (from the field of combustion) and an atmospheric scalar (tracer) probability density function (pdf). CMC predicts reactive scalar concentrations as a function of the statistics of a conserved scalar (conditional reactive scalar statistics). The Reaction Dominated Limit (RDL) is a simplified special case of CMC obtained by neglecting the effects of micromixing (dissipation). Such mixing occurs at small scales and acts to bring the reactants into molecular contact where chemical reactions can occur. Neglecting micromixing effectively assumes that the reactants are brought into contact instantaneously - leading to an overestimate of chemical reaction. Thus, RDL will always give conservative (upper-) estimates of NO_2 concentrations.

The conserved scalar pdf, $p(x)$, when integrated over $[0, \hat{C}]$, gives the probability that the conserved scalar is $\leq \hat{C}$. We choose the clipped-gamma form of Yee & Chan (1997). This pdf is particularly useful for inclusion in CMC modelling of reactive atmospheric species because one of its fundamental assumptions can be used to model one of the terms in the CMC equation. We thus ensure consistency between the chosen pdf and the CMC model.

A conserved scalar (ie. not affected by chemical reaction) is often used in dispersion modelling to describe the state of mixing of an atmospheric pollutant with the surrounding ambient fluid (with or without chemical reaction). In the present case, we use total oxides of nitrogen,

$$C_{NO_x} = C_{NO} + C_{NO_2},$$

where C_i is the concentration of species i. The corresponding mixture fraction (Bilger, 1993) is defined as,

$$\hat{C} = \frac{C_{NO_x}}{S_{NO}},$$

where S_{NO} is the initial concentration of NO in the plume and the corresponding ambient O_3 concentration is S_{O_3}.

The range of $\hat{C}$ is between 0 and 1, representing pure ambient fluid and pure plume fluid, respectively. The reactive and conserved scalars are related by:

$$\hat{C} = \frac{C_{NO} - C_{O_3} + S_{O_3}}{S_{NO} + S_{O_3}}.$$

An equally proportioned mixture is known as a stoichiometric mixture and the corresponding mixture fraction may be obtained from the equation above as:

$$\hat{C}_s = \frac{S_{O_3}}{S_{NO} + S_{O_3}}.$$

It is sometimes convenient to normalise the mixture fraction, $\hat{C}$, by $\hat{C}_s$ because the latter is representative of the region where most chemical reaction is likely to occur and consequently the region of greatest interest to us.

CONDITIONAL MOMENT CLOSURE

Klimenko and Bilger (1998) review the theory and use of CMC. We give here only a brief summary mainly following the approach of Bilger (1993). We note that the following derivation is not confined to any particular location in the plume. Moments *conditional* on the value of the conserved scalar, $\hat{C}$, are defined as:

$$Q_i = \prec C_i \mid \hat{C} = \eta \succ \qquad (1)$$

where η is a sample space variable for $\hat{C}$ and angle brackets denote conditional averaging. By substituting Equation (1) and conditional mean and fluctuating terms into the equation for conservation of species, averaging and neglecting minor terms we obtain:

$$\frac{\partial Q_{NO}}{\partial (x/H)} = -\frac{kH}{\overline{U}} Q_{NO}(Q_{NO} - \eta(S_{NO} + S_{O_3}) + S_{O_3}) + \frac{H}{2\overline{U}} < \chi \mid \eta > \frac{\partial^2 Q_{NO}}{\partial \eta^2}, \quad (2)$$

where $\overline{U}$ is the mean velocity, H is the plume height (used here as a length scale), k is the reaction rate constant and $<\chi|\eta>$ is the mean dissipation of conserved scalar fluctuations conditional on the value of the conserved scalar itself.

Finally, the pdf of the conserved scalar is needed to obtain mean values from the CMC predictions of the conditional reactive scalar statistics:

$$\overline{C}_i = \int_0^1 < Q_i \mid \eta > p(\eta) d\eta, \quad (3)$$

where $p(\eta)$ is the pdf of η and overbars represent conventional mean values. The accuracy of $\overline{C}_i$ depends on the accuracy of both $<Q_i|\eta>$ and $p(\eta)$. In atmospheric plumes, the pdf has the greatest uncertainty.

Brown & Bilger (1998) have successfully used the CMC approach for turbulent reacting plumes in smog chamber flows, which had a low mean velocity and large turbulence scale, similar to that in the atmosphere.

For the present implementation of the CMC model (Equation 2), we use the same simple linear relationship for the conditional scalar dissipation as that used by Yee & Chan (1997) to derive their pdf. From atmospheric plume measurements, Yee & Chan (1997) found that

$$\left\langle \left(\frac{\partial \hat{C}}{\partial t} \right)^2 \mid \eta \right\rangle \approx K\eta,$$

where K is a constant with dimensions of s^{-2}, which has not yet been thoroughly investigated for atmospheric plumes. Using Taylor's frozen-flow hypothesis to convert temporal gradients to spatial gradients gives

$$< \chi \mid \eta > = \alpha\eta, \quad (4)$$

where $\chi = 2D(\nabla \hat{C})^2$ and $\alpha = 2DK/\overline{U}^2$.

