

USE OF CONDITIONAL AVERAGING TO OBTAIN BIOGEOCHEMICAL REACTION
 RATES AND STOICHIOMETRIES UNDER TURBULENT MIXING

R.W. BILGER¹, L.V. KRISHNAMOORTHY¹ and L.R. SAETRAN²

¹Department of Mechanical Engineering,
 University of Sydney, NSW 2006, AUSTRALIA

²Division of Hydro and Gas Dynamics
 Department of Mechanical Engineering, University of Trondheim, Trondheim, NORWAY

ABSTRACT

Use of conditional averaging, conditional on a conserved scalar is proposed for obtaining mean reaction rates under turbulent mixing conditions. In this method, data is divided into narrow range of mixture fraction, say. The averages of these subsets are the conditional averages and are plotted against the central value of the mixture fraction. The second derivative of this function is proportional to the mean reaction rate divided by the mean scalar dissipation rate. Stoichiometries of reactions are thus directly obtained. The procedure is applied to data obtained in a mixing layer in grid generated turbulence in which reaction rates are obtained directly by spatially and temporally resolved measurements.

INTRODUCTION

It is notoriously difficult to obtain quantitative data on mean reaction rates and stoichiometries under turbulent mixing conditions that pertain in the field, whether this is the atmosphere, ionosphere, ocean, lake or an estuary. Much of the problem is due to compositional inhomogeneities in the system arising from the turbulent mixing process. Plots of mean values of reactive species concentrations against mean values of a conserved scalar such as salinity (Hartman and Hammond, 1985; Van Green et al., 1988) or radon concentration (Atlas, 1988) are often used in discussing the effects of mixing and reaction. Nonlinearities in these plots are usually ascribed as being due to biogeochemical reaction. In this present note a conditional averaging procedure, conditional on the conserved scalar, is proposed to obtain mean reaction rates. The validity of this method is discussed in the light of the mean rates estimated directly from the spatially and temporally resolved measurements made in a mixing layer in classical grid turbulence.

ANALYSIS

It is assumed that the reactive scalar Y and the conserved scalar S obey the equations

$$w_y = \rho \frac{\partial Y}{\partial t} + \rho \mathbf{u} \cdot \nabla Y - \nabla \cdot (\rho \mathcal{D} \nabla Y) \quad (1)$$

$$0 = \rho \frac{\partial S}{\partial t} + \rho \mathbf{u} \cdot \nabla S - \nabla \cdot (\rho \mathcal{D} \nabla S) \quad (2)$$

where w_y is the net rate of production of species Y from biogeochemical reactions. Also ρ is the density, \mathbf{u} the instantaneous velocity vector and \mathcal{D} the effective molecular diffusivity, assumed equal for all species. Defining Y_c as the conditional expectation of Y

$$Y_c \equiv \langle Y(x, t) | S = S \rangle, \quad (3)$$

we notice that if the turbulence is stationary and homogeneous Y_c is only a function of S. Let

$$Y = Y_c + y. \quad (4)$$

Substituting (4) into (1) we obtain

$$\begin{aligned} w_y &= \frac{\partial Y_c}{\partial S} \left\{ \rho \frac{\partial S}{\partial t} + \rho \mathbf{u} \cdot \nabla S - \nabla \cdot (\rho \mathcal{D} \nabla S) \right\} \\ &\quad - \rho \mathcal{D} \nabla S \cdot \nabla S \frac{\partial^2 Y_c}{\partial S^2} + \rho \frac{\partial y}{\partial t} + \rho \mathbf{u} \cdot \nabla y - \nabla \cdot (\rho \mathcal{D} \nabla y) \\ &= - \rho \mathcal{D} \nabla S \cdot \nabla S \frac{\partial^2 Y_c}{\partial S^2} + \rho \frac{\partial y}{\partial t} + \rho \mathbf{u} \cdot \nabla y \\ &\quad - \nabla \cdot (\rho \mathcal{D} \nabla y) \end{aligned} \quad (5)$$

using (2). In obtaining (5) terms arising from spatial and temporal variations of $Y_c(S)$ have been ignored. We note that $\langle y \rangle = 0$ so that averaging (5) yields

$$\begin{aligned} \langle w_y \rangle &= - \langle \rho \mathcal{D} \nabla S \cdot \nabla S \frac{\partial^2 Y_c}{\partial S^2} \rangle + \nabla \cdot (\langle \rho \mathbf{u}' y \rangle) \quad (6) \\ &\approx - \frac{1}{2} \langle \rho \rangle \epsilon_s \langle \frac{\partial^2 Y_c}{\partial S^2} \rangle \end{aligned} \quad (7)$$

