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A proposed test of two hypotheses related to concentration fluctuations and residence times

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ABSTRACT

An experimental test is proposed of the hypotheses behind 2 models of Junge's empirical result relating fluctuations in concentrations of atmospheric trace constituents to their residence times. The test, which probably could be performed using available data, involves calculating the coefficient of variation, F_c, for sampling periods of different duration, Δt_E, (or for portions of a single data record). For one theory, F_c would be independent of Δt_E; the second theory suggests that F_c will increase linearly with Δt_E, at least for small Δt_E. Moreover, the second theory suggests that the initial slope of the F_c versus Δt_E curve is related to the residence time T_r via $\lim(\Delta t_E \to 0)\{dF_c/d(\Delta t_E)\} = [\sqrt{12}T_r]^{-1}$.

1. Introduction

Junge (1974) demonstrated an empirical relationship between concentration fluctuations for trace atmospheric constituents and their atmospheric residence times, T_r. He found that the coefficient of deviation (the standard deviation divided by the mean) was inversely proportional to T_r, with the proportionality constant (0.14 years) the same for all chemicals. Subsequently, a number of authors have searched for a theoretical basis for Junge's relationship (Gibbs and Slinn, 1973; Baker et al., 1979; Jaenicke, 1982; Hamrud, 1983; Slinn, 1983, 1988a, b). As stated in Slinn (1988a) [hereinafter Sa]:

> Hamrud's analysis is particularly illuminating: he emphasizes that Junge's result is more appropriately interpreted, not as a relationship for fluctuations in time at a particular point, but as a measure of the spatial variability of the concentrations. If Hamrud's interpretation is coupled with a part of Jaenicke's concept of finite sampling-time, then the following simple model can be developed.

The resulting simple model has been criticized by Jaenicke (1989), who sees little difference between the model and the one developed in Jaenicke (1982). The response by Slinn (1989) suggests that there are differences and suggests that an experimental test might be able to distinguish between the different hypotheses. The purpose, here, is to describe the proposed test.

2. Eulerian versus Lagrangian times

Fig. 1 is used to elucidate measurable differences between the two theories. In Fig. 1a, curve 1a(i) shows hypothetical variations of the concentration, C, of some chemical as a function of local (Eulerian) time, t_E. As is well known, there can be many causes of concentration variations; here, to start, assume that the variation is primarily caused by differences in (Lagrangian) travel times between a single source and the detector. Under some conditions (see later), the case of multiple sources can be treated relatively easily, but as mentioned in Sa, there remain a number of restrictions of the theory for the case of a finite area source in a three- (or even two-) dimensional world. Hamrud's numerical calculations give informative examples of these complications and demonstrate that more theoretical studies are needed.