The parameter α has dimensions of inverse time. Two cases are considered for equation (4). Firstly a constant value of α at all axial locations and secondly, the decay of α with axial distance. The latter is more realistic of real atmospheric flows since scalar dissipation decays strongly in jets and plumes. For example, on the centreline of jets, dissipation decays approximately as $\overline{\chi}_c \propto x^{-4}$ and for the round plume in grid turbulence of Brown & Bilger (1998), as $x^{-3.6}$. As a first attempt for this atmospheric flow we assume that α is related to the scalar fluctuations in the plume:

$$\alpha = -K_1 \left(\overline{\hat{C}}_c \right)^2 i^2, \quad (5)$$

where i is the intensity of fluctuation. This is equivalent to modelling the decay of the dissipation as $\overline{\chi}_c \propto x^{-3}$, because for the present plume $\overline{\hat{C}}_c = x^{-1.5}$. This is not a rigorous model and is used to give a qualitative understanding of the behaviour of α.

The special case of α=0 s^{-1} is the reaction dominated limit (RDL). The second term on the right hand side of Equation (2) is eliminated in this case and the equation is simplified to a convective-reactive balance which has an analytical solution given in Brown & Bilger (1998).

Equation (2) is parabolic and is solved for Q_{NO} by stepping through in the x-direction from imposed initial conditions, with a non-uniform geometric progression discretised grid (expansion factor 1.07) in the η-direction and with a 200x30000 (η-x) grid. An explicit marching method with mixed Euler scheme is used. The differencing scheme is forward-Euler except for part of the convection term which is backward-Euler. It runs in about 30 seconds on a fast PC and is accurate and stable.

PROBABILITY DENSITY FUNCTION

Recently Yee & Chan (1997) presented a parameterised concentration pdf, suitable for surface-layer point sources under a range of commonly encountered atmospheric conditions. The only inputs required to specify the pdf are the first two moments of the conserved scalar. It takes the form of a clipped-gamma pdf (with three fitted parameters k_p, s and λ):

$$p\left(\frac{\hat{C}}{\overline{\hat{C}}}\right) = \left(\frac{1}{s}\left(\frac{\hat{C}}{\overline{\hat{C}}} + \lambda\right)\right)^{k-1} \frac{1}{s\Gamma(k_p)} \exp\left(-\frac{1}{s}\left(\frac{\hat{C}}{\overline{\hat{C}}} + \lambda\right)\right) + (1-\gamma)\delta\left(\frac{\hat{C}}{\overline{\hat{C}}}\right),$$

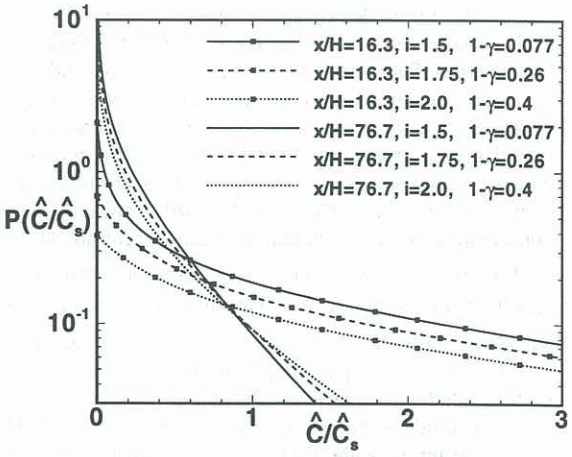

Figure 1. PDF of $\hat{C}$ at two downstream locations and three intensities of fluctuation as shown in the legend.

where Γ(k) denotes the Gamma function, δ is the Dirac delta function and γ is the scalar intermittency, (probability of plume fluid being present).

Examples of the pdf on the centreline at two downstream locations are shown in Figure 1. Three intensities of fluctuation are shown covering the expected range for this type of atmospheric plume. The Dirac delta function associated with the intermittency at $\hat{C}/\hat{C}_s = 0$ is omitted for clarity and its effective area (1-γ) is shown in the legend on the figure. Each pdf is normalised so that the total area including the Dirac delta function is unity.

