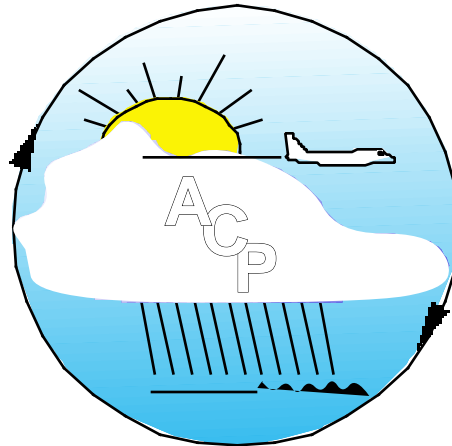


# Measurements of Nonmethane Hydrocarbons in Phoenix

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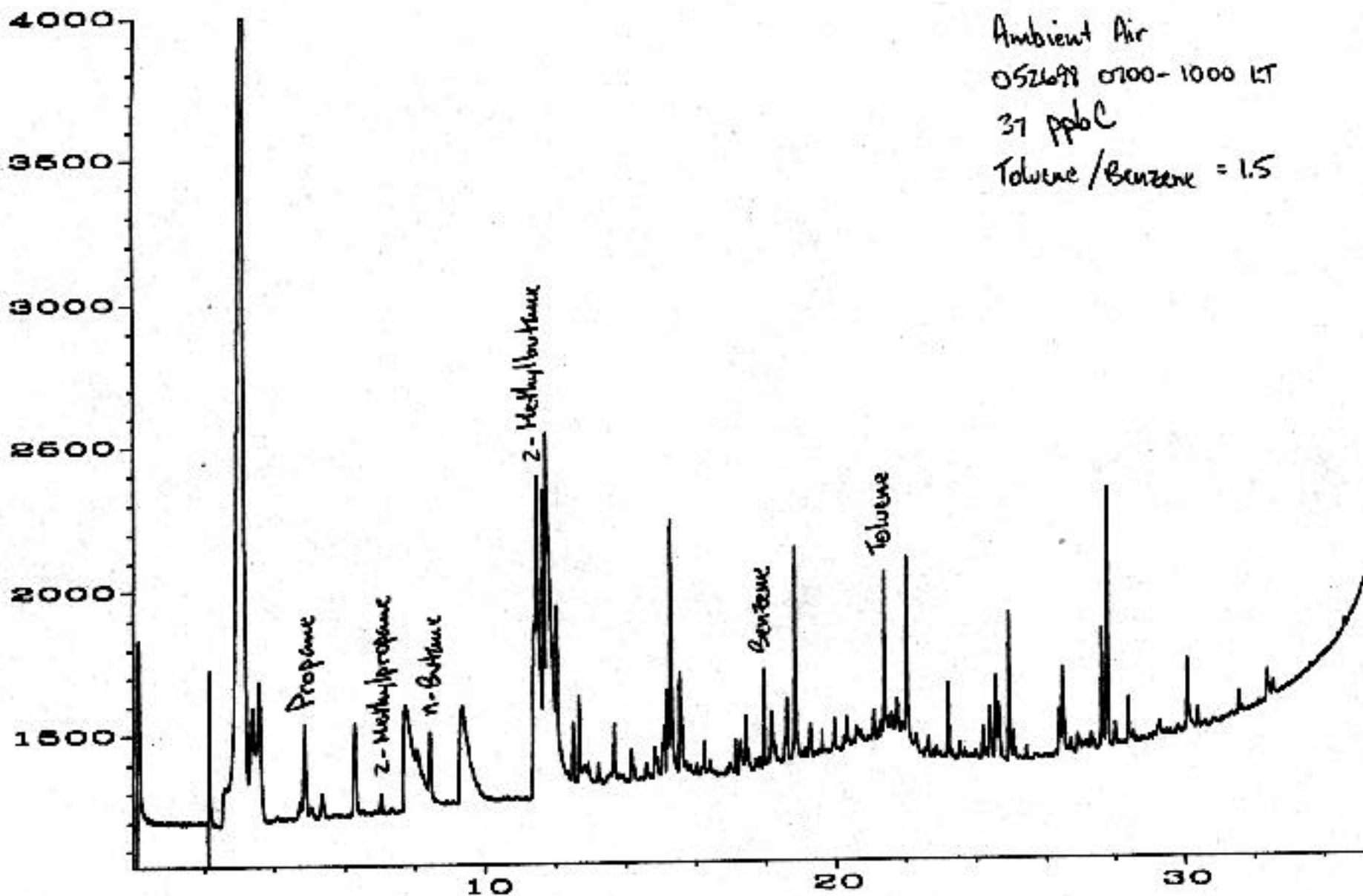
## **Measurements at Usery Pass, Mesa, Arizona**

