

Mixing of Atmospheric Gas Concentrations

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Atmospheric gas concentrations were measured at 1 s intervals in the upper troposphere during a flight through and near the anvil of a storm. The observed very high correlations between the concentrations of CO and CH₄ are interpreted as arising from the mixing of two distinct air masses with differing concentrations of each species, and is due to the nearly identical diffusivities of CO and CH₄ in air. We find that the correlations depend on the period over which each concentration measurement was made. Correlations in measurements made over short periods decay with time, while correlations over larger scales remain high. We interpret this using a simple mixing model.

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On May 8, 1996, as part of the SUCCESS project [1], a NASA DC-8 aircraft flew through and near the cirrus outflow of a large storm over the midwestern U.S. [2]. Measurements were made at 1 s intervals of various gas concentrations, aerosol particle concentrations, cloud surface area, and meteorological variables. An analysis of some of the chemistry associated with the observed oxides of nitrogen and ozone has already been reported [2]. In this paper we present some remarkable correlations in the observed gas concentrations, and provide a physical explanation of the observations based on a simple mixing model.

It is possible to construct correlation functions of a series of measurements of two variables, a and b , which we take to be the concentrations (measured in terms of mole fraction) of two atmospheric constituents:

$$C(a, b; t, \Delta t) = \frac{\sum_i (a_i - a_m)(b_i - b_m)}{\left(\sum_i (a_i - a_m)^2 \sum_i (b_i - b_m)^2 \right)^{1/2}} \quad (1)$$

The measurements a_i and b_i are labeled by the suffix i , and are mean values over periods regularly spaced within the time interval $t - \Delta t/2$ to $t + \Delta t/2$, while a_m and b_m are the mean values of a and b for this interval. The period τ over which data are gathered to make each measurement can vary: as τ is increased, the number of measurements in the interval Δt will clearly decrease.

The value of C must lie between $+1$ for perfect correlation, which occurs (in the absence of statistical noise) when the variables a and b are positively linearly related ($b = \lambda a + \mu$, where λ and μ are constants and λ is positive) and -1 when they are negatively linearly related ($b = \lambda a + \mu$, where λ and μ are constants and λ is negative). In general, we would expect C to lie between ± 1 , and to depend upon Δt as well as the time t and the measurement period τ .

Fairly high overall correlations of this type are often found in atmospheric trace gas measurements [3], a re-

flection of the origins and behavior of large air masses. In particular, they occur between CO and CH₄ during portions of this flight. These gaseous species are expected to originate mainly at the ground and to be relatively chemically unreactive in the upper troposphere. Measurements of gas concentrations were made by sampling air through an inlet into a 20 m folded path White Cell and the use of a mid-IR diode laser-based differential absorption instrument [3–5]. The data have precisions of 1 parts per billion by volume (1 s) for both gases [5]. We have performed correlation analyses using $\Delta t = 50$ s, with $\tau = 1$ s (the raw data) and $\tau = 50$ s (obtained by an averaging of the 1 s data over periods of 50 s).

In Fig. 1 we show the $\tau = 1$ s CO : CH₄ correlation and mean CO concentration during the time period when the aircraft was ascending through the anvil of the storm. From 70 650 to 71 000 s the correlation lies mostly between 0.8 and 1. In Fig. 2, we show the actual concentration data for the final 100 s of the period. In spite of variations in the CO concentration by about 30% during the interval, in

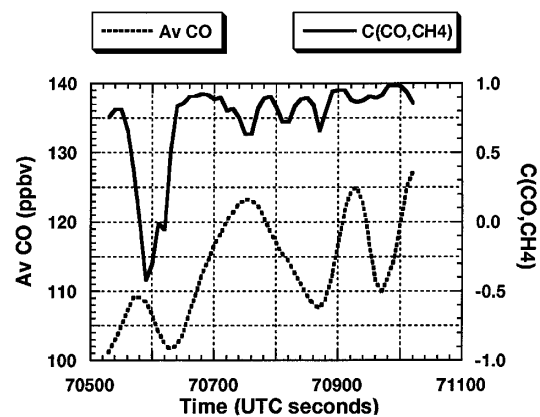


FIG. 1. The CO concentration averaged over 50 s intervals and the correlation between CO and CH₄ concentrations during the intervals as a function of time during the rising section of the flight.

