# Internal consistency tests for evaluation of measurements of anthropogenic hydrocarbons in the troposphere

D.D. Parrish,[1] M. Trainer,[1] V. Young,[2] P.D. Goldan,[1] W.C. Kuster,[1] B.T. Jobson,[1,3] F.C. Fehsenfeld,[1] W.A. Lonneman,[4] R.D. Zika,[5] C.T. Farmer,[5] D.D. Riemer,[5,6] and M.O. Rodgers[7]

**Abstract.** Measurements of tropospheric nonmethane hydrocarbons (NMHCs) made in continental North America should exhibit a common pattern determined by photochemical removal and dilution acting upon the typical North American urban emissions. We analyze 11 data sets collected in the United States in the context of this hypothesis, in most cases by analyzing the geometric mean and standard deviations of ratios of selected NMHCs. In the analysis we attribute deviations from the common pattern to plausible systematic and random experimental errors. In some cases the errors have been independently verified and the specific causes identified. Thus this common pattern provides a check for internal consistency in NMHC data sets. Specific tests are presented which should provide useful diagnostics for all data sets of anthropogenic NMHC measurements collected in the United States. Similar tests, based upon the perhaps different emission patterns of other regions, presumably could be developed. The specific tests include (1) a lower limit for ethane concentrations, (2) specific NMHCs that should be detected if any are, (3) the relatively constant mean ratios of the longer-lived NMHCs with similar atmospheric lifetimes, (4) the constant relative patterns of families of NMHCs, and (5) limits on the ambient variability of the NMHC ratios. Many experimental problems are identified in the literature and the Southern Oxidant Study data sets. The most important conclusion of this paper is that a rigorous field intercomparison of simultaneous measurements of ambient NMHCs by different techniques and researchers is of crucial importance to the field of atmospheric chemistry. The tests presented here are suggestive of errors but are not definitive; only a field intercomparison can resolve the uncertainties.

## 1. Introduction

A pervasive problem faces researchers in atmospheric chemistry: the veracity of field measurements cannot be established by repeating experiments under a range of controlled conditions. Such repetition is routine in laboratory measurements but impossible in field studies because of expense and inevitably changing meteorological conditions. Therefore atmospheric chemists have come to rely upon blind, rigorous field intercomparisons to support the accuracy and precision claimed for measurements [e.g., *Gregory et al.*, 1990a, b; *Fehsenfeld et al.*, 1990; *Williams et al.*, 1992, and references cited therein.] Such an intercomparison for

[1]Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado.
[2]Department of Chemical Engineering, Ohio University, Athens.
[3]Also at Cooperative Institute for Research in the Environmental Sciences, NOAA, and University of Colorado, Boulder.
[4]National Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.
[5]University of Miami, Rosenstiel School of Marine and Atmospheric Science, Miami, Florida.
[6]Now at National Center for Atmospheric Research, Boulder, Colorado.
[7]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia.

nonmethane hydrocarbons (NMHCs) is under way [*Apel et al.*, 1994]; however, results published thus far are limited to laboratory-prepared mixtures rather than ambient samples. Less formal intercomparisons [*Carsey*, 1991; *Donahue and Prinn*, 1993; *Shreffler*, 1993] show substantial disagreements between simultaneous measurements made by different investigators. This paper examines patterns in measured NMHC concentrations and develops tests of internal consistency to evaluate anthropogenic NMHC measurements.

Anthropogenic and natural NMHCs are a portion of the fuel for tropospheric photochemistry. They are the fraction of volatile organic compounds (VOCs) that contain only carbon and hydrogen, and they constitute the majority of anthropogenic VOC emissions. Ultimately, NMHCs are oxidized to carbon dioxide and water via various intermediates: radicals (e.g., hydroxyl, hydroperoxy, organic peroxy), organics (e.g., aldehydes, acids, alcohols, nitrates, peroxides), and inorganics (e.g., carbon monoxide, ozone, hydrogen peroxide, nitric acid). Thus the accurate and precise measurement of NMHCs is key to our understanding of tropospheric photochemistry.