Here ϵ_s is the mean rate of dissipation of the variance of S

$$\epsilon_s = \langle 2 \mathcal{D} \nabla S \cdot \nabla S \rangle \quad (8)$$

and the approximation involves neglect of the correlations between fluctuations in the density, in the square of the scalar gradient and in S. Further it involves neglect of the divergence of the turbulent flux $\langle \rho \mathbf{u}' y \rangle$. This is zero in homogeneous turbulence, but in inhomogeneous turbulence, it is likely to be the leading order correction term. Even then its neglect may not be too serious. It can be shown that

$$\langle \rho \mathbf{u}' y \rangle \approx \langle \rho \mathbf{u}' Y' \rangle - \frac{d \langle Y \rangle}{d \langle S \rangle} \langle \rho \mathbf{u}' S' \rangle \quad (9)$$

so that it is about the same as the error in using gradient modelling for the turbulent flux of Y with the turbulent diffusivity appropriate for S.

Equation (7) is the basis of the method proposed here. This method should be independent of the conserved scalar chosen. It will probably be found, however, that some conserved scalars work better than others, possibly due to influence of the neglected term $\nabla \cdot (\langle \rho \mathbf{u}' y \rangle)$. A conserved scalar with a source of inhomogeneity the same as the source of inhomogeneity for Y will probably work best.

EXPERIMENTAL FACILITY AND INSTRUMENTATION

A description of the Environmental Turbulent Reading Flow (ETReF) facility (Fig. 1) can be found in Saetran et al. (1989). The turbulence producing grid is made from 63 x 63 mm rectangular hollow section in aluminium on a grid of 320 x 320 mm(M) square pitch

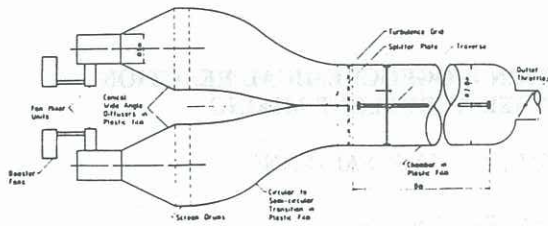


Figure 1 Schematic of ETReF facility

giving 65% open area. The facility is optimized to provide high Reynolds number flow together with a range of Damkohler numbers varying from those for nearly equilibrium chemistry to those for nearly frozen chemistry (Bilger, 1980). The maximum mean flow velocity in the working section is 0.55 m/s and the corresponding Reynolds number based on the grid spacing, M , is 11700. The mixing layer is obtained by doping one of the incoming streams with nitric oxide (NO) and the other with ozone (O_3). The concentration levels of these reactants are of the order of parts per million (ppm) and chemiluminescent analysers, developed in-house, are used for concentration measurements. Two channels of constant temperature hot wire anemometer operating an x -wire probe are used to measure u (longitudinal) and v (normal) components of velocity. The analog signals from the anemometers and chemiluminescent analysers are digitized and sampled at 128 Hz per channel by a LSI 11/28 terminal and sent to VAX780 computer. The sampling time at each measuring point is about 240 seconds.

FLOW FIELD AND MIXING

The flow field is that of a normal grid generated turbulent flow, i.e., the statistical properties of velocity vary only along the streamwise direction. The mean velocity profiles, except in the boundary layer region close to test section wall, are constant with spatial standard deviation of 2% in the transverse direction. The present experiments are performed in the region, $12 \leq x/M \leq 21$ downstream of the grid which according to Batchelor and Townsend (1948) lies within the initial period ($x/M < 100$) of the decay of homogeneous grid generated turbulence. The turbulence intensities and the degree of anisotropy corresponding to the present set of experiments can be found in Saetran et al. (1989).