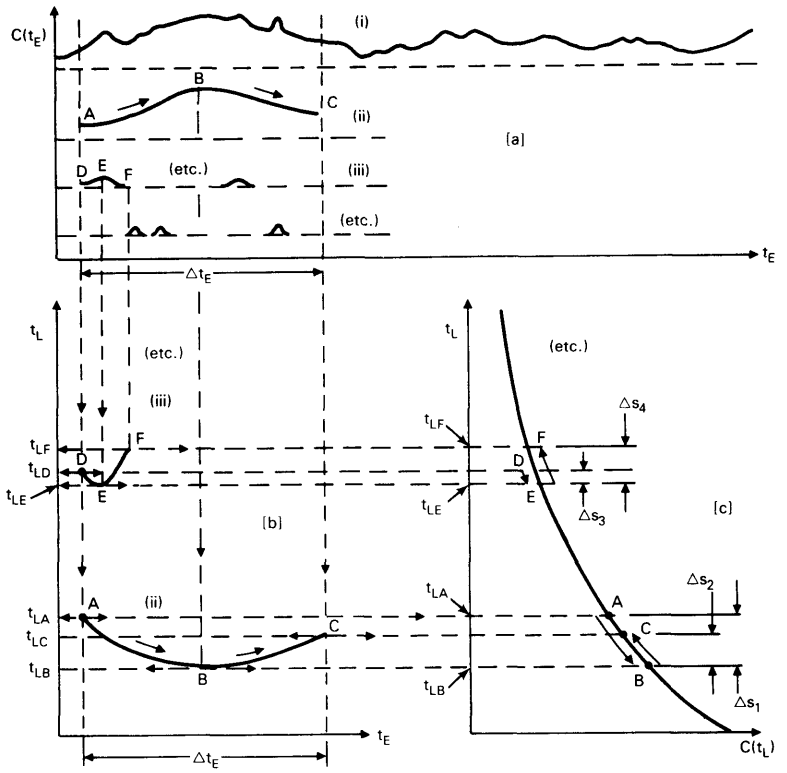

Fig. 1. Qualitative sketches of (a) sampled concentrations as a function of (Eulerian) time, (b) corresponding values of sampled Lagrangian times, and (c) corresponding sampled concentrations as a function of Lagrangian time (with corresponding intervals of Lagrangian time shown at the far right).

In Fig. 1a, curves a(ii), a(iii), etc., plotted only for an Eulerian time interval Δt_E (e.g., the duration of the sampling expedition or sampling campaign), suggest the decomposition of C into contributions from a single source but as a result of these different (Lagrangian) times during which the chemical is assumed to have been in the reservoir. If the detector has a minimum sensitivity or response time, then this decomposition could not proceed indefinitely, but whether or not such limits exist is peripheral to the main point to be demonstrated. Also, no restriction is placed on the duration of the Eulerian sampling interval.

In Fig. 1b, curves b(ii) and (iii) suggest distributions in Lagrangian times t_L (during which the chemical resided in the reservoir) for the corresponding curves in Fig. 1a. Thus, as illustrations, point A on a(ii) has a corresponding point A on b(ii), point B on a(ii) (with larger concentration than at A) corresponds to point B on b(ii) (larger concentrations corresponding to shorter Lagrangian times), and so on, and similarly for the distributions of Lagrangian times for curve b(iii), etc. By this means, one can hypothetically determine the distribution of Lagrangian times that have been sampled during Δt_E.

The curve in Fig. 1c (plotted in a left-handed coordinate system) is the presumed "decay curve" for the concentration as a function of the time during which the chemical has been in the reservoir. The single curve in Fig. 1c is for a single source, but the case of multiple sources

would seem to proceed similarly. Points A, B, etc. in Fig. 1c correspond to those in Fig. 1b (and Fig. 1a), and with them, corresponding Lagrangian time intervals, $t_{LA} - t_{LB} = \Delta s_1$, $t_{LC} - t_{LB} = \Delta s_2$, etc., can be identified. For example, in Fig. 1c, A to B corresponds to a time interval when the concentration continued to increase (e.g., because the chemical took a more direct route to the sampler), and then from B to C, continuously longer Lagrangian times are presumed to have been sampled. On the right-most edge of Fig. 1c are corresponding ranges of sampled times, Δs_j. In Sa, a "peculiar" coefficient of deviation, F_c (the standard deviation divided by the mean), is calculated by averaging over individual Lagrangian time intervals, Δs_j.

Importantly for what follows, this coefficient of deviation is found in Sa to be independent of the (absolute) Lagrangian time, dependent only on the interval of sampled Lagrangian times, Δs. Specifically, eq. (3b) in Sa, with a typographical error corrected, gives

$$F_c^2 + 1 = \frac{\Delta s}{2T_r} \frac{[1 - \exp\{-2(\Delta s)/T_r\}]}{[1 - \exp\{-(\Delta s)/T_r\}]^2}, \quad (1)$$

in which T_r is the chemical's residence time. Thus, for example, if a week of Lagrangian times are sampled from B to C in Fig. 1c (e.g., at an average "Lagrangian downwind time" of a month), then the calculated F_c would be the same as for a week of Lagrangian times from E to F (e.g., at an average downwind Lagrangian time of a year).