Most reported NMHC measurements have been made by gas chromatographic (GC) techniques, primarily with flame ionization detection (FID). The large number of NMHCs present in ambient air, coupled with the low specificity of FID, provides ample opportunity for errors, including coelution of multiple NMHCs and coelution with non-NMHC species to which the FID responds (e.g., oxygenated organic compounds or halocarbons). Mass spectrometric (MS) detectors with the GC separation can address some coelution problems but may

introduce additional calibration problems. Sampling presents additional challenges. Ambient compounds can be lost or interferants generated when samples are collected in containers or upon adsorbent materials. Field deployment of a GC system with direct sample collection avoids some problems, but the NMHCs in ambient air must still be concentrated and injected into the GC. The concentration process occurs in the matrix of ambient air containing water, ozone, peroxides, organic nitrates, and other species which may preferentially absorb, destroy, or produce particular NMHCs. Not surprisingly, measurement problems are often identified or suspected in reported NMHC data sets.

Measurements of NMHCs have been used in a variety of analyses. Examples include emission inventory evaluation [Goldan et al., 1995b; Scheff et al., 1996], monitoring changes of atmospheric levels to infer changes in emissions [Singh et al., 1985], source reconciliation studies [Nelson et al., 1983; Aronian et al., 1989; McLaren et al., 1996a, b; Zweidinger et al., 1988], evaluation of photochemical model calculations [Sillman et al., 1995], investigation of the seasonal cycle of photochemistry [Rudolph et al., 1989; Jobson et al., 1994b; Goldstein et al., 1995], and indirect determination of air mass history or radical concentrations [Calvert, 1976; Roberts et al., 1984; McKeen et al., 1990; Parrish et al., 1992]. Although possible measurement errors are generally ignored in such analyses, their potential influence on the results should be considered.

Fortunately, the large number of ambient NMHC species presents opportunities to identify measurement problems. Anthropogenic NMHCs are emitted by identifiable classes of sources and are removed by common mechanisms. Thus approximate patterns and relationships between anthropogenic NMHC species are expected. If these patterns are not present in reported data, then measurement problems should be suspected.

This paper analyzes NMHC data sets collected during the SOS 1995 Nashville/Middle Tennessee Ozone Study with regard to expected patterns and draws tentative conclusions

regarding the accuracy and precision of the data. Additional literature data sets are examined to support the general nature of the expected patterns, which should be generally applicable to anthropogenic NMHC data. Because all of the data sets considered were collected in North America, the patterns may be realized quantitatively only in that region, but analogous patterns are expected for other regions. Our analysis is guided by two hypotheses: first, that ambient anthropogenic NMHC data should reflect urban concentration patterns modified by dilution and photochemical removal and, second, that deviations from the expected patterns warrant examination for measurement problems.

The urban concentration patterns of NMHCs are well established. Table 1 presents results from the most extensive study in U.S. cities [Seila et al., 1989b]. Over 800 ambient air samples from 39 cities collected from 1984 to 1986 are represented in this table. The median concentrations of the 48 compounds found at the highest ambient levels, as shown in Table 1, are presumed to characterize the urban NMHC pattern. These data for the 25 most abundant compounds are more widely available in the work of Seinfeld [1989]. The measurements of Table 1 represent only half of the study, which continued through 1988 and totaled over 1600 samples from 88 sites in 71 U.S. cities. In the present work, the variability in this complete data set is assumed to represent the variability of the urban NMHC pattern.

During transport from urban to suburban to rural to remote sites, urban NMHC patterns should be modified by progressively greater dilution and photochemical removal. The primary process for removal of NMHCs from the atmosphere is attack by OH radicals. Figure 1 presents the reactivity of several NMHCs toward OH. The approximate summertime lifetimes span the range of tens of days for ethane for typical diurnally averaged OH concentrations to approximately 1 hour for the more reactive species at midday OH concentrations. Removal by ozone plays a secondary role for the alkenes [e.g., Singh and Zimmerman, 1992]. Removal by $NO_3$ [Platt et al., 1990; Winer et al., 1984] and halogen

