Do Photochemical Clocks Keep Time? The Interaction of Mixing and Aging in the Troposphere

D.D. Parrish, A. Stohl, C. Forster, E.L. Atlas, P.D. Goldan and W.C. Kuster

1. Introduction

Nonmethane hydrocarbons (NMHC) are ubiquitous trace species of the troposphere that provide useful indicators of atmospheric oxidation and transport processes. No air parcel is ever transported and photochemically aged in isolation; transport is always accompanied by dispersion and mixing to a greater or lesser extent. Many studies have utilized NMHC as indicators of photochemical processing and have attempted to account for the confounding effects of mixing and dispersion through a variety of strategies. The use of ratios of NMHC are useful since they minimize the effect of dilution. Our goal here is to examine the effect of atmospheric mixing on two photochemical clocks based on the ratios of light alkanes in order to determine if they provide robust measures of the extent of photochemical processing.

2. Required Formalism

In an isolated air parcel NMHC concentrations, [A], [B], etc. are simply described by 3 equations if oxidation is only by OH. $[A]_0$ is the concentration at the initial emission time, t_E, and k_A is the reaction rate constant. Equation (2) suggests the physical meaning and an operational definition of photochemical age, t_a. Equation (3) shows the utility of NMHC ratios, where $[A]_0/[B]_0$ is the emission ratio of 2 NMHC.

$$\ln[A] = \ln[A]_0 - \int_{t=t_E}^{t} k_A[OH]dt \quad (1)$$

$$t_a = \int_{t=t_E}^{t} [OH]dt = -\frac{1}{\langle k_A \rangle} \ln\left(\frac{[A]}{[A]_0}\right) \quad (2)$$

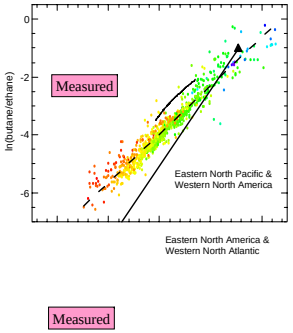
$$t_a = -\frac{1}{\langle k_A - k_B \rangle} \left\langle \ln\left(\frac{[A]}{[B]}\right) - \ln\left(\frac{[A]_0}{[B]_0}\right) \right\rangle \quad (3)$$

The effects of mixing between air parcels are treated by considering continuous emissions into a sampled air parcel. Each emission element has its own, well-defined emission time. $[A](t_E)$ is the concentration of the NMHC that was emitted at time t_E and remains in the air parcel at sampling time t_M. The integral sums emissions from the distant past ($t_E = 0$) up to the measurement time.

$$[A] = \int_{t_E=0}^{t_E=t_M} [A](t_E)dt_E \quad (4)$$

$$[A](t_E) = [A]_0(t_E) \exp\left\{-\int_{t=t_E}^{t} k_A[OH]dt\right\} \quad (5)$$

3. Comparison of Two Clocks: Observations



Measured

Comparison of 2 photochemical clocks should follow the relationship of the above equation, and yield a slope of 2.61 in Figure 1. However, this relationship fails, even though each clock gives precise results over several e-foldings, or > 2 months of aging at [OH] of 10^6 cm^{-3}. This failure is commonly attributed to the effects of mixing of air with different histories.

$$\ln\left(\frac{[A]}{[C]}\right) = -\frac{\langle k_A - k_C \rangle}{\langle k_B - k_C \rangle} \ln\left(\frac{[B]}{[C]}\right) + c$$

Conclusion: Hydrocarbon ratio clocks are precise, but do not agree quantitatively.

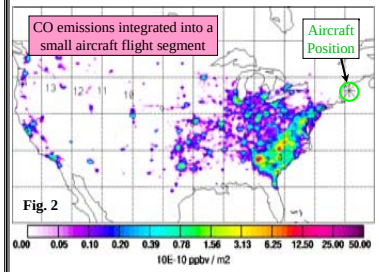
Fig. 1. Correlation between two photochemical clocks for all samples from two field studies. Slopes and r^2 for linear least-squares fits (dashed lines) are given. The straight solid line indicates aging of an isolated air parcel beginning at the estimated Northern Hemisphere average emission ratios (triangle), while the curved solid line indicates mixing of fresh emissions into the well-stirred reactor model (circle).

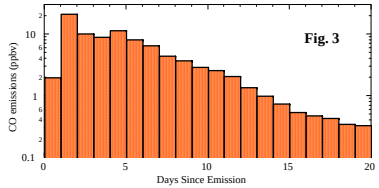
4. Well-Stirred Reactor Model of Troposphere

A well-stirred reactor model is useful conceptual limit for the effects of mixing on NMHC ratios. If it is assumed that emitted NMHC are mixed throughout the troposphere much faster than they are removed by reaction, then the ratio of two NMHCis simply a function of their emission ratio and rate constants. This result isgiven by the circle for the two NMHC ratios compared in Figure 1. Mixing of fresh emissions into the background troposphere defines the curved solid line in that figure.