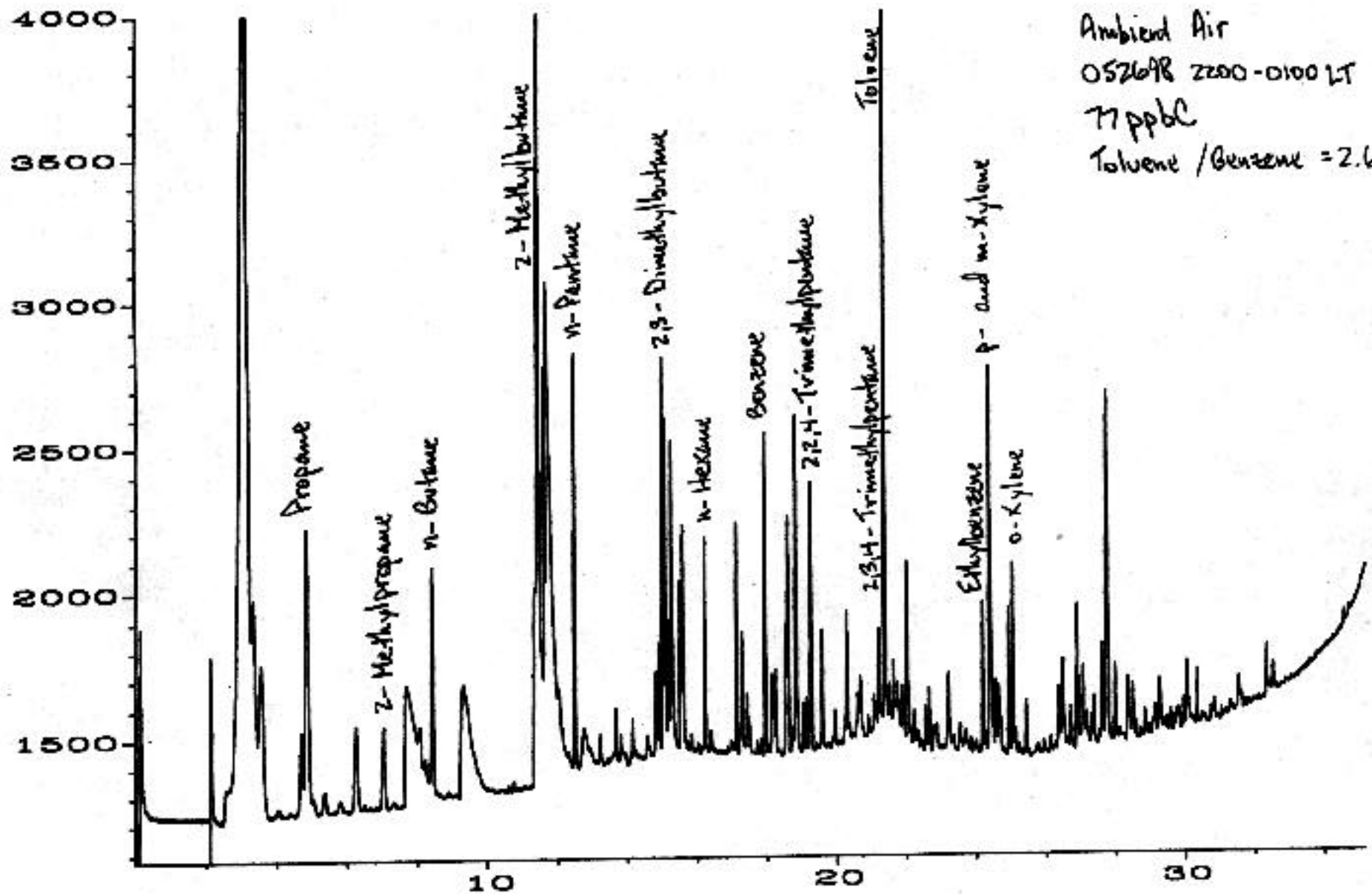
Nonmethane hydrocarbons (NMHCs) were measured during May 1998 at a surface site located in a hilly region to the east of Phoenix. Ambient air was collected in Summa<sup>®</sup> passivated stainless steel canisters and analyzed at Argonne National Laboratory by a cryogenic preconcentration/high-resolution gas chromatographic technique with flame ionization detection. Three-hour integrated samples were collected over 24 hour periods to examine diurnal variations of the NMHC concentrations.