Also important for what follows is that, if the range of sampled times, Δs, is much smaller than the chemical's residence time, then a second-order expansion of (1) for $\Delta s \ll T_r$ gives

$$F_c \to \frac{1}{\sqrt{12}} \frac{\Delta s}{T_r}, \quad (2)$$

i.e., F_c becomes linearly proportional to $(\Delta s/T_r)$. The result (2) therefore not only reflects Junge's empirical result, it permits a linear addition of contributions from different sources (superposition), and it suggests that the largest Δs contributes most to F_c. But to suggest that the total F_c can be estimated simply by summing contributions from different records implies that there are no correlations between these records, an assumption that needs investigations, especially for pulsating sinks and sources (e.g., the biosphere). However, a pulsating source, alone, would make no contribution to this F_c, because when the Lagrangian travel times are identical, the corresponding Δs would be zero (Slinn, 1989).

3. Distributions of sampled Lagrangian times

To explain the proposed experimental test of the two theories, it is useful to introduce the concepts shown in Fig. 2. To see how Fig. 2 might be conceptually constructed, first choose one value for Δt_E (as in Fig. 1) and plot a histogram (or probability density function = pdf) describing the distribution of the Δs_j values that were sampled during this one expedition (e.g., a histogram of the Δs_j values shown on the far right-hand side of Fig. 1c). Then, what is sketched in Fig. 2 (rotated vertically and using a left-handed coordinate system) above the specific Δt_E value is this pdf of sampled Lagrangian times. Note that all of Fig. 1 is for one sampling expedition (viz., one Δt_E, say for 10 h) and therefore corresponds to only one pdf on the abscissa of Fig. 2 (viz., at $\Delta t_E = 10$ h).

It is then assumed that pdfs could be found similarly for all other Δt_E values and the hypothetical results are sketched in Fig. 2. Thus, suppose that a number of sampling expeditions had been conducted (or divide one long data record into a number of subintervals, possibly overlapping), with data record "i" of duration Δt_{E_i} (e.g., a week, a month, etc.). For each, as shown in Figs. 1a–c, there is a distribution of sampled Lagrangian time intervals (e.g., from 1 year to 1 year plus a day, from 10 years to 10 years plus a week, etc.). Then the many pdfs sketched in Fig. 2 attempt to show the range in Lagrangian intervals Δs that would have been sampled as a function of the duration of each sampling expedition (viz., the pdfs for Δs plotted at each Δt_{E_i}).

The following notes are added to help the reader through other assumed features of this qualitative Fig. 2.

The short-dash line at the top of Fig. 2 reflects the suggestion that, for different instruments, there is expected to be a maximum Δs that could be sampled because of minimum instrument sensitivity (i.e., for large enough Δs, it is assumed that the signal would be lost in instrument noise).