For a one step, irreversible, second order reaction in isothermal flow, the difference between the instantaneous concentrations of reacting species A and B ($\Gamma_A - \Gamma_B$) is a conserved scalar (Bilger, 1976). The mixture fraction F is based on this conserved scalar and is defined as

$$F = \frac{\Gamma_A - \Gamma_B + \Gamma_{B_2}}{\Gamma_{A_1} + \Gamma_{B_2}} \quad (10)$$

where Γ_{A_1} and Γ_{B_2} are the inlet concentrations of A and B. The subscripts A and B denote NO and O_3 respectively. The chemical behaviour in the flow is adjustable in the sense that the speed of chemical reaction rate can be varied with respect to the speed of mixing. We characterize the ratio of these two speeds by the Damkohler number

$$N_D \equiv k_3(\Gamma_{A_1} + \Gamma_{B_2}) \frac{M}{U} \quad (11)$$

where $\tau_M \equiv M/U$ is the typical time scale of mixing and $\tau_c = [k_3(\Gamma_{A_1} + \Gamma_{B_2})]^{-1}$ is the time scale of chemical reaction. The reaction rate constant $k_3 = 0.37 \text{ ppm}^{-1} \text{ s}^{-1}$ at 298K (Chameidas and Stedman, 1977) for the reaction

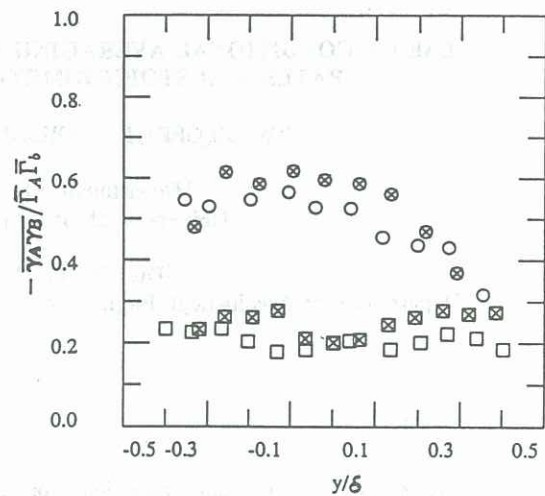
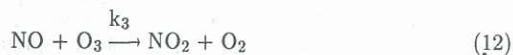


Figure 2 Distribution of concentration covariance. Open symbol, $x/M = 16$; crossed symbol, $x/M = 21$. \circ , low inlet concentration ($N_D = 0.3$) \square , high inlet concentration ($N_D = 1.8$)

MEAN REACTION RATES

The mean reaction rate $\langle \dot{w} \rangle$, for the second order reaction considered in this study, can be expressed as

$$-\langle \dot{w} \rangle / k_3 = \Gamma_A \Gamma_B \left[1 + \frac{\overline{\gamma_A \gamma_B}}{\Gamma_A \Gamma_B} \right] \quad (13)$$

The second term on the RHS of (13) contains the reactants concentration covariance. The covariance is normalized by the product of the local mean concentrations is shown as a function of y/δ (Figure 2) where δ is the width of the mixing layer between the points where $\overline{F} = 0.1$ and $\overline{F} = 0.9$. In Fig. (2) the covariances correspond to two different inlet conditions ($N_D = 1.8$, high concentration run; $N_D = 0.3$, low concentration run) and two downstream locations ($x/M = 16$ and 21). In the limit $N_D \rightarrow \infty$, that is of equilibrium chemistry, $\overline{\gamma_A \gamma_B} / \Gamma_A \Gamma_B \rightarrow -1$. In the limit $N_D \rightarrow 0$, that is of frozen chemistry, $\overline{\gamma_A \gamma_B} / \Gamma_A \Gamma_B \rightarrow -f'^2 / \overline{F(1-F)}$, $\sim 10^{-1}$ in this flow. The results in Fig. (2) show that the normalized covariance is consistent with these limits and reaches values of about -0.55 in the central portion of the mixing layer for the high N_D case.

The correlation coefficient defined as

$$R_{AB} = \overline{\gamma_A \gamma_B} / (\gamma'_A \gamma'_B) \quad (14)$$

where $(\gamma'_A \gamma'_B)$ is the product of standard deviations, reach values of about -0.6 (Figure 3) for the high N_D runs. In the limit of frozen chemistry, the reactant concentrations are linear functions of the mixture fraction and the limiting value for R_{AB} is -1 . The low Damkohler number results show a significant influence of slow chemistry with R_{AB} values reaching close to the limiting value given by frozen chemistry condition.

The conditional averaging procedure described in the 'Analysis' section has also been used to obtain the mean reaction rate. The chosen conserved scalar S is the mixture fraction F and the reactive scalar Y is Γ_B the

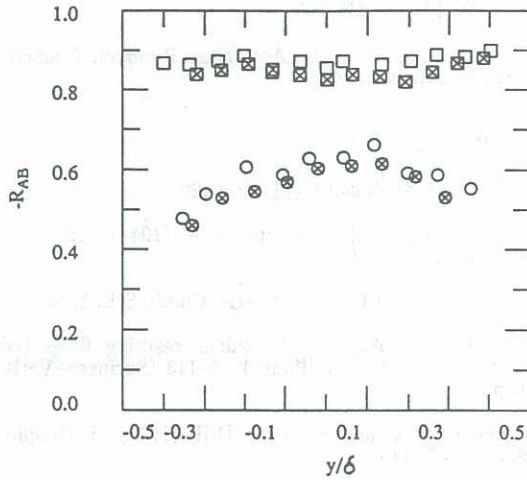


Figure 3 Distribution of correlation coefficient of concentrations
Symbols as in Figure 2.

