Photochemical histories of nonmethane hydrocarbons inferred from their stable carbon isotope ratio measurements over east Asia

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[1] The first airborne measurements of stable carbon isotope ratios (δ13C) of nonmethane hydrocarbons (NMHCs) were made over east Asia and its downwind regions as part of the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia). The measured δ13C values for ethane, n-butane, and n-pentane varied from approximately −30‰ to −20‰. In contrast, acetylene showed much higher δ13C with a wide variation (−10‰ to +20‰). These are consistent with the high δ13C values of combustion-derived acetylene and a significant isotopic fractionation due to photochemical removal process. Vertical profiles of δ13C-derived photochemical ages of NMHCs differed from one NMHC to another: less reactive ethane and acetylene showed linear increases in age with altitude (8 days below 1 km to 20 days at about 6 km altitude), whereas more reactive n-butane and n-pentane (4 days) had no age gradient. This suggests that less reactive NMHCs in high-altitude air are transported from upwind source regions and mixed with fresh emissions from east Asia, while reactive NMHCs, even in the free troposphere, have recently been emitted. Thus vertical profiles are caused by the mixing of fresh emissions with aged air masses containing reactivity-determined amounts of photochemically aged NMHCs. This mixing causes the difference in the photochemical ages calculated by two methods (the “hydrocarbon clock” method using n-butane/ethane ratios and the “isotopic hydrocarbon clock” method using δ13C values of ethane).


1. Introduction

[2] Anthropogenic emissions of nonmethane hydrocarbons (NMHCs) into the urban atmosphere play an important role in the atmospheric chemistry of OH radicals, ozone and other oxidants. They are emitted primarily from surface sources (e.g., industrial activities, fossil fuel production and consumption, and biomass burning) with relatively well known emission ratios. After emission to the atmosphere, NMHCs are subjected to photochemical degradation mainly by OH radicals, which react at unique rates with each species. Hence, concentration ratios of NMHCs have been widely used to estimate the “photochemical age” of air masses [Rudolph and Johnen, 1990; Parrish et al., 1992; Blake et al., 1996a; Kleinman et al., 2003; de Gouw et al., 2005] and to estimate concentrations of OH [Roberts et al., 1984; Blake et al., 1993; Kramp and Voll-Thomas, 1997] and other radicals [Jobson et al., 1994; Wingenter et al., 1996; Penkett et al., 2007].

[3] Recent developments in stable carbon isotopic (δ13C) measurement of NMHCs [Rudolph et al., 1997] allow us to estimate the photochemical age of each hydrocarbon [Rudolph and Czuba, 2000]. During the last decade, several studies have determined NMHC isotopic signatures for some important emission sources [Czapienski et al., 2002; Rudolph et al., 2002; Nara et al., 2006] and the isotopic fractionation factors associated with the degradation of NMHCs [Rudolph et al., 2000; Anderson et al., 2004]. These observational and laboratory studies have revealed that δ13C of the various NMHCs in emission sources are similar, in contrast to other volatile organic compounds (e.g., methyl chloride [e.g., Thompson et al., 2002; Saito and Yokouchi, 2008]). They also showed that the magnitude...
of kinetic isotopic fractionation in the atmosphere is high enough to be observed, suggesting that \( \delta^{13}C \) can be used as an indicator of atmospheric processing. Measurements of ambient \( \delta^{13}C \) have been made [Rudolph et al., 1997; Tsunogai et al., 1999; Rudolph et al., 2000, 2002; Saito et al., 2002; Rudolph et al., 2003; Naka et al., 2007; Redeker et al., 2007] and used, in some cases, to estimate photochemical age. However, these studies are all limited to surface sites, so there are no reports of vertical trends in isotopic composition.

[4] Vertical mixing and changes in NMHC concentrations during long-range atmospheric transport have been studied from aircraft [e.g., Blake et al., 1996b]. We made stable carbon isotopic (\( \delta^{13}C \)) measurements of NMHCs from an aircraft over east Asia and its outflow regions (the western North Pacific) in spring, when the continental outflow of Asian pollution is most significant [Liu et al., 2003]. We use the observed variations of \( \delta^{13}C \) to estimate the degree of photochemical processing of NMHCs and to determine the factors controlling NMHC composition in east Asian air masses.