$$\frac{[A]}{[B]} = \frac{E_A \langle k_B \rangle}{E_B \langle k_A \rangle}$$

5. Mixing defined by FLEXPART Age Spectra





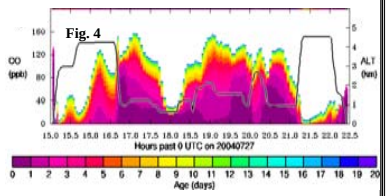


Fig. 2. For each short flight segment FLEXPART calculates 40,000 back trajectories to derive the CO emission footprint integrated into air sampled at that position. **Fig. 3.** FLEXPART sums the emissions to yield an age spectrum for each sample. **Fig. 4.** FLEXPART age spectra calculated for one flight

To properly evaluate the simultaneous effects of mixing and aging, a global chemical transport model is required. For our purposes here we combine an ultra-simple chemical module (constant [OH]) with the transport described by FLEXPART, a Lagrangian particle dispersion model. The FLEXPART results (Figure 2) show that every sample represents a wide history of emissions that is described by its age spectrum. Here we use the age spectra for the ITCT 2K2 (3657 calculated for 30 day periods) and NEAQS/ITCT 2004 (4459 for 20 days) aircraft campaigns to calculate the alkane ratio relationships expected for the analysis illustrated in Figure 1. This calculation entails applying Eq. (2) to each of the three alkanes through integration by summing over the each histogram bin (e.g. Figure 3) with Eq. (3) applied. For each alkane, $[A]_0(t_E)$ is taken proportional to the FLEXPART CO emissions, so as to agree with the Northern Hemisphere average emission ratios (triangle in Figure 1) and the ratio of global emissions of ethane to CO.

Figure 5 compares the average age spectra for the two field studies. After the FLEXPART calculation period the age spectra are assumed to be identical (solid lines), and to relax to the limit of uniform mixing of total emissions throughout the Northern Hemisphere (arrow) with a 30 day time constant. The results are insensitive to the details of the extrapolation.

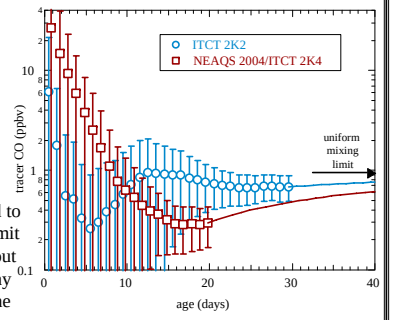
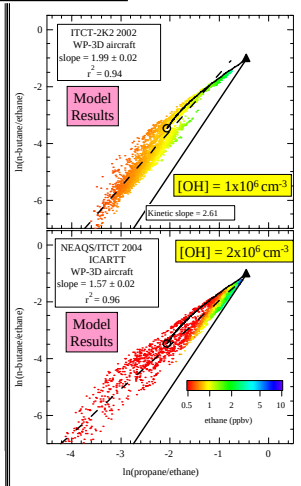


Fig. 5. Average and standard deviation of CO emissions in each bin of age spectra, compared to uniform mixing limit.



6. Comparison of Two Clocks: Model Results

Applying Eqs. (2) and (3) to all of the age spectra from each field study for all three alkanes predicts the photochemical clock behavior shown in Figure 6. This plot can be compared directly to the observed behavior shown in Figure 1. The constant [OH] was set to values appropriate for the spring ITCT 2K2 and summer NEAQS/ITCT 2004 studies. The model results well approximate the observations; the differences in the slopes of the linear fits are due more to differences in the fresh emissions than in the aging and mixing behavior. Even the absolute concentration of ethane indicated by the color-coding is approximately correct.

Fig. 6. Correlation between two photochemical clocks for all FLEXPART age spectra calculated for two field studies. The format is the same as in Figure 1.

7. Interpretation of Photochemical Age

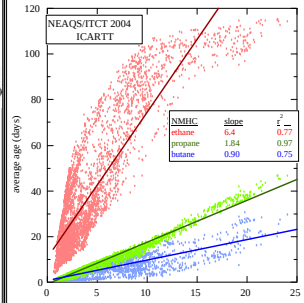


Fig. 7. Average FLEXPART age from Eq. 6 for three alkanes compared to photochemical age derived from FLEXPART butane/ethane ratio and Eq. (3).

$$\langle age \rangle = \int_{t_E=0}^{t_E=t_M} t_E[A](t_E)dt_E \Big/ \int_{t_E=0}^{t_E=t_M} [A](t_E)dt_E \quad (6)$$

The average age of any NMHC can be calculated From Eq. (6) using the FLEXPART age spectra. In Figure 3 average age of three alkanes are compared with the photochemical age derived from the butane/ethane ratio using Eq. (3). The butane/ethane ratios are also from the FLEXPART age spectra. The average ages do correlate reasonably well with the photochemical age. However, the slopes deviate significantly from unity, and this deviation can be quite large when the time constant of the photochemical clock, $(k_A\text{-}k_B)^{-1}$, is much different from the time constant for the NMHC, k_C^{-1}. Any interpretation of aging using NMHC ratios should account for such mixing effects.

7. Conclusions

- **Mixing and OH oxidation can quantitatively explain the evolution of light alkane ratios; there is no evidence for a significant contribution from other oxidants (e.g. Cl atoms).**
- **The age of an air parcel is ill-defined; each species has its own average age.**
- **Photochemical clocks based on light alkane ratios do keep "time", but we must interpret the "time" correctly.**