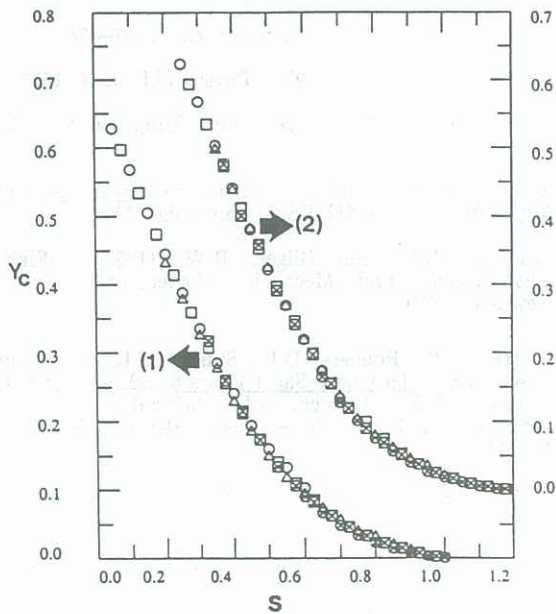


Figure 4 Distribution of conditional averages for $N_D = 0.3$
(1) $x/M = 16$; (2) $x/M = 21$
 \circ , $y/\delta = -0.4$; \square , -0.2 ; Δ , 0.0 ; \blacksquare , 0.2 ; \otimes , 0.4

concentration of O_3 . The data is sorted into subsets of narrow range (40 bins) of width $\delta S = 0.025$. The average value of each bin is taken as the conditional value Y_c corresponding to the central value of the mixture fraction for the subset. Figure 4 is a typical plot of the conditional averages in the mixture fraction space for test case corresponding to low inlet concentrations. It is seen that $Y_c(S)$ is independent of the transverse location in the mixing layer. The streamwise variation of $Y_c(S)$ is also seen to be quite small. These findings endorse the use of the homogeneity assumptions in deriving Eqn (6). Very similar plots were obtained (not shown here) for high inlet concentration runs, except that they gave lower values of Y_c near $S = 0.5$ and consequently higher second derivatives $d^2 Y_c / ds^2$ there. Similar results were obtained when NO was chosen as the reactive scalar instead of O_3 .

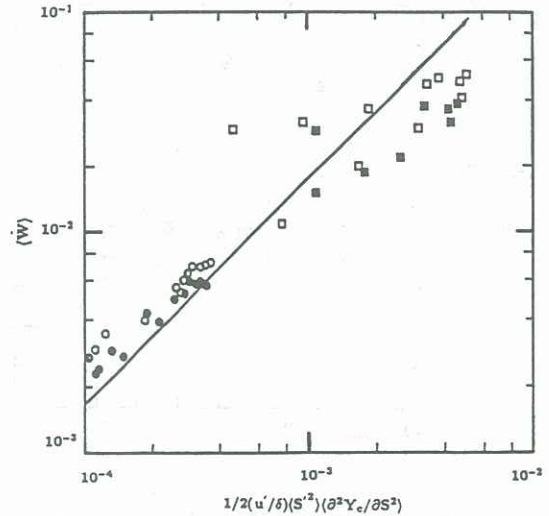


Figure 5 Variation of measured reaction rate against the modelling in equation (16). Symbols as in Figure 2.

