The Use of Photochemical Ages To Describe Emissions and Chemistry of VOCs in the LA Basin

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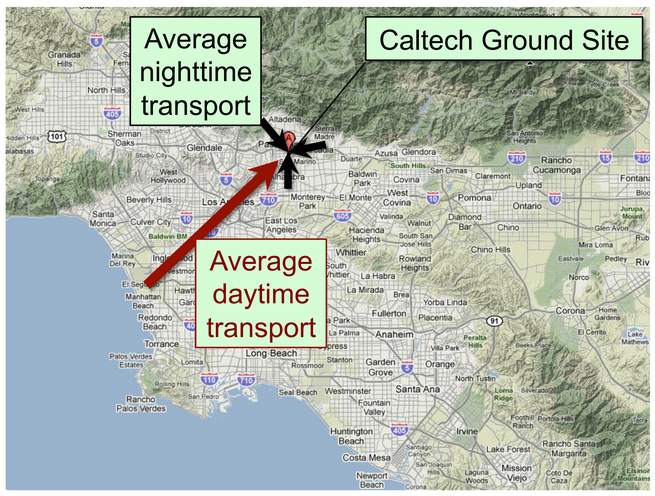
1. Introduction

An extensive set of VOCs was measured by GC-MS on the Caltech campus during CalNex. Here, we attempt to describe the variability in measured VOCs using 2 simplifying assumptions:

1. VOC emissions have the same composition across the basin
2. Aging of VOCs is dominated by OH chemistry and can be described using a photochemical age



The photochemical age Δt of an air mass is determined from the ratio of 2 measured hydrocarbons:

HC_1 + OH ➔ products k_1
HC_2 + OH ➔ products k_2

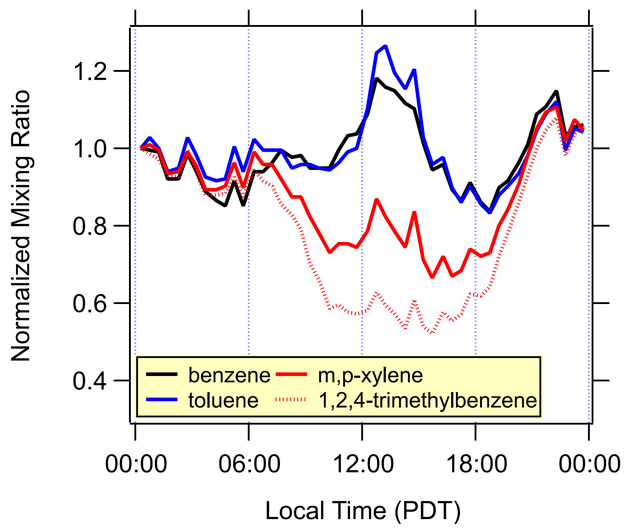
The ratio between HC_1 and HC_2 is:

$$\frac{HC_1}{HC_2} = ER_{12} \times \exp\left(-(k_1 - k_2)[OH]\Delta t\right)$$

where ER_{12} is the emission ratio of HC1 vs. HC2. This can be solved for Δt:

$$\Delta t = \frac{\ln(ER_{12}) - \ln(HC_1/HC_2)}{(k_1 - k_2)[OH]}$$

Benzene/toluene ratios were used in the past [*de Gouw et al.*, 2005], but this clock is too slow for this data set. Instead, we use here the ratio between benzene and the more reactive 1,2,4-trimethyl benzene.



2. Hydrocarbon Removal

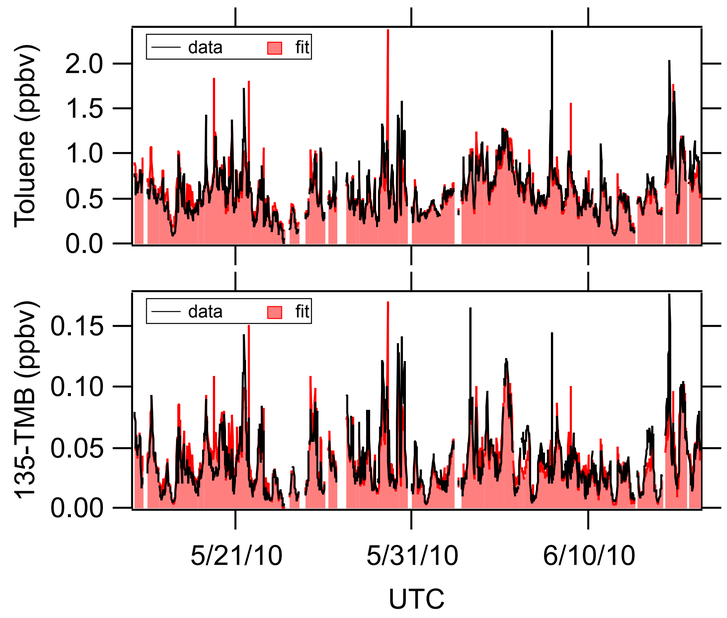
We assume that hydrocarbons are removed by OH:

HC + OH ➔ products

The ratio of HC relative to the combustion tracer ethyne (C_2H_2) is:

$$\frac{HC}{C_2H_2} = ER_{HC} \times \exp\left(-(k_{HC} - k_{C_2H_2})[OH]\Delta t\right)$$

The measurement of HC can be fit using the measured ethyne, the photochemical age Δt, and with 2 fit parameters: the emission ratio vs. ethyne (ER_{HC}) and the rate coefficient (k_{HC}).