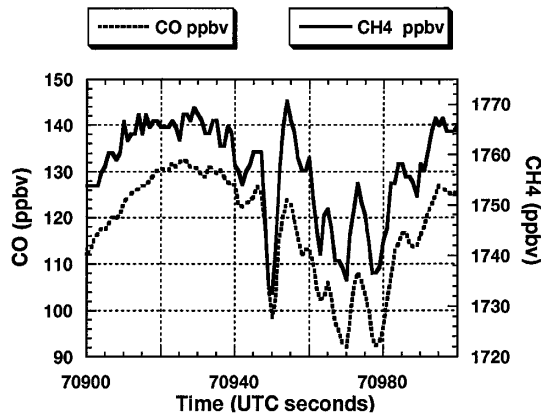


FIG. 2. CO and CH₄ concentrations at 1 s intervals during a 100 s interval.

contrast to a variation of only about 2% in the CH₄ concentration (note the different scales), their fluctuations are almost perfectly correlated. The following model provides a possible explanation of this result, which is consistent with the fine precision quoted for the measurements, and has further implications.

We consider two trace constituents of the air with concentrations c_1 and c_2 , respectively, referring to the gases CO and CH₄, for example. Over long time periods, the concentrations of any gaseous constituents in well-mixed air will tend to become uniform in space through the two processes of turbulent mixing and molecular diffusion. These processes are included in the following transport equation for the concentrations, valid when the c_j are small, where $j = 1, 2$ labels the species:

$$\frac{\partial c_j}{\partial t} + \mathbf{v} \cdot \nabla c_j - D_j \nabla^2 c_j = 0, \quad (2)$$

where D_j are the molecular diffusivities in the ambient air and \mathbf{v} is the flow velocity of the air. There are no source or sink terms in Eq. (2) if the region of the atmosphere concerned is far from ground-based sinks and the constituents are not involved in local chemical reactions.

The proposed model is based on the mixing of two uniform air masses A and B in which the concentrations of the constituents are c_{1A} , c_{2A} and c_{1B} , c_{2B} , respectively. The first case we consider is when the concentrations are both larger in the first air mass:

$$\text{Model 1 : } \quad c_{1A} > c_{1B}, \quad c_{2A} > c_{2B}. \quad (3)$$

Now we define the scaled variables

$$\begin{aligned} c'_1 &= (c_1 - c_{1B}) / (c_{1A} - c_{1B}), \\ c'_2 &= (c_2 - c_{2B}) / (c_{2A} - c_{2B}). \end{aligned} \quad (4)$$

As these variables are linear in c_1 and c_2 , the c'_j obey the same Eq. (2). But in the initial air masses A and B , $c'_j = 1$ and 0 , respectively, so that their difference, $c'_1 - c'_2$, initially vanishes everywhere. This difference obeys the equation

$$\frac{\partial (c'_1 - c'_2)}{\partial t} + \mathbf{v} \cdot \nabla (c'_1 - c'_2) = D_1 \nabla^2 c'_1 - D_2 \nabla^2 c'_2. \quad (5)$$

So we immediately obtain the result that, if the diffusivities of the two species are equal, the solution for all t satisfying the initial conditions is

$$c'_1 = c'_2. \quad (6)$$

This produces a positive linear relation between c_1 and c_2 , and by the earlier arguments this would lead to a perfect correlation between the two species in the mixing process.

Before investigating possible corrections due to unequal diffusivities, we show how a different initial condition would lead to a perfect anticorrelation:

$$\text{Model 2 : } \quad c_{1A} > c_{1B}, \quad c_{2A} < c_{2B}. \quad (7)$$

In this case we define different scaled variables,

$$\begin{aligned} c'_1 &= (c_1 - c_{1B}) / (c_{1A} - c_{1B}), \\ c'_2 &= (c_{2B} - c_2) / (c_{2B} - c_{2A}). \end{aligned} \quad (8)$$

Again the initial values of these variables are 1 in region A and 0 in region B so that $c'_1 - c'_2$ vanishes everywhere. This difference still obeys Eq. (5) so the solution for equal diffusivities is again Eq. (6). However, this is now a negative linear relation between c_1 and c_2 giving a perfect anticorrelation.

Now consider corrections to these correlations due to unequal diffusion coefficients. These are tabulated [6] for both gases in air at standard pressure (1.01325×10^5 Pa) and temperatures from 293.15 to 673.15 K. These data can be fitted within an accuracy of 2.9% for CH₄ and 1.3% for CO by the following expressions, with temperature T in K:

$$D_1 = 3.476 \times 10^{-9} T^{3/2} + 2.279 \times 10^{-12} T^{5/2} \quad (9)$$

for CO, and

$$D_2 = 3.299 \times 10^{-9} T^{3/2} + 2.754 \times 10^{-12} T^{5/2} \quad (10)$$

for CH₄, both in units of $\text{m}^2 \text{s}^{-1}$. For the dilute gases in question, in a mixture at total pressure p of order 1 atm, the diffusivities will be inversely proportional to p , so that we can estimate the diffusivities for typical flight conditions of $T = 215$ K and $p = 2 \times 10^4$ Pa. We obtain a diffusivity for CO of $0.633 \times 10^{-4} \text{m}^2 \text{s}^{-1}$, and for CH₄ a value of 0.621×10^{-4} . For this difference in diffusivities of only 1.9% we can see how the good correlations shown in Fig. 2 can arise.