2. Experimental Procedure

[5] Air samples (n = 49) were collected aboard the NCAR Lockheed C-130 aircraft over the east Asian region during the research flights (RF01, RF03, RF05, RF10, RF13, and RF19) of the ACE-Asia campaign [Huebert et al., 2003], between 30 March and 3 May 2001, at altitudes up to 7 km (Figure 1). Eleven additional samples were collected during ferry flights over the western North Pacific from Iwakuni, Japan to Hawaii at altitudes of 5800–6500 m, from 7 to 9 May 2001. Air samples were pressurized (using a metal bellows pump) to about 40 psi into preevacuated 2-L electrochemically polished canisters. Twelve canisters were fixed in a stainless steel rack on board the C-130. Filled canisters were sent to the laboratory at Hokkaido University and analyzed within 1 week of collection.

[6] We measured stable carbon isotope ratios of NMHCs with a cryogenic vacuum extraction line and a gas chromatograph-combustion-isotope ratio mass spectrometer (GC-C-IRMS), using the method described by Rudolph et al. [1997]. Details of the experimental setup are documented by Tsunogai et al. [1999]. Briefly, each air sample (~6 L) was condensed in a three-stage preconcentration process in a bath of liquid N\(_2\). During the process, bulk air gases (mostly N\(_2\) and O\(_2\)), water vapor, and CO\(_2\) were removed. The purified air matrix including NMHCs was then introduced to the GC equipped with a PoraPLOT-Q capillary column (25 m long \( \times \) 0.32 mm internal diameter) after a cryofocusing step at liquid N\(_2\) temperature at the head of the capillary column. The stable carbon isotope ratios of the NMHCs were measured with an IRMS (Finnigan MAT 252) in continuous flow mode, following combustion of the NMHCs to CO\(_2\).

[7] The accuracy of the isotopic measurements was estimated to be better than 0.3\% by measuring a National Institute of Standards and Technology (NIST) RM 8560 (International Atomic Energy Agency (IAEA) NGS2) isotopic standard. The reproducibilities derived from repeat analyses of a working standard were less than 0.5\% for GC injection >200 pmol C, <1.5\% for 80–200 pmol C, and <2\% for 30–80 pmol C. The mixing ratios of ethane, \( n \)-butane, and \( n \)-pentane were calculated by comparing each \(^{44}\text{CO}_2 \) peak area (m/z 44) with that of a calibrated amount of working standard gas mixture. The mixing ratio of acetylene was determined from its \(^{44}\text{CO}_2 \) peak area relative to that of ethane. The reproducibility of the concentration measurements was better than 10\%. We do not report on propane because of a sporadic contamination peak during the measurement of propane’s \( \delta^{13}C \). Similarly, \( i \)-butane and \( i \)-pentane are not discussed owing to large uncertainties (>±4\%) caused by low mixing ratios and broad chromatographic peaks.

3. Results and Discussion

3.1. Air Mass Classification Based on Back Trajectory Analysis

[8] To estimate recent histories of the sampled air masses, we analyzed air mass trajectories for each sample on the
basis of 5-day back trajectories using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT 4) model (http://www.arl.noaa.gov/ready/hysplit4.html). Trajectory analyses showed that most of the sampled air masses had passed over east Asia. We classified air masses into two categories on the basis of the trajectories. The first category was air masses that stayed below 2 km altitude for more than 6 h over China, Korea, or Japan. We classified these as “fresh emissions.” The second category included air masses that stayed above 2 km. We called these “aged emissions.” This approach is similar to that of Blake et al. [2003].

Among the total 49 samples, 23 and 25 samples were classified as “fresh” and “aged” emissions, respectively. The remaining sample had traveled over the Sea of Japan below 2 km for the previous 5 days, so it was not classified. Air mass classification is discussed in sections 3.2.2 and 3.3.1.

3.2. Vertical Profiles of NMHC Mixing Ratios and Stable Carbon Isotopic Ratios

Vertical profiles of NMHC mixing ratios and stable carbon isotopic ratios are shown in Figure 2. The mixing ratios of all the NMHC components decreased as a function of altitude. For example, the average mixing ratio of ethane decreased from about 2600 pptv in the boundary layer to 1300 pptv at 6 km. The vertical distributions of ethane and acetylene were comparable to those over the western North Pacific during PEM-West B [Blake et al., 1997] and TRACE-P [Blake et al., 2003].