RESULTS

The conditional reactive scalar means, Q_{NO}, Q_{O_3} and Q_{NO_2} at x/H=41 are shown in Figures 2abc, and were obtained from CMC calculations using Table 1 data and the linear model (equation 4) for the conditional scalar dissipation. Parameter α was varied through four values from α=0 to 8×10^{-7} s^{-1} without any axial change for each selected value. The case of α=0 s^{-1} is the RDL and is shown on the figure with symbols for emphasis. It is a maximum limit on the extent of reaction and so forms a lower bound on Q_{NO} and Q_{O_3} and an upper bound on Q_{NO_2}. Also shown on Figures 2 is the equilibrium limit and the frozen limit (for details see Brown & Bilger, 1998) which represent, respectively, instantaneous chemical reaction ($k\to\infty$) and no chemical reaction ($k\to0$). Plots of Q_{NO} at additional x/H to those shown in Figure 2abc are shown in Figure 2d. A constant value of α=5×10^{-8} s^{-1} has been used for all x/H. A problem with the value of α not changing with axial distance can be seen in this figure. At x/H>25, all Q_{NO} collapse and do not approach the equilibrium limit. This is because at downstream locations the micromixing (dissipation) term in equation (2) is too large relative to the other terms.

We introduce some axial dependence to the modelling of $\langle\chi|\eta\rangle$ by using equation (5). This is not a rigorous model but can qualitatively investigate the effect of $\langle\chi|\eta\rangle$ on Q_i. Figure 3a shows Q_{NO} at x/H=25 for decaying α. The parameter K_1 is varied from 0 to 50 and Q_{NO} appears to be behaving in a similar way to that in Figure 2a. Figure 3b shows Q_{NO} at various x/H for K_1=50.

Table 1. Emissions & conditions for the reactive plume for the reactive plume of Janssen *et al.* (1988).

Initial Concentration of NO	S_{NO}	877 ppm
Emission of NO		0.2 kg s^{-1}
Flow Rate		100 m^3 s^{-1}
S_{NO}/S_{NO_x}		90%
Stability Class (Pasquill)		D
Effective Plume Height	H	215 m
Wind Speed at Plume Height	$\overline{U}$	10 m s^{-1}
Ambient Ozone	S_{O_3}	15 ppb
Reaction Rate Constant	k	0.37 ppm^{-1} s^{-1}
Fluctuation Intensity	i	1.75

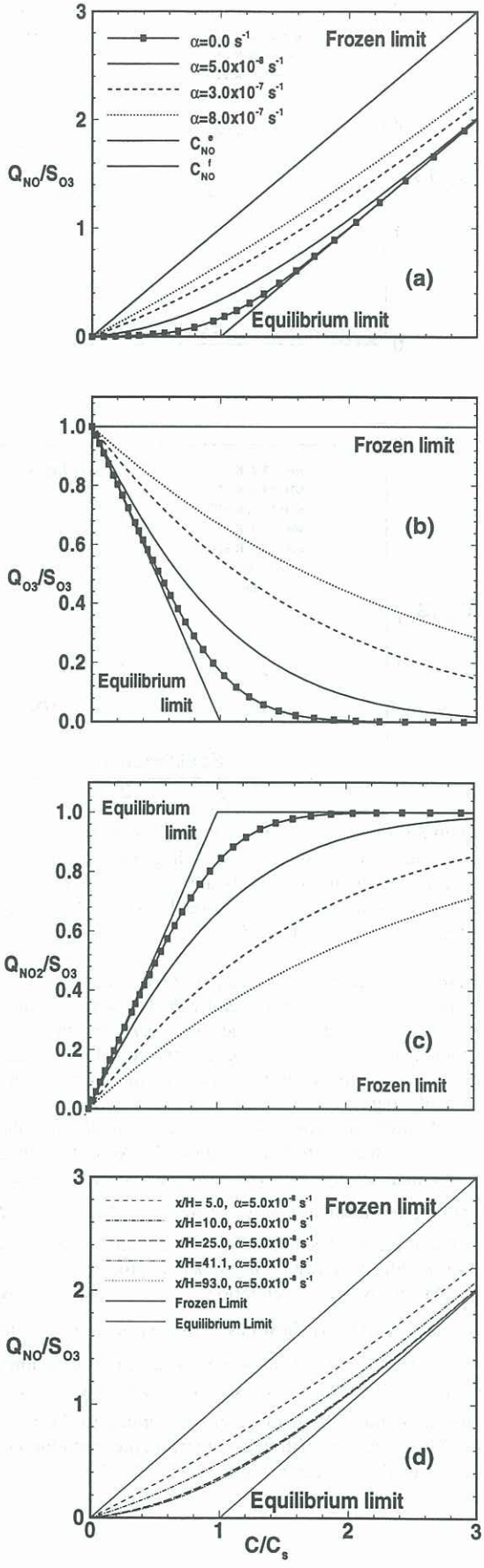

Figure 2. Conditional reactive mean concentrations, Q_i, calculated using the linear model of equation (4) for the conditional scalar dissipation with constant α. Frozen and equilibrium limits are also shown. The case α=0 s^{-1} is the reaction dominated limit. At x/H=41.1: (a), Q_{NO}; (b), Q_{O_3}; (c), Q_{NO_2}. At additional x/H: (d), Q_{NO}.