## **Distributions in Ambient Air**

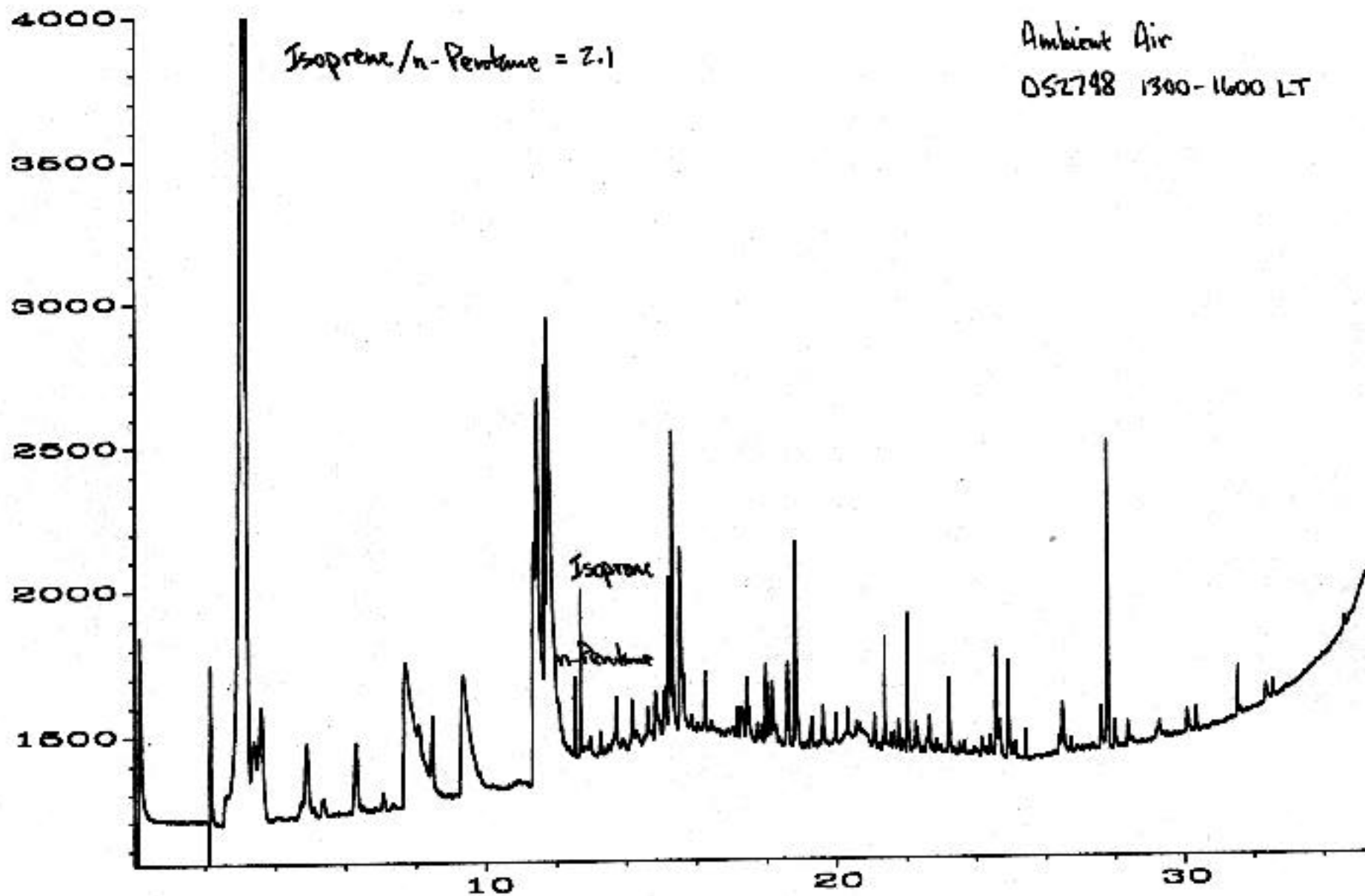
Distributions of the NMHCs were typical of photochemically processed and partially reacted vehicle exhaust. Levels of the saturated, unsaturated, and aromatic hydrocarbons reached maximum values between 0100 and 0400 local time (LT). During this period the toluene/benzene ratios were approximately 2.0 and characteristic of partially reacted emissions from vehicles. Biogenic emissions of isoprene were evident during the daylight hours. Samples collected within close proximity of shrubs at the site exhibited concentrations of isoprene that were much greater than the levels observed in ambient air. Toluene/benzene ratios in samples collected before 1600 LT were usually between 1.0 and 1.5 and typical of vehicle emissions that had been photochemically oxidized.