3.2.1. Ethane

The stable carbon isotopic ratio of ethane in our samples ranged from −27.4‰ to −23.4‰ with a mean of −25.8‰ (+1.1‰). The most striking feature of the ethane data is an increasing trend of δ13C from −28 ‰ at low altitude to −24 ‰ in the middle troposphere (∼6 km), whereas the mixing ratios showed a decrease. In the 11 samples collected during the flights from Japan to Hawaii, only ethane was above the limit of determination (less than ±4‰) for δ13C measurements; these data are plotted in Figure 3 against longitude. The δ13C values of ethane were higher (−24.5‰ to −20.5‰) than those near the western rim of the Pacific. Interestingly, they showed a gradual increase from west to east, while mixing ratios decreased.

The observed change in the δ13C values of ethane, as well as those of other NMHCs, can be explained by the δ13C values of their emissions, isotopic fractionation associated with their removal process, and the mixing of different air masses. On a global scale, biomass burning and leaking of natural gas are important sources of ethane [Rudolph, 1995]. Isotopic studies of ethane emitted from biomass burning have reported δ13C values of around −28‰, comparable to those of plant materials. The burning of C4 plants cause higher δ13C values [Czapiewski et al., 2002; Nara et al., 2006]. A wide variety of δ13C values have been reported for ethane in natural gas: −25.8 ± 3.4‰ in Japan [Sakata, 1991; Igarı, 1999] and −30.8 ± 6.4‰ in China [Xu et al., 1997]. Our observed δ13C values for ethane at lower altitudes (about −27‰) are within the range reported for fresh biomass burning and natural gas emissions.

The major sink for NMHCs is reaction with atmospheric OH radicals. Because OH radicals more rapidly attack hydrogen atoms in the molecules consisting of 13C [Rudolph et al., 2000], the δ13C values of NMHCs remaining in the atmosphere increase as a result of this loss. Figure 4 shows a good correlation between mixing ratios of ethane and its δ13C values. The increase of δ13C with decreasing mixing ratios is consistent with a positive kinetic isotope effect (KIE) for the removal of ethane. However, the slope of a least squares fit to the measurements (apparent KIE, εapp = 2.8 ± 0.6‰) is smaller than that predicted by the Rayleigh dependence between isotope ratio and mixing ratio for the reaction of ethane with OH radicals (εapp = 8.57 ± 1.9‰ [Anderson et al., 2004, Table 1]). The other NMHCs also have ambient KIEs lower than laboratory KIEs for reaction with OH (Figure 4). The Rayleigh dependence is based on the assumption that an air mass is closed (no dilution or mixing). However, the real atmosphere often violates this assumption: mixing generally lowers the apparent KIE in a polluted atmosphere. This is because dilution causes a more pronounced change in the mixing ratio than in the isotope ratio. Hence, the lower apparent KIE suggests there was substantial impact of dilution (mixing with cleaner air). Although OH oxidation is generally thought to dominate the atmospheric removal of NMHCs, some authors have suggested a significant role for chlorine atoms in the marine boundary layer [e.g., Pszeny et al., 2007]. However, the KIEs in reactions with Cl atoms are not significantly different from those with OH radicals [Anderson et al., 2007].

Mixing ratio-dependent changes of δ13C for ethane have also been reported in previous studies in the western North Pacific [Tsunogai et al., 1999; Saito et al., 2002]. The apparent KIE in this study is consistent with that reported by Tsunogai et al. [1999] (εapp = 3 ± 1‰), but lower than that by Saito et al. [2002] (εapp = 5.5 ± 1.3‰). The difference with Saito et al. [2002] may be due to dilution. Assuming two-end point mixing (such as dilution of emissions by background air), dilution would lower the apparent KIE for the measurements made near a source. Our study area is closer to sources in east Asia than Saito et al.’s [2002] study area was, leading to higher mixing ratios in this study. However, owing to the complicated relationship between isotope ratios, mixing ratios, emissions, atmospheric removal, and mixing of air masses, interpreting differences in apparent KIEs requires additional information.