To understand how deviations from perfect correlation would arise from unequal diffusivities, we can integrate Eq. (5) over a sample volume V whose boundaries are moving with the flow. Because of turbulence, such a volume will change shape considerably with time, but the relation between its surface area, S , and the volume gives us a length scale, $L_s = V/S$, important in estimating

deviations. We obtain

$$\begin{aligned} \frac{d}{dt} \int_V (c'_1 - c'_2) dV &= \int_V (D_1 \nabla^2 c'_1 - D_2 \nabla^2 c'_2) dV \\ &= \int_S (D_1 \nabla c'_1 - D_2 \nabla c'_2) \cdot d\mathbf{S}. \end{aligned} \quad (11)$$

Using Eq. (6) as a first approximation, we can take $\nabla c'_1 = \nabla c'_2$ so that the right-hand side becomes $(D_1 - D_2) \int_S \nabla c'_1 \cdot d\mathbf{S}$. Dividing by an average value over the sample volume, $\overline{c'_1}$, we obtain an estimate:

$$\frac{1}{\overline{c'_1}} \frac{d}{dt} \overline{(c'_1 - c'_2)} = \frac{(D_1 - D_2)}{V \overline{c'_1}} \int_S \nabla c'_1 \cdot d\mathbf{S}. \quad (12)$$

It should be borne in mind that the surface integral is a fluctuating time dependent quantity. However, on average, values of the c'_j will diverge with time, and so, to represent this, we need to make a simple (positive) estimate of the right-hand side.

For a given flow field there will be a length scale L_t characterizing the dominant eddies responsible for mixing. This will be the characteristic distance over which significant changes in concentrations will be seen. If the dimensions of the sample volume are much smaller than this scale, then the surface integral of the concentration gradient will be close to zero. On the other hand, if a dimension of the sample is of order L_t , the integral may be approximated by $S \overline{c'_1} / L_t$. Large gradients in c'_1 are to be expected across the sample. But if a dimension of the sample greatly exceeds L_t , then the integral is again small, this time due to cancellation between contributions from different parts of the surface.

The data c_{1i} that enter the calculation of correlation functions in Eq. (1) are just the averaged values of the concentration c_1 over the volume sampled in the measurement interval τ , and similarly for c_{2i} . Both are related to the $\overline{c'_j}$ just considered. A departure from $\overline{c'_1} = \overline{c'_2}$ will lead to a reduction in the correlation function C between c_1 and c_2 . This can be studied using Eq. (12), written in the form

$$\frac{1}{\overline{c'_1}} \frac{d}{dt} \overline{(c'_1 - c'_2)} = \frac{1}{t_0} \leq \frac{1}{t_c} = \frac{|D_1 - D_2|}{L_s L_t}. \quad (13)$$

This equation shows how measurements of c'_1 and c'_2 diverge as time progresses. If $c'_1 = c'_2$ at $t = 0$, then $c'_1(t) \approx c'_2(t) + \overline{c'_1}(0)(t/t_0)$, and, since c'_1 is of order unity, the time needed to introduce significant decorrelation is t_0 . The lower limit for this time scale is $t_c = L_s L_t / |D_1 - D_2|$.

Now, the measurements are made in a sample volume which takes the form of a long thin cylinder, introduced through an inlet of diameter 0.5 cm into the aircraft [3]. Its geometry will have evolved from some initial form due to turbulence, but the measurement chamber has $L_s = V/S = 0.125$ cm, and we assume that this is a reasonable guess for the whole cylinder. The difference in the gas diffusivities is $0.012 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ so that, with turbulent

length scales in the range 0.1 to 1 m, we obtain $t_c = 100$ to 1000 s.

By how much t_0 exceeds t_c will depend on the size of the sample volume, or equivalently the measurement period τ . For $\tau = 1$ and 50 s, the length of the cylinder would be about 200 m and 10 km, respectively, if the aircraft travels at about 200 ms^{-1} . These sample volumes may be mapped out by calculating backtrajectories in the flow starting from the inlet. In fact, we would more realistically have to abandon the notion that the sample volume is quasicylindrical in the $\tau = 50$ s case, since turbulence will cause the backtrajectories to diverge. In any case, we would expect the time scale t_0 for the $\tau = 1$ s measurements to be smaller than the time scale for $\tau = 50$ s, and so the correlations in c_1 and c_2 should fall more rapidly for the measurements taken over short intervals than for long intervals.