A knowledge of the distribution of the mean rate of dissipation of the scalar variance, ϵ_s , is necessary to estimate the mean reaction rate using Eqn (7). As the dissipation occurs at the higher end of the frequency spectrum, direct measurement of it is always limited by spatial resolution of the probes used. An approximate modelling for ϵ_s is

$$\epsilon_s = R \frac{u'}{\delta} \langle s'^2 \rangle \quad (15)$$

where u' is the rms of the longitudinal velocity fluctuation and R is a modelling coefficient expected to be close to constant in value. Substituting (15) into (7) we obtain

$$\langle w_y \rangle_{cs} = \frac{1}{2} \langle \rho \rangle R \frac{u'}{\delta} \langle s'^2 \rangle \langle \frac{\partial^2 Y_c}{\partial S^2} \rangle \quad (16)$$

The second derivative $\partial^2 Y_c / \partial S^2$ is obtained from a fourth order polynomial least squares curve fit to the $Y_c(S)$ correlations as shown in Fig. 4. A value for $R = 34$ was obtained from the intercept of best fit line of unity slope (Figure 5) when the reaction rates given by eq. (13) and (16) are plotted in log-log form. Note that Figure 5 shows correct trend over range of factor of about 25 in the mean reaction rate. The present value of R is about ten times higher than the value of about 3 which can be deduced from the modelling used by Libby (1975) in his analysis of non-reacting mixing layer. Present value of R may be due to low values of x/M considered in the present experiments whereas Libby's analysis is more suitable to regions of large x/M where there is a balance between convection, diffusion and production of scalar fluctuations. R can also be overestimated due to the neglect of the divergence of turbulent flux $\langle \rho u' y' \rangle$ and the correlation of the scalar and its dissipation in Eq. (6). Further the concentration field is found to be weakly dependent on x . We are currently estimating R taking into account the sources of the discrepancies mentioned above.

The ratio of the mean reaction rates obtained using Eq. (16) with $R = 34$ and Eq. (13) are plotted in Figure 6 as a function of (y/δ) . Values somewhat less than unity (~ 0.8) are obtained for the low N_D runs. Higher values are obtained for high N_D case and are found to be a strong function of (y/δ) . Since the mixing layer develops in a grid-generated nearly homogeneous turbulent flow, such variations with N_D seem unreasonable. This may be due in part to inaccuracies in measuring the reactant covariances in Eq. (13), these inaccuracies arising from the limited spatial and temporal resolution of the concentration measurements.

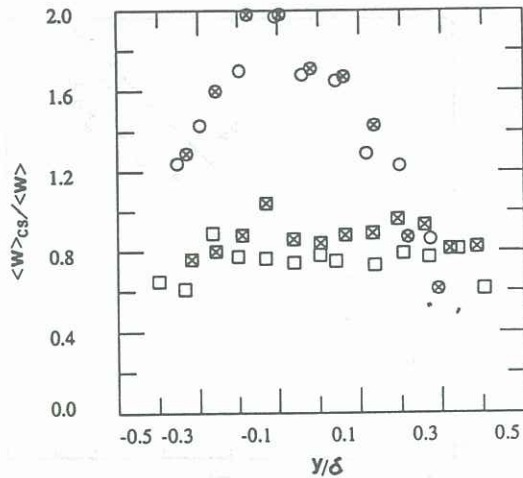


Figure 6 Distribution of the ratio of mean reaction rates across the layer. Symbols as in Figure 2.

The modelling coefficient R in Eq. (16) is related to the dissipation time scale ratio $R_s = (\epsilon_{sk})/(\epsilon_s'^2)$. R_s varies widely in flows. Launder's (1976) review show that R_s has roughly two-fold variation while considering only homogeneous turbulent flows. There is a considerable sensitivity of R_s to the relationship between the sources of scalar and velocity fluctuations (Warhaft and Lumley, 1978; Sirivat and Warhaft, 1982), however, due in part to interference phenomena (Warhaft, 1984). It should be possible to deduce a mean value of ϵ_s from the streamwise variations in the mixture fraction measurements. More accurate measurements of the mean mixture fraction field to enable this check to be made are currently being undertaken.

CONCLUSION

A new analytical result is obtained relating the mean reaction rate in a turbulent mixing flow to the mean rate of dissipation of a conserved scalar and the second derivative of conditional averages of the reactive scalar with respect to the conserved scalar. This analytical result has been tested against measurements made in a reacting scalar mixing layer downstream of a turbulence generating grid.

The experimental results are in generally good qualitative agreement with the new analytical result. A best fit value of the modelling coefficient for the scalar dissipation is somewhat larger than values deduced from the literature. This coefficient also shows some dependence on the Damkohler number, a result that can only be attributed to inaccuracies in measurement of the reactive scalar correlations. A finding of some significance is the lack of dependence of the conditional averages on position across the shear layer. This supports the use of homogeneity assumptions in the analysis and may have other useful implications. Suggestions are made as to the possible sources of discrepancy in the modelling coefficient for the scalar dissipation and means for investigating these.

ACKNOWLEDGEMENT

The support of the Australian Research Council is gratefully acknowledged.

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