3.2.2. Acetylene

To our knowledge, there have been no isotopic studies of ambient acetylene outside urban areas. Acetylene in our study was substantially enriched in 13C (mean δ13C of +5.0‰) compared to the other NMHCs (means: −25.8‰ for ethane, −25.4‰ for n-butane, and −25.3‰ for n-pentane). Vertical profile of acetylene δ13C shows a strong upward increase from −1.5‰ (0–1 km) to +15.3‰ (5–7 km), which is more distinct than the vertical profile of δ13C for ethane. Such a large variation (∼30‰) can be attributed to the large KIE (15.8 ± 0.6‰ [Andrew et al., 2000]) for the reaction of acetylene with OH radicals in the atmosphere. This KIE is the second largest (after ethylene) for the reactions of NMHCs [Anderson et al., 2004]. The mixing ratio of acetylene decreased with altitude, resulting in a positive correlation (R2 = 0.77, Figure 4) between the δ13C values and mixing ratios. The apparent KIE (10.9 ± 1.7‰) is lower than the laboratory KIE for the reaction with
Figure 2. Vertical trends of mixing ratios of ethane, acetylene, $n$-butane, and $n$-pentane and their stable carbon isotopic ratios in air samples from the ACE-Asia research flights (solid gray circles). Error bars of the gray circles denote 1σ uncertainty of the individual isotope measurements. Solid black circles show mean mixing ratios and isotopic ratios for intervals of 1 km altitude; horizontal error bars indicate standard deviation. V-PDB is Vienna PeeDee belemnite.
OH radicals, probably owing to dilution. However, we cannot rule out a contribution by Cl atoms, since there is no published KIE for the reaction of acetylene with Cl.

The acetylene $^{13}$C values we measured are much higher than those of ethane even at low altitudes (0–1 km, Figure 2), indicating the importance of an isotopically heavy source of acetylene. One approach for estimating the composition of major emissions uses the relationship between the reciprocal of mixing ratios and $^{13}$C values. If

![Figure 2](image_url)

**Figure 2.** Mixing ratio versus stable carbon isotope ratio plots for (a) ethane, (b) acetylene, (c) $n$-butane, and (d) $n$-pentane from samples collected on the research flights (solid circles) and the Japan-Hawaii flights (open circles). Error bars indicate 1σ uncertainty of the isotope measurements. V-PDB is Vienna PeeDee belemnite.

![Figure 3](image_url)

**Figure 3.** Mixing ratios and isotopic ratios of ethane plotted as a function of longitude for samples from the research flights (solid circles) and the Japan-Hawaii flights (open circles). Error bars indicate 1σ uncertainty of the isotope measurements. V-PDB is Vienna PeeDee belemnite.

![Figure 4](image_url)

**Figure 4.** Mixing ratio versus stable carbon isotope ratio plots for (a) ethane, (b) acetylene, (c) $n$-butane, and (d) $n$-pentane from samples collected on the research flights (solid circles) and the Japan-Hawaii flights (open circles). Error bars indicate 1σ uncertainty of the isotope measurements. The open squares indicate the mean mixing ratios and isotopic ratios in an urban atmosphere as reported by Tsunogai et al. [1999]. The straight lines show the linear least squares fit to all flight data. The dashed lines indicate Rayleigh dependence for reactions of NMHCs with OH radicals based on the average urban values.
two-end-point mixing is responsible for changes in both mixing ratios and $^{13}$C for a compound, the plot of $^{13}$C against the reciprocal of the mixing ratio produces a linear correlation, and the intercept represents the $^{13}$C value of the emission source. However, the application of this approach to reactive compounds such as acetylene is somewhat uncertain because of the effect of the KIE: mixing is not the only process affecting the $^{13}$C of acetylene. [16] Figure 5 shows a linear least squares fit to the “fresh emission” data. The emission source signature (mean with 95\% confidence interval: $-9.3 \pm 3.2$) estimated from the intercept is similar to that of urban areas ($-9.2 \pm 4.2$\% [Tsunogai et al., 1999]; $-5.8 \pm 4.2$\%, [Redeker et al., 2007]). This is consistent with acetylene originating mostly from urban sources. The source composition is slightly larger than those for burning of C3 plant material (Manuka) ($-13.0 \pm 1.6$\% [Rudolph et al., 1997]) and pine (about $-13$\% [Nara et al., 2006]), but lower than that for burning Eucalyptus and Musasa ($-0.4 \pm 4.1$\% [Czapiewski et al., 2002]) and car exhaust ($>0$\%, [Rudolph et al., 2002]).