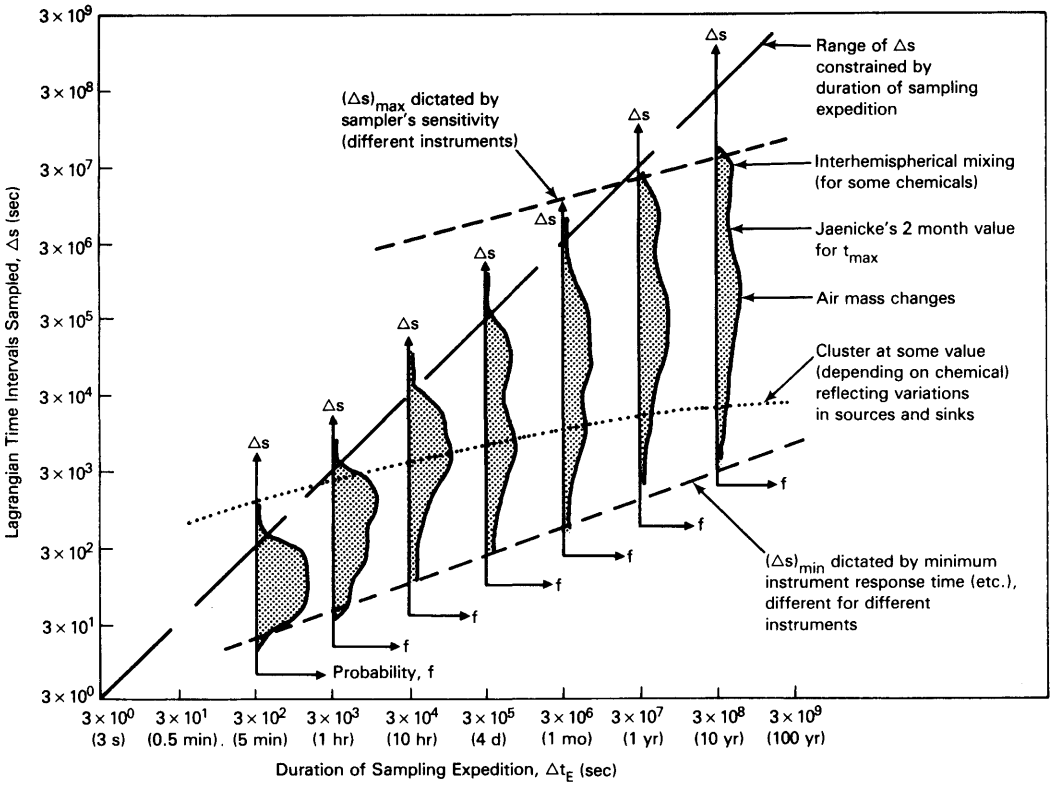

Fig. 2. Qualitative sketches of the distributions of Lagrangian time intervals sampled during each measurement expedition.

The long-dash diagonal line with unit slope, important in what follows, represents an equivalence of the two time intervals, i.e., Lagrangian time intervals equal to the duration of the sampling expedition. It is expected that rarely would one be able to sample *differences* in Lagrangian times larger than the Eulerian time of the expedition (e.g., during a week's expedition, sample differences in Lagrangian times larger than a week, on a single curve of concentration versus Lagrangian time). However, the possibility that $\Delta s > \Delta t_E$ is not inconceivable: transport of the chemical past the sampling station could result in sampling, say during a week, a single "plume" whose differences in Lagrangian times were, say, 2 weeks. But these are expected to be exceptional cases; consequently, the "tails" of the pdfs barely extend past this line defined by $\Delta s = \Delta t_E$.

The dotted line in Fig. 2 schematically suggests that there might be a cluster of sampled Lagrangian times (i.e., a local maximum in each pdf) that reflects some characteristic frequencies for variations in the spatial distributions of either the sources or sinks (or both) for the chemical; this dotted line is curved, since new variations might become apparent as the expedition time increased. Additional clusters in the pdfs are suggested for characteristic times for air mass changes (at times of the order of a week) and for interhemispheric mixing (which might be relevant for some chemicals whose source distributions are not globally uniform).

Finally, the short-dash line at the bottom of Fig. 2 suggests a minimum Δs that could by detected because of limited instrument response time. This line is curved to suggest that different instruments might be used for different Eulerian sampling periods.

Also shown in Fig. 2 is the single t_{max} value

suggested by Jaenicke and the subject of much of what follows.

4. Differences in hypotheses

In contrast to the method in Sa, in which averages were performed over an arbitrary Lagrangian time period, Δs (or, equivalently, over space, as Hamrud perceived), Jaenicke (1982) forms averages of the concentrations from (Eulerian) time zero to a time t_{max}. In his paper he states: "It immediately becomes obvious that a time t_{max} has to be introduced as upper limit of the averaging period." With respect to this t_{max}, Jaenicke (1982) states:

> We now will try estimating a value of t_{max} for the troposphere. Obviously t_{max} is determined from meteorological parameters and the general mixing of the troposphere and is independent from the individual trace gas species. . . . The gases with the smallest relative standard deviation . . . as compared to our model . . . suggest an apparent $t_{max} = 3$ months. We tend to assume a $t_{max} = 2$ months as valid for transport in the troposphere. It remains for future research to (prove) the validity of the above model and the meteorological significance of t_{max} in general and $t_{max} = 2$ months as a quantity.