**Table 1.** Median Concentrations of the 48 Most Abundant Ambient Air Hydrocarbons in 39 U.S. Cities

| Rank | Compound | ppbC | Rank | Compound | ppbC |
|---|---|---|---|---|---|
| 1 | i-pentane | 45.3 | 25 | n-heptane | 4.7 |
| 2 | n-butane | 40.3 | 26 | 2,3-dimethylbutane | 3.8 |
| 3 | toluene | 33.8 | 27 | c-2-pentene | 3.6 |
| 4 | propane | 23.5 | 28 | 1,2,3-trimethylbenzene | 3.4 |
| 5 | ethane | 23.3 | 29 | methylcyclohexane | 3.4 |
| 6 | n-pentane | 22.0 | 30 | n-decane | 3.3 |
| 7 | ethene | 21.4 | 31 | 1,3,5-trimethylbenzene | 3.0 |
| 8 | m&p-xylene | 18.1 | 32 | C11 aromatic | 3.0 |
| 9 | 2-methylpentane | 14.9 | 33 | t-2-pentene | 2.9 |
| 10 | i-butane | 14.8 | 34 | o-ethyltoluene | 2.9 |
| 11 | acetylene | 12.9 | 35 | p-ethytoluene | 2.8 |
| 12 | benzene | 12.6 | 36 | C10 aromatic | 2.8 |
| 13 | n-hexane, 2-ethyl-1-butene | 11.0 | 37 | n-octane | 2.6 |
| 14 | 3-methylpentane | 10.7 | 38 | 2-methyl-1-butene | 2.6 |
| 15 | 1,2,4-trimethylbenzene | 10.6 | 39 | 1,2-dimethyl-3-ethylbenzene | 2.5 |
| 16 | propene | 7.7 | 40 | t-2-butene | 2.5 |
| 17 | 2-methylhexane | 7.3 | 41 | 2,3,4-trimethylpentane | 2.5 |
| 18 | o-xylene | 7.2 | 42 | 2-methylheptane | 2.5 |
| 19 | 2,2,4-trimethylpentane | 6.8 | 43 | 1,4-diethylbenzene | 2.4 |
| 20 | methylcyclopentane | 6.4 | 44 | 3-methylheptane | 2.2 |
| 21 | 3-methylhexane | 5.9 | 45 | n-nonane | 2.2 |
| 22 | 2-methylpropene, 1-butene | 5.9 | 46 | cyclohexane | 2.2 |
| 23 | ethylbenzene | 5.9 | 47 | 2,4-dimethylpentane | 2.2 |
| 24 | m-ethyltoluene | 5.3 | 48 | cyclopentane | 2.1 |

Taken from Seila et al. [1989b].
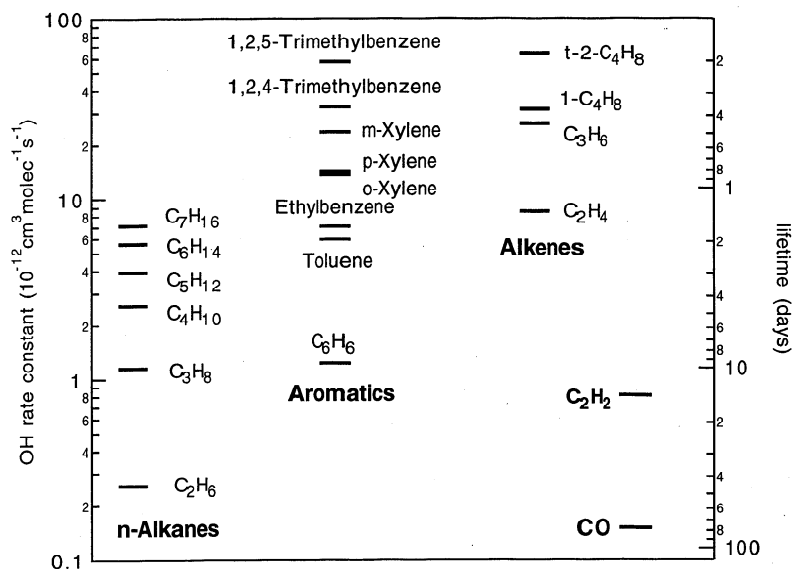
**Figure 1.** Rate constants (left ordinate) and approximate tropospheric lifetimes (right ordinate) for the less reactive nonmethane hydrocarbons (NMHCs). Carbon monoxide is included for comparison. Rate constant data are taken from *Atkinson* [1994]. To estimate lifetimes, a concentration of OH equal to $10^6$ molecules $cm^{-3}$ and a temperature of 298 K were assumed.

radicals [*Keene et al.*, 1996; *Jobson et al.*, 1994a] have also been proposed for specific environments. However, OH reactions generally are believed to dominate.