These results are consistent with the $\Delta t = 50$ s, $\tau = 1$ s correlation function for CO and CH₄ observed when the aircraft flew away from the storm horizontally just above the anvil, shown in Fig. 3. The initial mixing of the distinct air volumes *A* and *B* probably took place many minutes earlier, and then we see the correlations decaying, on average, with time and distance from the storm, becoming considerably less than unity.

On the other hand, the large length scale changes in concentration in this region are still very well correlated. This is illustrated using the average concentrations for $\tau = 50$ s intervals plotted in Fig. 4. The correlation function at $t = 71\,300$ s with $\Delta t = 150$ s (employing the seven $\tau = 50$ s averages for t between 71\,150 to 71\,450 s) is as high as 0.978. These features strongly support the idea that the loss in correlation is due to differential diffusion of species in a mixture of two originally uniform air masses.

We can present the same ideas in another way. For large volumes where V/S is large, such as spheres, it is easy to show from Eq. (11) or from Eq. (12) that average values of $c'_1 - c'_2$ must remain very small for long times following mixing. The average value can only be changed

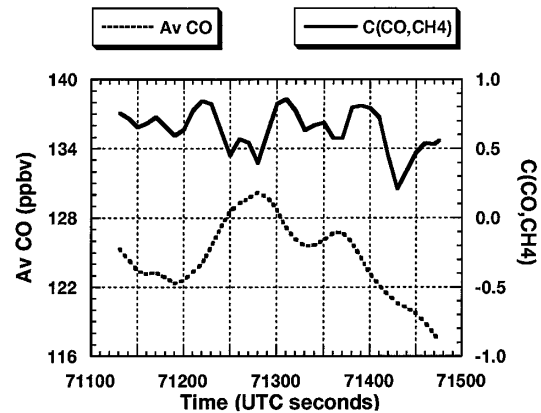


FIG. 3. As for Fig. 1 during a later horizontal section of the flight above the anvil.

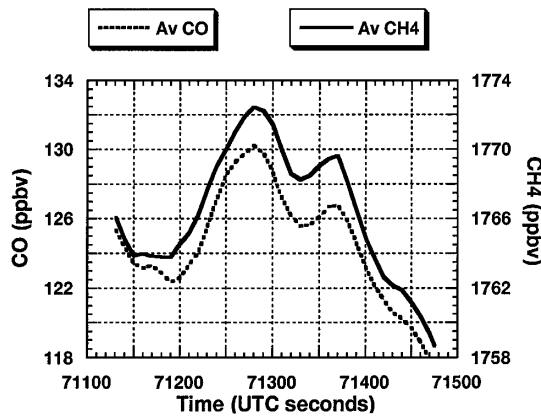


FIG. 4. CO and CH₄ concentrations averaged over 50 s intervals during the time interval of Fig. 3.

by the net diffusive flux through the boundary, and as the volume increases, and the V/S ratio with it, the effect of unequal diffusion across the boundary upon the mean concentrations decreases. It takes a longer time to cause the average concentrations to decorrelate. The aircraft, however, collects a volume of air over a long time as a long tube with a value of V/S which remains constant as V increases, and the same argument does not apply. Instead, however, we can argue that if there is random mixing within large volumes the average value of $c'_1 - c'_2$ even for a tube should also remain small, unless the tube volume is small enough to capture the fluctuations to be expected in species concentrations due to diffusion. This result arises from the character of the turbulent mixing as well as diffusion. The observation of larger correlations between mean concentrations in larger samples is then a reflection of turbulent mixing in the atmosphere.

In summary, the model explains the excellent correlations observed between the CO and CH₄ concentrations:

they arise from the mixing of uniform air masses in which the concentration of both gases are higher in one air mass than in the other. We have also described major differences in correlations at different times, and also a dependence upon different length and time scales, and have given a partial description of their origin. It is clear that there are many other implications of such observations and results that can be deduced from them. The correlations reflect on the accuracy of the measuring instruments and their sampling procedure. It is important to examine different time averages as these can reflect on atmospheric mixing properties. Finally, comparisons can be made to observations of other concentrations and atmospheric properties observed at the same time. For the flight in question, we shall report elsewhere on deductions which can be made concerning the behavior of other atmospheric constituents at the time, including aerosol. Altogether, the fact that the diffusivities of the two trace gases are very close so that their mixing correlations can be very high offers a very promising way to explore mixing and other properties of the atmosphere.

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