In what follows, the goal is to suggest measurements that might be capable of distinguishing between the 2 models.

Stripped of the theoretical differences between the two models (related to calculations using Lagrangian versus Eulerian times), the practical difference is that Jaenicke has proposed that the constant in Junge's empirical result (0.14 years) has meteorological significance, whereas in Sa, Junge's empirical "constant" is, unfortunately, not a constant, but is found to depend on the Lagrangian times that have been sampled. Thereby, according to Fig. 2, it is suggested that Junge's constant depends on a number of variables, including (1) the duration of the sampling expedition, (2) a (complicated) dependence on source and sink distributions, trajectories, etc., and (3) characteristics of the sampling instrument. Of most significance for the present purpose, however, is the suggestion that—especially for short-duration sampling expeditions—the most important Δs values (at least, those most important for the calculation of F_c, viz., the largest Δs values) will be essentially the (Eulerian) sampling time.

5. Suggested test of hypotheses

Fortunately, some data may already be available that would allow a test of the 2 hypotheses. To define the suggested test, let δt_E be the time required to obtain a single sample (e.g., 1 s for some instruments, perhaps 1 h for a filter pack or similar integrator, and possibly longer for other sampling strategies). Choose a number of sampling periods (or "sampling expedition periods" or "averaging periods"), Δt_{E_i} (e.g., a day, week, month, etc.), which can overlap, and calculate the coefficient of deviation F_c for each Δt_{E_i} (i.e., calculate F_c, simply by evaluating the means and standard deviations from each record, for the number of samples $N_i = \Delta t_{E_i}/\delta t_E$). Finally, plot F_c versus Δt_E for the chosen values of the Eulerian averaging periods Δt_{E_i}.

If this were done for gases with fairly long residence times compared to the maximum expedition time Δt_E (e.g., for CH_4, use a maximum Δt_E no longer than a month or so, and for CO_2, no longer than a few months), then it is suggested that the linear result (2) would hold, and therefore, it is expected that F_c would increase essentially linearly with Δt_E, especially for small Δt_E. That is, summing over contributions from many Δs_j would primarily give the contribution from the largest Δs, which would be essentially Δt_E, especially for small Δt_E. In contrast, if Jaenicke's model is correct, then it is expected that F_c will be independent of Δt_E.

Although it is readily admitted that the approximations used herein are crude (calculated correctly, the appropriate mean and mean-square values would need to be averaged over the (unknown) distribution of Δs values), it is nevertheless suggested that if experimentalists do find that F_c increases linearly with this $\Delta t_E \approx \Delta s$, especially for small Δt_E, then the initial slope of this line $[\lim(\Delta t_E \to 0)\{dF_c/d(\Delta t_E)\}]$ should give a better estimate of the residence time than the estimates given by Junge's empirical result or by Jaenicke's model. Specifically, for $\Delta s \ll T_r$, then from (2) the inverse of this slope is predicted to be $\approx \sqrt{12}T_r$.

However, because of the many approximations introduced, not much stock should be put in the constant $\sqrt{12}$. For example, this constant could easily be made a factor of 2 larger by choosing the representative Δs to be half the value of Δt_E.

Also, Hamrud has shown, for example, that variations in the areal distributions of the sources can make large contributions to F_c. Nevertheless, the point emphasized here is that neither Jaenicke's model nor Junge's empirical result predicts any variation of F_c with the duration of the sampling, and if the theory in Sa has any validity, it may then have some value in suggesting how better estimates for T_r can be obtained from F_c measurements by at least eliminating the dependence of F_c on the sampling time. Moreover, it seems that this same technique would apply for chemicals in other reservoirs, e.g., various hydrocarbons in lakes and various carbon compounds in the ocean.

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