Ambient Air  
052698 0700-1000 LT  
37 ppbC  
Toluene/Benzene = 1.5



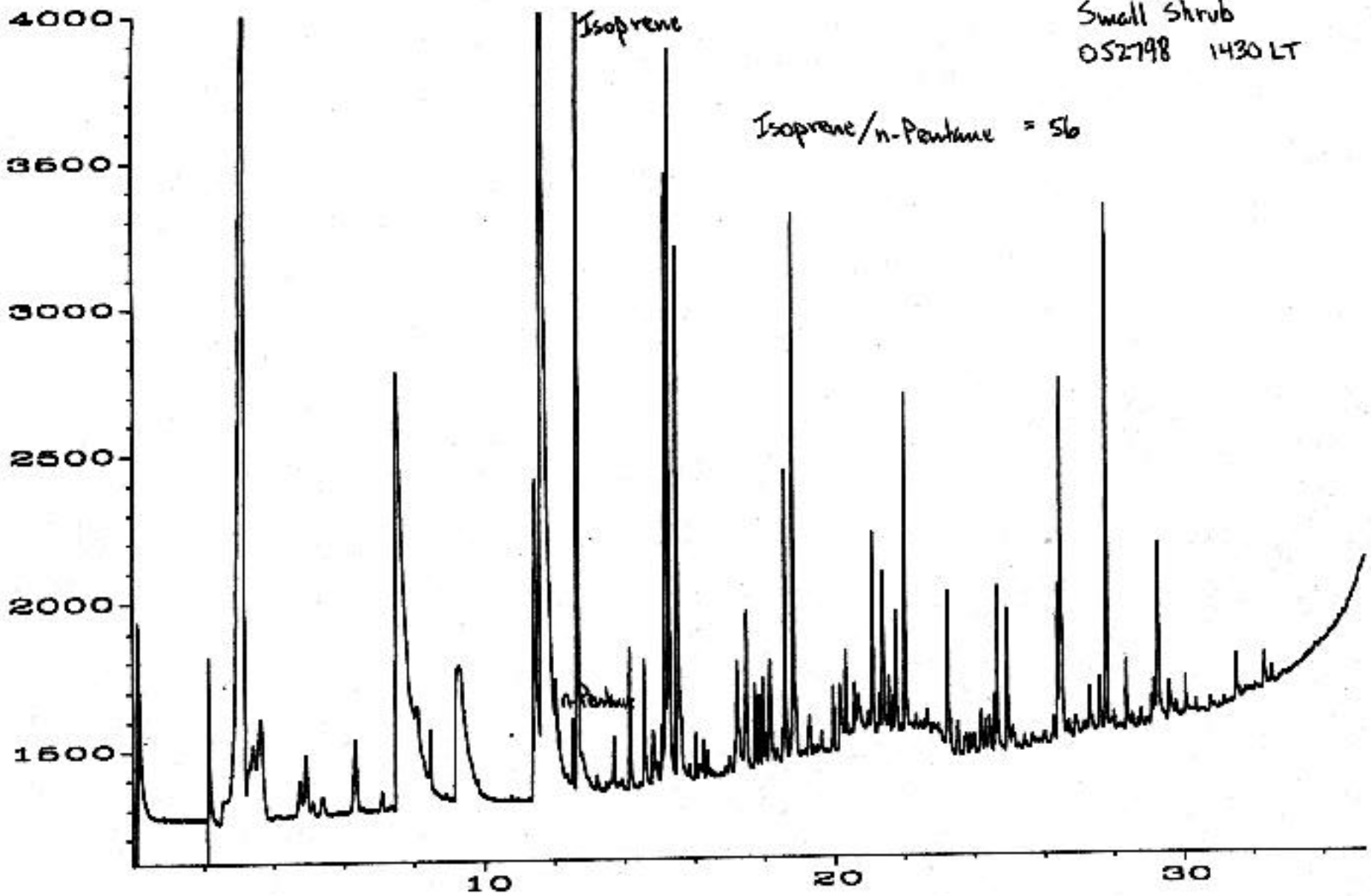