### 3.3. Butane and Pentane

[17] In contrast to ethane and acetylene, the $^{13}$C values of n-butane and n-pentane did not show a clear altitude trend, although their mixing ratios decreased with altitude (Figure 2). Further, unlike ethane and acetylene, their average values ($-25.9 \pm 2.3$\% for n-butane, $-25.3 \pm 2.6$\% for n-pentane) were similar to those reported in urban areas ($-27.6 \pm 1.1$\% for n-butane, $-24.6 \pm 0.4$\% for n-pentane [Tsunogai et al., 1999]), even though their mixing ratios were much lower than those of urban air. The observed small variations of the $^{13}$C are likely to be due to the relatively small KIE values for the reaction with OH radicals (Table 1). In addition to the small KIEs, relatively large uncertainty ($\sim$2\%) of the $^{13}$C measurements leads to a weak correlation of the $^{13}$C values with mixing ratios ($R^2 = 0.18$ for n-butane, $R^2 = 0.04$ for n-pentane, Figure 4). These variations of measured $^{13}$C values will be discussed below from the viewpoint of air mass mixing.

### 3.3. Photochemical Ages of NMHCs

[18] In section 3.2, we found an increase of $^{13}$C for ethane and acetylene with increasing altitude, but not for n-butane and n-pentane. To interpret the difference in these vertical profiles, we apply the approach of Rudolph and Czuba [2000]. This technique uses the change in the isotope ratios of NMHCs to quantify the “average extent of photochemical processing of each NMHC.”

#### 3.3.1. Calculations of Photochemical Ages Using $^{13}$C

[19] The photochemical ages of NMHCs, $t$, were calculated using [Rudolph and Czuba, 2000]

$$t = \frac{^{13}C_i - ^{13}C_f}{\varepsilon_{OH} \times k_{OH} \times [OH]},$$

where $^{13}C_i$ and $^{13}C_f$ are temporal and initial isotopic ratios, respectively. $\varepsilon_{OH}$ and $k_{OH}$ are the kinetic isotope effects and rate constants in the reactions between NMHCs and OH radicals, respectively. [OH] represents the average OH radical concentration.

[20] For the calculation of photochemical ages, we assumed the initial values of $^{13}C_i$ were $-31 \pm 1.2$\% for n-butane and $-29 \pm 1.6$\% for n-pentane on the basis of urban source compositions such as tailpipe emissions and fuel evaporation [Rudolph et al., 2002]. We also assumed $^{13}C_i$ value of ethane to be $-28 \pm 1.5$\% [Thompson et al., 2003] and of acetylene to be $-9.6 \pm 4.1$\% [Tsunogai et al., 1999] on the basis of urban air measurements. Parameters related to OH reactions ($\varepsilon_{OH}$ and $k_{OH}$) are summarized in Table 1, and [OH] was assumed to be $10^6$ cm$^{-3}$. The OH radical concentration is similar with the model estimated global annual mean value ($1.16 \times 10^6$ cm$^{-3}$ [Spivakovskiy et al., 2000]) and the model estimate on Jeju island, Korea ($33.17^\circ$N, 126.10$^\circ$E) during the ACE-Asia experiment ($7 \times 10^5$ cm$^{-3}$ [Shon et al., 2004]).

### Table 1. Rate Constants, Estimated Lifetime, and Kinetic Isotope Effects for the Reaction of NMHC With OH Radicals

<table>
<thead>
<tr>
<th>Compound</th>
<th>OH Rate Constant(^a) (10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Lifetime(^b) (days)</th>
<th>KIE(^c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.254</td>
<td>46</td>
<td>8.57 \pm 1.95</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.090</td>
<td>13</td>
<td>15.80 \pm 0.61</td>
</tr>
<tr>
<td>n-butane</td>
<td>2.44</td>
<td>5</td>
<td>5.16 \pm 0.67</td>
</tr>
<tr>
<td>n-pentane</td>
<td>4.00</td>
<td>3</td>
<td>2.85 \pm 0.79</td>
</tr>
</tbody>
</table>

\(^a\)Rate constant data are from Atkinson [1997] for alkanes and from Atkinson [1994] for acetylene.

\(^b\)Lifetimes are estimated using [OH] $= 1 \times 10^6$ cm$^{-3}$.