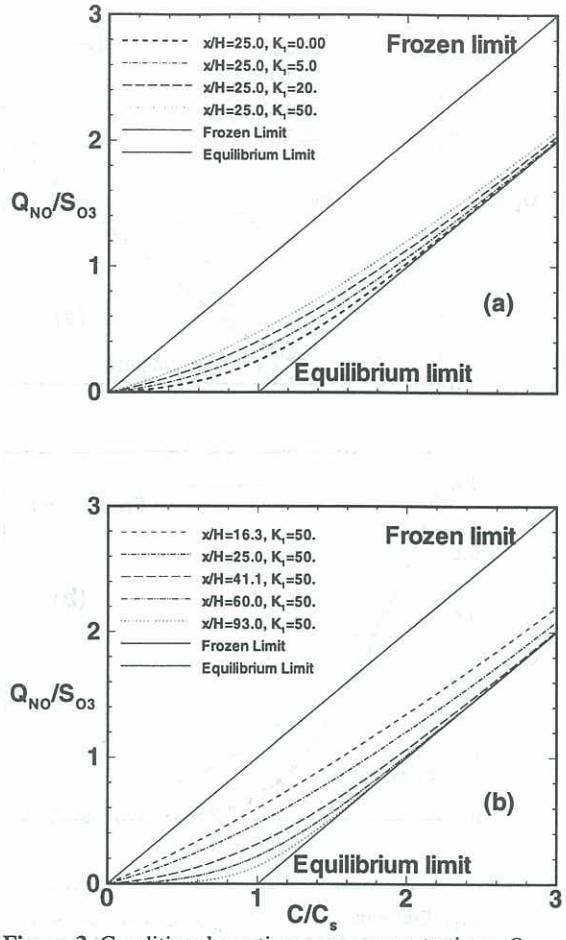

Figure 3. Conditional reactive mean concentrations, Q_{NO}, calculated non-constant α according to equation (5) Frozen and equilibrium limits are also shown. The case of α=0 s^{-1} is the reaction dominated limit. At x/H=25: (a). At additional x/H: with K_I=50. (b).

Unlike the behaviour of Q_{NO} in Figure 2d it is now behaving as would be expected by gradually approaching the equilibrium limit with increasing x/H. We therefore conclude that axial development of the conditional scalar dissipation is important and should be incorporated into its modelling

A problem arises when using a model for the dissipation such as that in equation (5). As $x/H \rightarrow 0$ then $\alpha \rightarrow \infty$ and so $\overline{\chi}_c \rightarrow \infty$. This problem is overcome by limiting the calculation of $\overline{\chi}_c$ at some small value of x/H so that it can not become infinite. The small value of x/H does not affect the rest of the numerical procedure.

Mean NO_2 concentration, $\overline{C}_{NO_2}$, produced by chemical reaction is shown as a fraction of local $\overline{C}_{NO_x}$ in Figure 3. Model predictions were obtained by weighting Q_{NO_2} from Figure 2c with the pdf from Figure 1 and integrating through the range of η according to Equation (3). The agreement with field data (from the centreline) is best when the parameter α is selected as 3×10^{-7}.

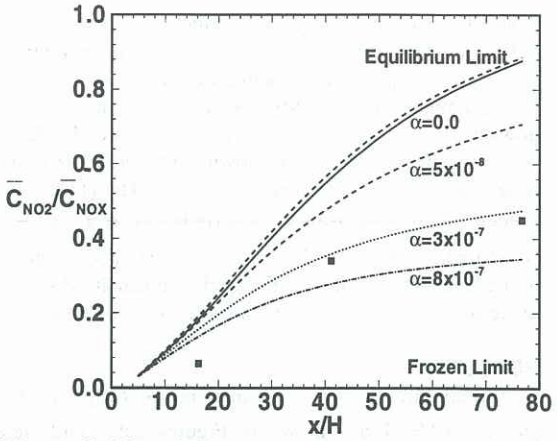

Figure 4. Mean NO_2, produced by chemical reaction shown as a fraction of local $\overline{C}_{NO_x}$, $\overline{C}_{NO_2}/\overline{C}_{NO_x}$. ■ Janssen *et al.* (1990) data as shown in Table 1.

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A first attempt has been made at modelling a chemically reactive atmospheric plume using conditional moment closure and a probability density function. From the limited comparison above, it can be seen that the CMC method for calculating mean NO_2 concentrations follows similar trends to that of field data. The RDL is also found to form a limiting maximum concentration of NO_2. Future development of the CMC model will concentrate on an operational sub-model for the conditional scalar dissipation, use of other forms for the conserved scalar pdf and extension to additional field data sets.

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