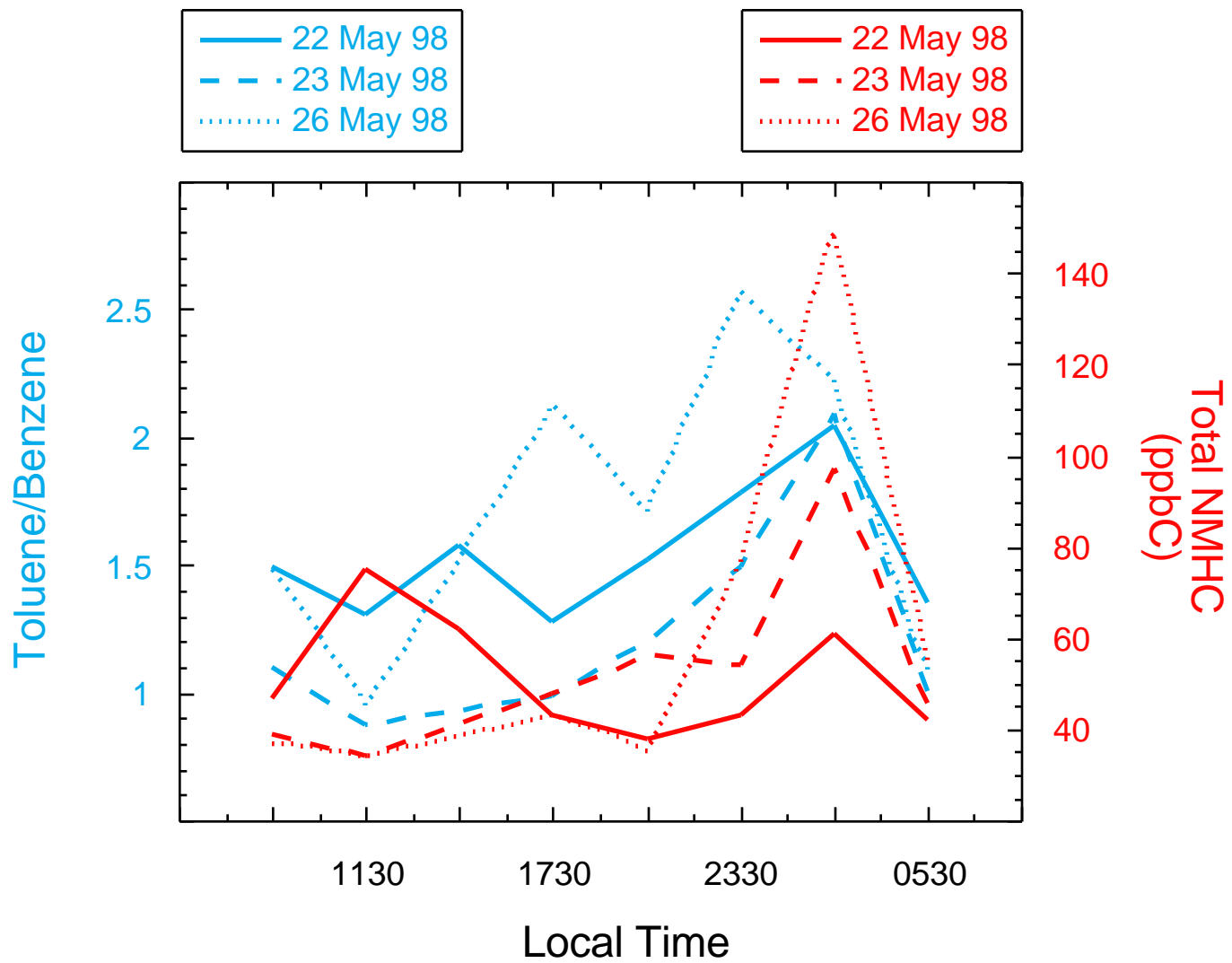
Ambient Air  
 052698 2200-0100 LT  
 77 ppbC  
 Toluene / Benzene = 2.6