\(^c\)KIE denotes kinetic isotope effect. Mean values and errors are those reported by Anderson et al. [2004] for alkanes and Rudolph et al. [2000] for acetylene.
Notably, the application of equation (1) to our observations is based on the assumption that the observed NMHCs were derived dominantly from the sources with a uniform isotope ratio (anthropogenic emissions, in this case). Although contributions of other sources (e.g., oceanic emissions) to the observed variations cannot be excluded, it seems unlikely that oceanic emissions of NMHCs were substantial in the western North Pacific, where atmospheric compositions are heavily controlled by outflows from the Asian continent under the conditions of westerly winds [e.g., Kawamura et al., 2003; Kondo et al., 2004]. This conclusion is supported by higher concentration ratios of $i$-pentane to $n$-pentane ($2.3 \pm 0.7$). Lower ratios would imply that oceanic emissions were significant [e.g., Saito et al., 2004]. Our observed ratios far exceed the reported values for seawater (0.6 [Broadgate et al., 1997]), but are consistent with those measured in urban environments (2.1 [Seila et al., 1989]).

### 3.3.2. The $\delta^{13}$C-Derived Photochemical Ages

We plotted the calculated photochemical ages of NMHCs against sampling altitude (Figure 6). As expected from equation (1), the vertical trends of the ages were similar to those of $\delta^{13}$C values; that is, increases in $\delta^{13}$C with altitude are evident for relatively long-lived ethane ($\sim 8–18$ days) and acetylene ($\sim 7–19$ days), but not for short-lived $n$-butane ($\sim 5$ days) and $n$-pentane ($\sim 4$ days). The observed differences in the photochemical ages are caused to some extent by mixing of different air masses, since the observed dependences between isotope ratios and mixing ratios deviate from the theoretical lines for the chemical removal of NMHCs (Figure 4). In general, mixing of air masses will generate a weighted-average age of a substance in the resulting air mass [Rudolph and Czuba, 2000]. An aged air mass would contain photochemically more aged NMHCs with reduced amounts of individual NMHCs, depending on their reactivity. (Free tropospheric substances are probably older than boundary layer ones, since the sources are mostly in the boundary layer.) Less reactive NMHCs would be relatively enriched whereas more reactive NMHCs would be depleted in the atmosphere relative to recently polluted air masses. The effect of mixing air masses with different photochemical ages would be greater for less reactive NMHCs than for more reactive NMHCs, simply because the longer-lived compounds are more likely to be present in background free tropospheric air. Therefore, mixing of a boundary layer air with surrounding air, including that from higher elevation, could explain the increase in the photochemical ages of less reactive NMHCs with altitude. On the contrary, similar ages of the reactive NMHCs with altitude can be interpreted by a mixing with background air containing negligible amounts of these readily removed NMHCs; this process has an insignificant effect on the photochemical age computation.

Our results thus demonstrate that the photochemical ages are different for each NMHC, reflecting their different photochemical histories, and suggest that the variation of

![Figure 6](image-url)
\( \delta^{13}C \) for NMHCs, in addition to their mixing ratios, is largely controlled by mixing of air masses that have experienced different degrees of photochemical processing. This is consistent with the study of Stein and Rudolph [2007], who simulated \( \delta^{13}C \) values of ethane in global chemical transport models and concluded that in the source latitudinal band around 40\(^\circ\)N, dilution of the pollutants with background air is the most important cause for variations in NMHC concentrations.

[24] To better understand the relation between the photochemical ages of NMHCs and the recent histories of air masses, we calculated the average photochemical ages associated with the trajectory-based classifications (i.e., “fresh emissions” and “aged emissions”; see section 3.1). The average ages of ethane and acetylene for “aged emissions” subset (mostly in the free troposphere) were as long as 15 days (Figure 7), suggesting that NMHCs in aged free tropospheric air were predominantly transported from source areas much further upwind. The ages for the “fresh emissions” subset (7–9 days) were shorter than those for the “aged” subset and qualitatively consistent with our classification. However, the computed ages were longer than 5 days, despite the fact that the air left Asia less than 5 days earlier. This would be due to mixing with air masses already containing substantial amount of the aged NMHCs.

[25] The average ages of \( n \)-butane and \( n \)-pentane for the “fresh” air mass subset (3–5 days) were consistent with the air mass histories, suggesting that they were recently emitted from sources in east Asia. Surprisingly, ages in the “aged” subset were nearly identical to the “fresh” subset, even though the “aged” air had not contacted land in the previous 5 days. This might be explained in part by recalling that a back trajectory represents the (quite uncertain) path of a single point. A transport model to represent the dispersion of the pollutant in time and space [Stohl et al., 2002] might better account for dispersion. Thus, in this case, the estimated short ages of \( n \)-butane and \( n \)-pentane in the aged emissions suggest that the air masses have been influenced by more recent emissions prior to be sampled.