Dilution and OH reaction have predictable effects on the NMHC pattern. When unexpected patterns appear, experimental problems should be suspected. These problems could arise from instrumental sources, or possibly from contamination of a sampling site by local sources (e.g., nearby solvent usage) that are not regionally representative. Because a consistent urban pattern modified only by dilution and OH reaction is assumed, other atmospheric processes or significant differences in regional emissions will also produce unexpected patterns. However, it is prudent to consider possible measurement problems before concluding that the atmospheric NMHC levels are affected by new or unusual factors.

This paper will describe the data sets (section 2), examine the difficulty of evaluating absolute concentrations (section 3), introduce the evaluation of relative concentrations (section 4), and apply this evaluation to measurements of long-lived (section 5) and short-lived (section 6) NMHCs. In section 7 the concentration patterns of the alkanes, the aromatics and the alkenes will be examined as separate classes. *Goldan et al.* [1995b] pointed out that correlations within the alkane and aromatic classes are generally higher than between species from different classes; this is believed to reflect a different source composition for the two classes. The alkenes also present special experimental problems. In section 8, conclusions are summarized and the original hypotheses and assumptions reevaluated.

## 2. Data Sets

We investigate five NMHC data sets collected during the Southern Oxidant Study (SOS) 1995 Nashville/Middle Tennessee Ozone Study. Five additional published data sets provide comparisons and contrasts of different techniques and site locales; these are referred to as literature data sets. Finally, the complete U.S. Urban data set partially reported in

Table 1 has been provided to us; it includes 1984-1988 data from 88 sites in 71 cities. Since it represents a wide variety of sampling locations, its variability suggests the deviation from the pattern in Table 1 that might be expected in any particular data set. Table 2 summarizes some parameters of the 11 data sets. The 1992 Rural Oxidants in the Southern Environment (ROSE 92) [*Goldan et al.*, 1995a], Harvard Forest [*Goldstein et al.*, 1995], and Colorado [*Goldan et al.*, 1996] data sets are representative of isolated rural areas in the southeastern, northeastern, and western United States, respectively. The Boulder, Colorado site [*Goldan et al.*, 1995b] and the Los Angeles sites [*Mayrsohn et al.*, 1976] represent western U.S. suburban and urban locations, respectively.

The 11 data sets encompass different, independently developed GC measurement techniques at surface sites and on aircraft platforms. Apart from the Boulder winter data set, all were collected in the summer. Although the Harvard Forest site is operated continuously, only the results from August 1995, which provides a large number of samples from the same time period as the SOS study, are considered here. The Air Cans and Air GC data sets are of particular value; they were collected on the same aircraft during the SOS study with many simultaneous samples. These simultaneous measurements allow an objective determination of the accuracy and precision for the respective measurements. Together, the 11 data sets include over 5200 samples.

The units of the data of Table 1 and in much of the NMHC literature are parts per billion carbon (ppbC) based on molar ratios to dry ambient air. We will consistently use an alternative unit: parts per billion by volume of compound (ppbv), which is calculated from ppbC by dividing by carbon number of the compound.

## 3. Evaluation of Absolute Measurements

It is difficult to specify limits for possible absolute ambient NMHC concentrations. The photochemical lifetimes of the hydrocarbons (Figure 1) are usually short compared to

**Table 2.** SOS (First Five Rows) and Literature Data Sets Used for Evaluation

| Data Set | Research Group | Study Period, Method, Site Type and Location | Number of Samples |
|---|---|---|---|
| SOS Cans | ----- | SOS 1995, canisters, 11 surface sites and 2 aircraft in southern U.S. | 663 |
| GC/MS A | ----- | SOS 1995, in situ GC-MS, suburban surface site in southern U.S. | 132 |
| GC/MS B | ----- | SOS 1995, in situ GC-MS, rural surface site in southern U.S. | 132 |
| Air Cans | York Univ.[a] | 6/26 to 7/20 1995, canisters, aircraft collection in southern U.S. | 159 |
| Air GC | NOAA AL[b] | 6/7 to 7/22 1995, in situ GC, aircraft in southern and western U.S. | 418 |
| ROSE 92 | NOAA AL[b] | 5/11 to 7/4 1992, in situ GC-FID, rural surface site in southern U.S. | 488 |
| Harvard Forest | Harvard Univ.[c] | August 1995, in situ GC-FID, rural surface site in northeastern U.S. | 647 |
| Colorado | NOAA AL[b] | 8/26 to 10/1 1993, in situ GC-FID, rural surface site in western U.S. | 417 |
| Boulder | NOAA AL[b] | 2/3 to 2/15 1991, in situ GC_FID, suburban surface site in western U.S. | 279 |
| L.A. Sites | Mayrsohn et al.[d] | June-September 1975, Tedlar bag, 4 urban sites in Los Angeles basin | 233 |
| U.S. Urban | U.S. EPA[e] | Summers, 1984-1988, canisters from 39 urban sites in U.S. | 1646 |