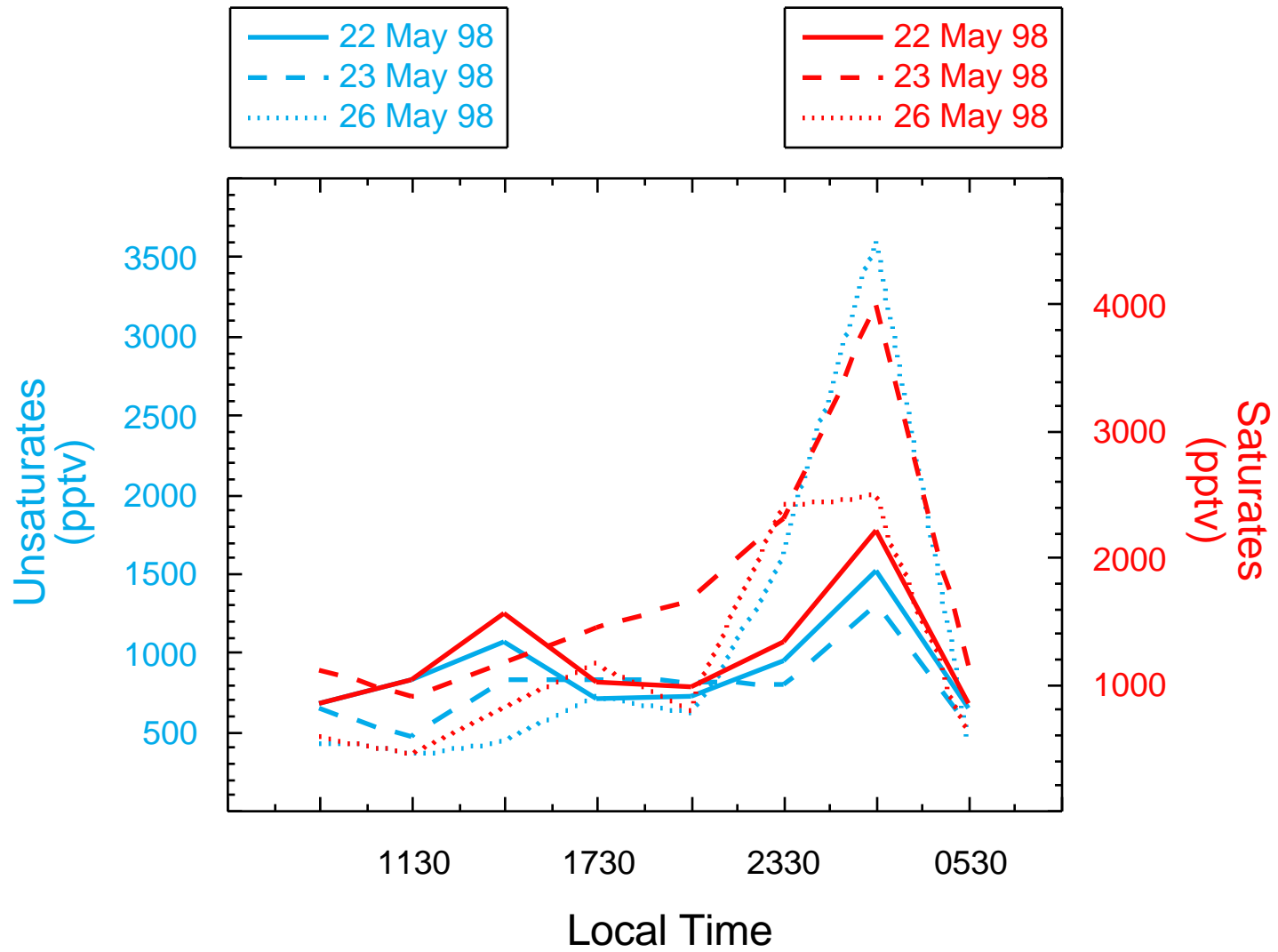
Small shrub  
052798 1430 LT

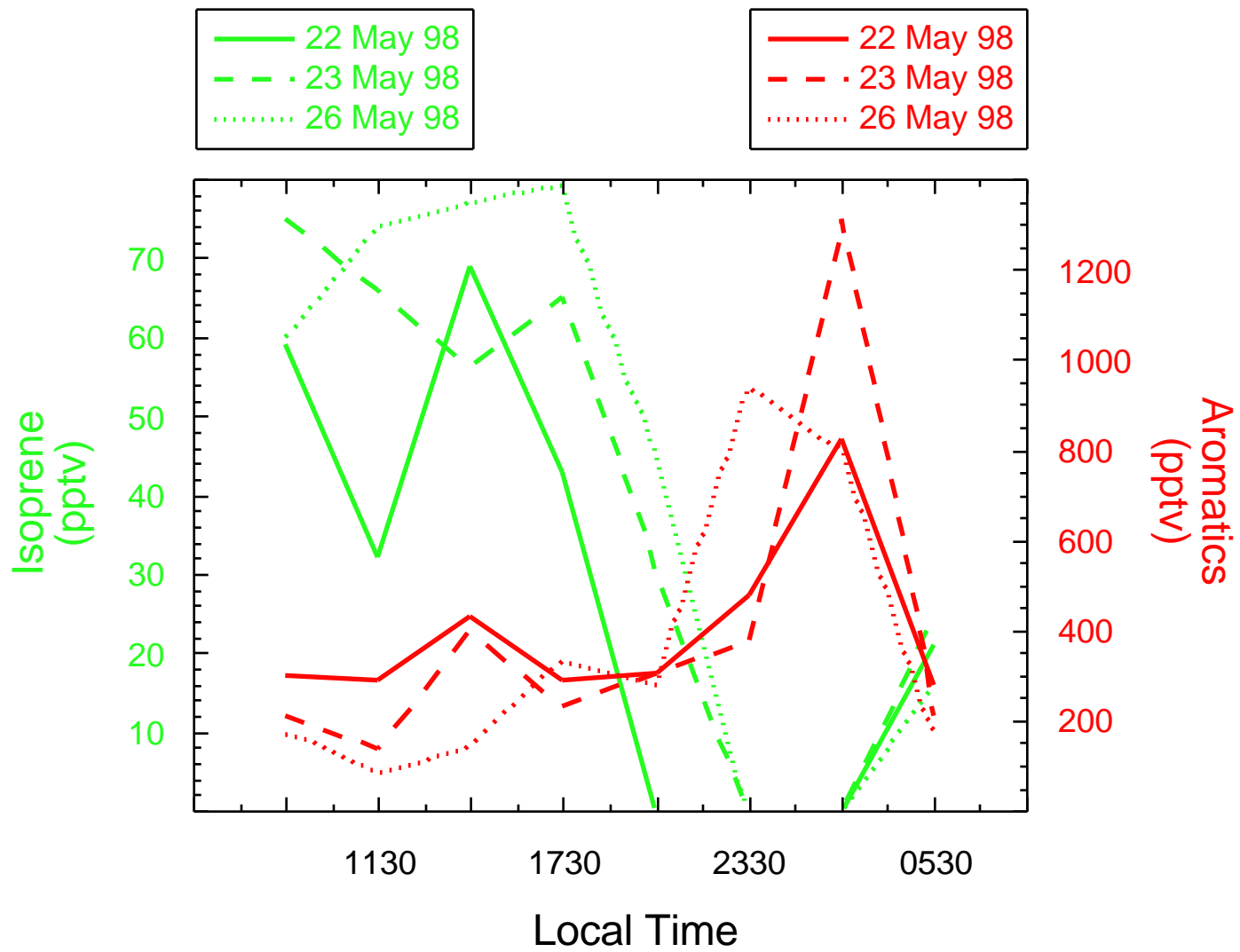
Isoprene/n-Pentane = 56





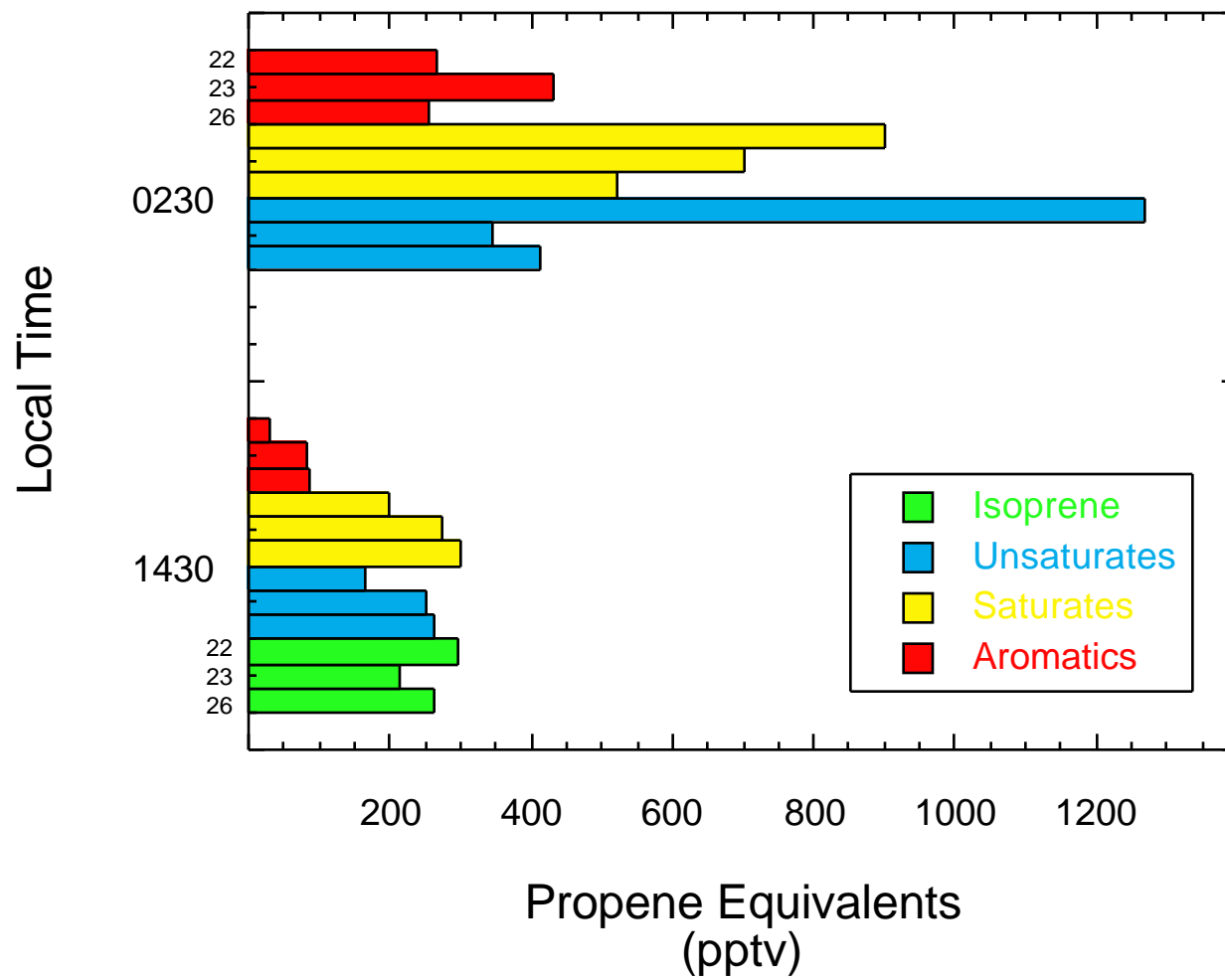






## Reactivity

The propene equivalent concentrations of isoprene and the saturated, unsaturated, and aromatic hydrocarbons were calculated by multiplying the concentration of each NMHC by the ratio of its hydroxyl radical rate constant to the hydroxyl radical rate constant of propene. Propene equivalent concentrations have been used to estimate the relative contribution of hydrocarbon species to the production of ozone. The reactivity values of the hydrocarbon mixture in ambient air at 0100-0400 LT were greater than reactivity levels at 1300-1600 LT. Isoprene contributed a significant fraction of the hydrocarbon reactivity during the daylight hours.