[26] To some extent this conundrum also highlights weaknesses in the photochemical age models, which tacitly assume that trace gases are emitted at a single moment into a pristine air mass. Such pollution “events” may not represent the reality of partially polluted air masses that are more or less continually receiving fresh emissions. Nonetheless, deviations from this simple conceptual model are useful for highlighting those compounds with significant sources well upwind of east Asia and the extent to which fresh emissions have been mixed with these air masses.

[27] Figure 8 demonstrates that the average photochemical ages increase with a decrease in the rate constants for the OH reactions, except for ethane. This is reasonable: substances that are removed more slowly will remain airborne longer. However, despite the longer atmospheric life of ethane than acetylene by a factor of three (Table 1), similar apparent photochemical ages (~12 days) were unexpectedly found. If the contribution of fresh emissions to the aged NMHCs in the background atmosphere were greater for ethane than that for acetylene, the average photochemical age of ethane in the mixed air mass would be reduced and might be similar to that of acetylene. An alternative explanation is that the uncertainty for the age determination caused the similar average ages for ethane and acetylene. If we used the lowest end of the reported KIE for ethane within the confidence interval (5.26% [Anderson et al., 2004]), the average photochemical age of ethane would increase to 19 days and thus be longer than that of acetylene.
We compared our results with the only previous study [Saito et al., 2002] that reported photochemical ages of NMHCs in the marine boundary layer. Our results in the marine boundary layer (8.2 ± 6.7 days for ethane and 4.4 ± 2.5 days for \(n\)-butane) are consistent for \(n\)-butane, but substantially lower for ethane compared to the previous study (26.5 ± 10.8 days for ethane and 4.1 ± 3.0 days for \(n\)-butane, recalculated using the parameters \((e_{\text{OH}}\) and \(d^{13}\text{C}\)) used in this study). In both studies, the photochemical ages of \(n\)-butane in the marine boundary layer were generally consistent with the trajectory results, suggesting that the ages reflect the recent input timing. The different ages for ethane might be related with the degree of mixing: that is, ethane in this study was less affected by mixing with background air than in the previous study, since this study area is closer to source regions than the previous study was.

For the flights from Japan to Hawaii, only ethane can be used to calculate photochemical ages; therefore, we could not consider the possible effect of air mass mixing on age. Nevertheless, the high \(^{13}\text{C}\) enrichment of ethane suggests photochemical ages of 20–40 days, increasing from the Asian continent toward the subtropical central North Pacific (Figure 9). These long ages suggest that ethane in the free troposphere over the subtropical central North Pacific was relatively isolated from recent emissions. The longitudinally increasing trend in photochemical age suggests that some ethane originated in east Asia and was photochemically processed during easterly transport over the North Pacific. Higher-than-assumed OH concentrations in the subtropics may also increase apparent NMHC photochemical ages.

### 3.3.3. Hydrocarbon-Ratio-Based Photochemical Ages

Although we described photochemical ages estimated from isotopic measurements above, other approaches have been used to estimate photochemical ages; these are known as “hydrocarbon clocks” [Roberts et al., 1984; Rudolph and Johnen, 1990; Parrish et al., 1992]. Here, we compare photochemical ages estimated by one such “clock” with that from the \(\delta^{13}\text{C}\) method above. The conventional hydrocarbon clock is based on pseudo-first-order decay of alkane as a result of OH radical reactions:

\[
[A]_t = [A]_0 \exp(-k_A \times [OH] \times t),
\]

where \([A]_0\) is the initial concentration of alkane A, \([A]_t\) is its concentration at time \(t\) after emission to the atmosphere, and \(k_A\) is the rate constant for the reaction of hydrocarbon A with OH radicals. From simultaneous measurements of alkanes A and B, which have different reactivities, the hydrocarbon-ratio-based photochemical age can be calculated as follows [Roberts et al., 1984]:

\[
t = \frac{1}{[OH]} \left( \frac{[A]_t}{[B]_t} \right) \ln \left( \frac{[A]_0}{[B]_0} \right).
\]

We used \(n\)-butane and ethane for A and B, which are widely used in this type of analysis. The \(k\) values were taken from Atkinson [1997]. The initial hydrocarbon ratio, \([n\text{-butane}]_i/[\text{ethane}]_i\), was assumed to be 0.35, the average emission ratio in the Northern Hemisphere (as estimated by Parrish et al. [2007] using values reported by Goldstein et al. [1995] and Swanson et al. [2003]). However, it should be noted that the emission ratio has a great variation depending on source types and thus on urban areas (e.g., 0.63 for Taipei [Ding and Wang, 1998]; 0.15–0.22 for Hong Kong [Wang et al., 2003]; 0.46–1.28 for Tokyo [Shirai et al., 2007]).