[a]*Young et al.*, [1997].
[b]*Goldan et al.*, [1995b].
[c]*Goldstein et al.*, [1995].
[d]*Mayrsohn et al.*, [1976].
[e]*Seila et al.*, [1989a].

atmospheric mixing times. Consequently, there is no definite lower concentration limit; observations vary from levels of tens or hundreds of ppbv in emission regions to the low parts per trillion by volume of compound (pptv) range or less in remote regions. The exception is ethane; its photochemical lifetime is of the order of tens of days. Measurements indicate that the minimum concentration that can be found in the troposphere of the northern hemisphere is about 0.3 ppbv [*Rudolph*, 1995]. This expected lower limit provides a useful test for ethane data sets.

Figure 2 presents measurement distribution plots for the data sets that include ethane. The median urban concentration from Table 1 is included for comparison. In most respects the data sets fit the expected patterns. The maximum concentration from each data set is below the median urban concentration, consistent with these generally nonurban measurements. However, the SOS Can data include some samples collected in downtown Nashville, and the larger values of this data set approach the urban median. The large fraction of the Air GC data set that was collected in the free troposphere accounts for the lower concentrations in the lower half of that distribution; similarly, a smaller fraction of free troposphere samples account for the low concentration tail of the Air Cans distribution. Although not evident from Figure 2, the simultaneous ethane samples from the Air Cans and Air GC data sets agreed well (P.D. Goldan et al., manuscript in preparation, 1998). The distribution of ethane from the ROSE 92 data set (Figure 2b) is displaced to larger concentrations compared to the Harvard Forest data; this may reflect leakage from the natural gas distribution lines in the ROSE 92 study region.

Figure 2 reveals one experimental problem. Approximately 50% of the ethane measurements from the SOS Cans data in Figure 2a are clearly too low; 29% of the results are reported as not detected, i.e. below the minimum reported ethane level of 0.026 ppbv. Yet the minimum expected ethane concentration is 0.3 ppbv. There must be a problem in this

analytical system for ethane measurements. The existence of a lower limit for the ambient concentration of this one NMHC does provide a useful indicator for suspect ethane data.

## 4. Evaluation Through Ratios of Concentrations

For NMHCs more reactive than ethane, definite concentration ranges cannot be defined, but concentration ratios of many NMHCs are predictable. Ratios should reflect the average emission ratios modified by the differing rates of photochemical removal for the two NMHCs. Ratios of NMHCs with similar reactivity should remain constant at the average emission ratio, since neither NMHC is preferentially removed. Ratios of NMHCs with different OH reactivities do vary but in a predictable manner. The variability of the observed ratios should be particularly small for NMHCs with long photochemical lifetimes, since a wide variety of sources will have the opportunity to contribute significantly to the sampled air parcel. Ratios of NMHCs with relatively short photochemical lifetimes (e.g., alkenes and substituted aromatics) may be treated similarly, although their ratios may be more strongly affected by specific local sources. Also, their reactivity may present sampling and analytical difficulties.