## Nighttime Chemistry

Elevated levels of  $\text{NO}_x$ , which could possibly produce significant concentrations of the nitrate radical ( $\text{NO}_3$ ), were typically observed between 0100-0400 LT at the Usery Pass location. Evidence of nighttime chemistry was not observed in the measured NMHC distributions. The rate constants for the branched alkanes are more than a factor of 2 greater than their straight chain homologs; however, the lifetimes of the straight chain and branched alkanes are on the order of days. Reaction rates of the olefins with  $\text{NO}_3$  are approximately four orders of magnitude greater than their saturated homologs; however, no trends were observed in the olefin distribution. Many biogenic hydrocarbons that are emitted from woody and herbaceous vegetation react rapidly with  $\text{NO}_3$ . Better evidence of nighttime chemistry might be observed in a location where high  $\text{NO}_x$  levels intercept, for example, a coniferous forest. Pinenes are emitted from coniferous vegetation throughout the day and night.

Table 1. Atmospheric lifetimes of anthropogenic hydrocarbons in polluted air.

Compound	Atmospheric Lifetime <sup>a</sup>		
	OH	O <sub>3</sub>	NO <sub>3</sub>
<b>Alkanes</b>			
2-Methylpropane	12 h		9.9 d
<i>n</i> -Butane	11 h		23 d
2-Methylbutane	7.1 h		6.6 d
<i>n</i> -Pentane	7.1 h		13 d
2,3-Dimethylbutane	4.6 h		2.4 d
<i>n</i> -Hexane	5.0 h		10 d
<b>Olefins</b>			
Ethene	3.3 h	2.9 d	5.1 d
Propene	63 min	11 h	2.7 h
2-Methylpropene	32 min	9.8 h	4.6 min
<i>cis</i> -2-Butene	30 min	53 min	4.3 min
<i>trans</i> -2-Butene	26 min	35 min	3.9 min

<sup>a</sup> Calculated for conditions in polluted air where O<sub>3</sub> = 2.5 × 10<sup>12</sup> molecules cm<sup>-3</sup> (100 ppbv), OH = 1 × 10<sup>7</sup> molecules cm<sup>-3</sup>, and NO<sub>3</sub> = 1.1 × 10<sup>10</sup> molecules cm<sup>-3</sup> (430 pptv).

Table 2. Atmospheric lifetimes of biogenic hydrocarbons in clean continental air.

Compound	Atmospheric Lifetime <sup>a</sup>		
	OH	O <sub>3</sub>	NO <sub>3</sub>
<b>Dienes</b>			
Isoprene	1.8 h	1.2 d	49 min
<b>Aliphatic Oxygenates</b>			
<i>trans</i> -2-Hexenal	4.2 h	7.7 d	1.9 d
<i>trans</i> -3-Hexen-1-ol	2.7 h	1.2 h	1.4 h
<i>cis</i> -3-Hexen-1-ol	1.7 h	5.8 h	2.1 h
<i>cis</i> -3-Hexenylacetate	2.4 h	6.9 h	2.2 h
<i>trans</i> -2-Hexenylacetate	2.8 h	1.2 h	1.4 h
1-Octen-3-ol	4.6 h	21 h	1.9 d
<b>Acyclic Monoterpenoids</b>			
Myrcene	52 min	47 min	3.0 min
<i>cis</i> -Ocimene	44 min	45 min	1.5 min
<i>trans</i> -Ocimene	44 min	41 min	1.5 min
Linalool	1.2 h	52 min	3.0 min
<b>Monocyclic Monoterpenoids</b>			
-Phellandrene	35 min	7.5 min	24 s
-Terpinene	31 min	1.1 min	11 s
Limonene	1.1 h	1.8 h	2.7 min
-Terpinene	1.0 h	2.6 h	1.1 min
Terpinolene	49 min	12 min	21 s

### Bicyclic Monoterpenoids

-Pinene	3.4 h	3.8 h	5.4 min
Camphene	3.5 h	17 d	51 min
-Pinene	2.3 h	1.0 d	13 min
<sup>3</sup> -Carene	2.1 h	8.3 h	3.7 min

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<sup>a</sup> Calculated for conditions in clean continental air where  $O_3 = 7.5 \times 10^{11}$  molecules  $cm^{-3}$  (30 ppbv),  $OH = 1.5 \times 10^6$  molecules  $cm^{-3}$ , and  $NO_3 = 5 \times 10^8$  molecules  $cm^{-3}$  (20 pptv).