3. Formation of Oxygenates

We assume that oxygenated VOCs (OVOC) are formed and removed by:

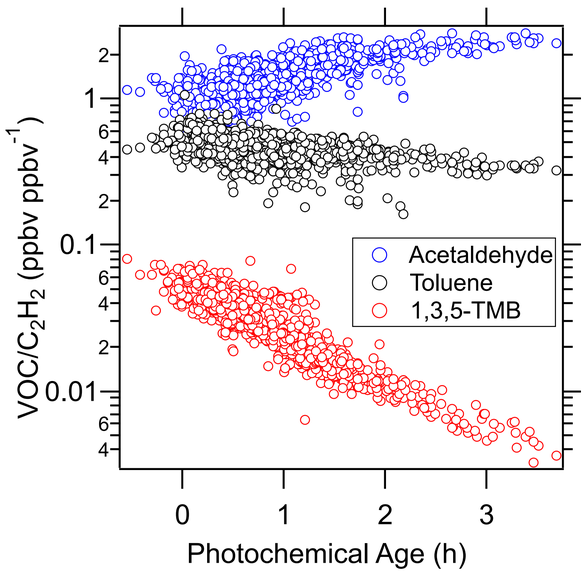
P + OH ➔ OVOC
OVOC + OH ➔ products

The ratio of OVOC relative to ethyne is:

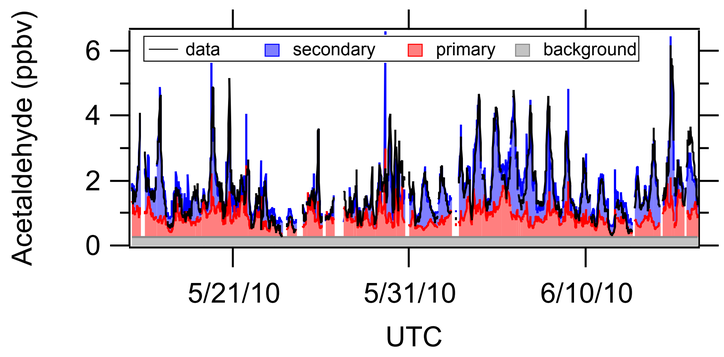
$$\frac{OVOC}{C_2H_2} = ER_{OVOC} \times \exp\left(-(k_{OVOC} - k_{C_2H_2})[OH]\Delta t\right) \quad \text{Direct emissions}$$

$$+ ER_P \times \frac{k_P}{k_{OVOC} - k_P} \times \frac{\exp(-k_P[OH]\Delta t) - \exp(-k_{OVOC}[OH]\Delta t)}{\exp(-k_{C_2H_2}[OH]\Delta t)} \quad \text{Secondary production}$$

$$+ background$$

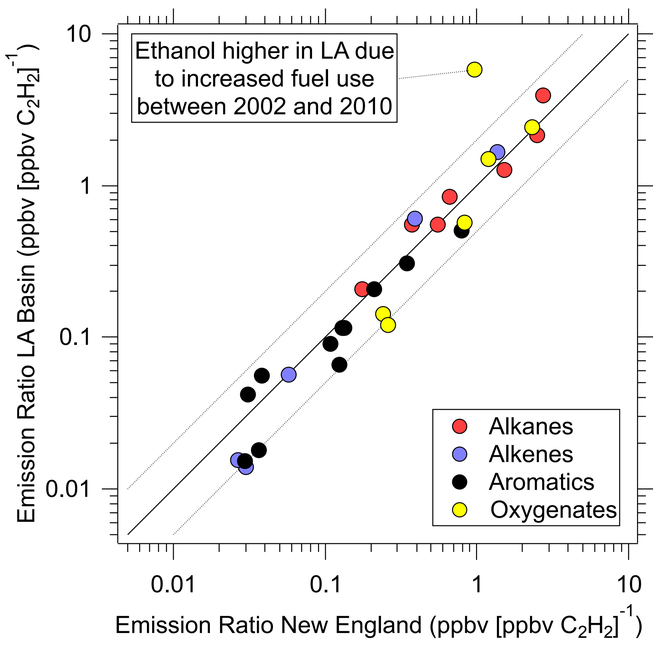


The measurement of OVOC can be fit using (1) the measured ethyne, (2) the photochemical age Δt, and with 4 fit parameters: the OVOC emission ratio (ER_{OVOC}), the emissions ratio (ER_P) and rate coefficient (k_P) of precursor P, and a constant background.



4. Emission Ratios

From the fits, we can estimate emission ratios. The results agree within a factor ~2 with previous estimates from New England [*de Gouw et al.*, 2005] except for ethanol, which use as a gasoline additive has strongly increased in the last decade.



de Gouw, J.A., et al. (2005), Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, J. Geophys. Res.-Atmos., 110, D16305, doi: 10.1029/2004JD005623.