**Figure 9.** Estimated photochemical age of ethane from samples from the research flights (solid circles) and Japan-Hawaii flights (open circles) plotted as a function of longitude. Error bars show overall uncertainties of the photochemical ages.

**Figure 10.** Correlation of the photochemical ages estimated from \(\delta^{13}\text{C}\) of ethane with those estimated from \(n\)-butane/ethane ratios. Error bars show overall uncertainties of the photochemical ages.
We compared the photochemical ages estimated from \( n \)-butane/ethane ratios with those from the \( \delta^{13}C \) value of ethane. Because both \( n \)-butane/ethane ratios and the \( \delta^{13}C \) value of ethane are based on the same compound (\( ^{12}\text{C}_2\text{H}_6 \)), the comparison is useful for considering the potential effect of different reactivities on the estimated ages. Figure 10 presents the correlation of the photochemical ages estimated by the two methods. Although both estimated ages are similar below \( \approx 10 \) days, the isotope-based estimate shows much higher values for longer periods. Such a difference between the two methods can be semiquantitatively explained by a simple model, similar to the approach of Parrish et al. [1992]. In this model, we considered mixing of an equal amount of two air masses: an air mass with an age of 0 days (a fresh emission), and an aged air mass of different photochemical age (reacted and diluted). The apparent ages of the mixed air masses were calculated with the isotope-based photochemical clock (\( ^{13}\text{C}_2\text{H}_6/^{12}\text{C}_2\text{H}_6 \)) and also with the concentration-based \( (n\text{-butane}/\text{ethane}) \) photochemical clock according to equation (3). The chemical decay of the alkanes was calculated according to equation (2) using the rate constants [Atkinson, 1997] and KIE values [Anderson et al., 2004] for the reactions of hydrocarbons with OH radicals.

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Figure 11. Apparent age of new air masses formed by mixing equal amount of fresh emissions and diluting air versus the age of the diluting air masses. Ages were calculated using a very simple mixing model and two indicators. See text for details.

Figure 12. Photochemical ages estimated from \( \delta^{13}C \) of ethane versus those estimated from \( n \)-butane/ethane ratios calculated using a very simple mixing model (see text). Fresh emissions mixed with diluting air masses making up 50%, 90%, and 99% of the total volume after mixing are shown.
The comparison above demonstrates that the $\delta^{13}C$-based photochemical age is concentration-weighted average of the ages of the specific compounds in the air mass, which is not necessarily equal to the time since most of that compound was added to the air mass. The hydrocarbon-ratio-based photochemical age is biased to varying extents by the mixing of air masses with different photochemical age. The advantages of the technique for estimating the photochemical age of NMHCs using $\delta^{13}C$ over that using hydrocarbon ratio have been first proposed by Rudolph and Czuba [2000]. Unlike the isotope-based photochemical age, the hydrocarbon-ratio-based photochemical age is not compound-specific; however, Parrish et al. [2007] recently asserted that the average age of any NMHC could be approximated by the concentration ratio of an appropriate pair of hydrocarbons. The $n$-butane/ethane ratio, for instance, gives a good estimate for the average age of propane. A comparison between photochemical age derived from $\delta^{13}C$ of propane and that from $n$-butane/ethane ratio should provide further test of these techniques.

4. Conclusions

The altitude profiles of NMHCs and their isotopic ratios can largely be explained by the mixing of fresh emissions with aged background air. For longer-lived substances there will be a larger background concentration (with a greater photochemical age) in the diluting air, thus creating a significant vertical gradient in $\delta^{13}C$. For more reactive hydrocarbons, their short lifetimes reduce background concentrations so that the diluting air has little or no impact on their $\delta^{13}C$ vertical profiles. All the short-lived material is recently emitted, essentially. Isotopic ratio profiles can therefore be used to evaluate the relative importance of mixing and removal on various hydrocarbons. Photochemical age models can be misleading if upwind sources and mixing are not properly considered.

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