Mathematically, the use of concentration ratios presents at least two statistical difficulties: codependence and proper calculation of the mean and standard deviation of a set of ratios. In the analysis, related variables are often plotted, such as the ratio of two NMHCs versus the concentration of one of them. Such plots necessarily have some correlation arising from the codependence of variables. This codependent correlation results from a statistical artifact, not atmospheric behavior or instrumental characteristics. Codependence is minimized by placing the NMHC measured more precisely (usually the one of higher concentration) in the denominator. It is difficult to interpret the arithmetic mean and standard deviation of an ensemble of experimental determinations of
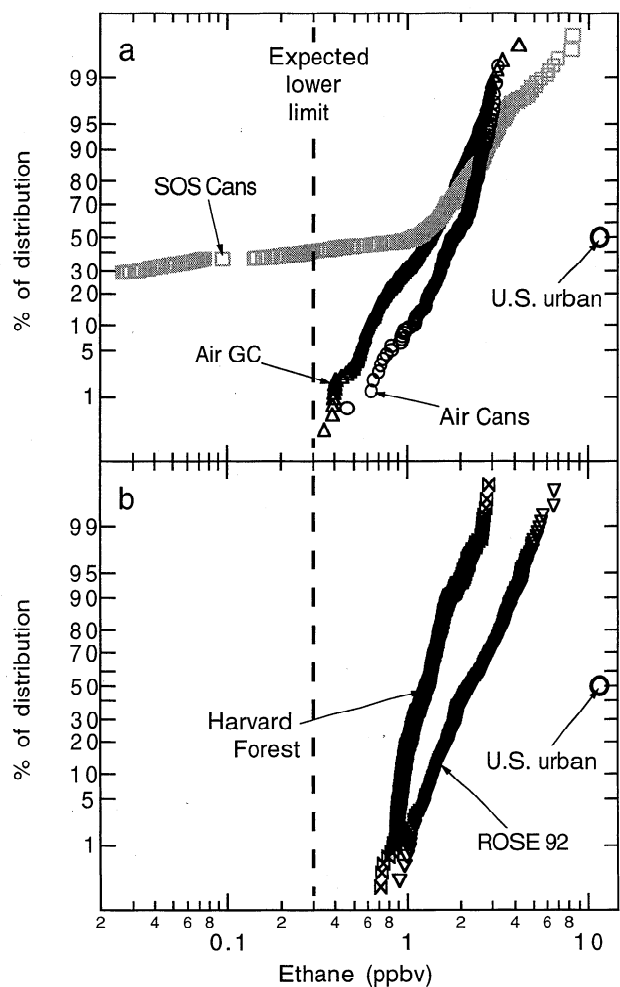
**Figure 2.** Ethane concentrations plotted on cumulative probability axes for the Southern Oxidant Study (SOS) data sets (a) compared to two literature data sets (b). Each panel includes the median U.S. Urban concentration from Table 1. The ordinate gives the percentage of the data set reporting ethane at or below the concentration given on the abcissa.

the ratio. Small values in the denominator give large, positive ratios. Because concentration ratios cannot have large negative values, the arithmetic mean of the ratios is distorted and generally larger than the median. As a result, the conclusion reached regarding a particular ratio will generally depend upon which NMHC is chosen for the denominator. This problem becomes more pronounced as the variability of the ratio approaches the magnitude of the ratio. In this paper the geometric mean ratio (the antilog of the mean of the logs of the ratios), which avoids this problem, is used exclusively. The logs of the ratios tend to form a symmetric distribution around the log of the median ratio and can extend to negative as well as positive values. Thus the geometric mean approximates the median of the ensemble of ratios.

The use of geometric means of NMHC ratios can be justified mathematically. The observed concentrations of primary pollutants, such as NMHCs, tend to be distributed lognormally [see *Parrish et al.*, 1991]. Thus the log-transformed data are distributed approximately normally. The log of the ratio of two NMHCs is equal to the difference of their logs, and the distribution of the difference of two distributions that are normally distributed is itself normally distributed [e.g., *Larsen*

*and Marx*, 1981]. Therefore the ratio of two NMHCs is approximately lognormally distributed.

Since the ratios approximately define a lognormal distribution, the standard deviation of the natural logs of the ratios $\sigma_{lnz}$ is a useful statistic. It is the approximate number of times that the geometric mean ratio must be multiplied and divided by $e$ to encompass 68% of the ratio determinations. Also, $\sigma_{lnz}$ is approximately equal to the $1\sigma$ fractional variability about the geometric mean if $\sigma_{lnz}$ is small with respect to unity; this follows from the differential of the natural log function: $d(\ln z) = dz/z$. Further, if $z$ is the ratio of $x$ and $y$ (e.g., the ratio of the measurements of two NMHCs), if the measurement imprecisions of $x$ and $y$ are statistically uncorrelated, and if the variability of the observed ratios is dominated by this measurement imprecision, then the fractional uncertainty in the ratio, $\sigma_{lnz}$, is given by

$$\sigma_{lnz} = (\sigma_{lnx}^2 + \sigma_{lny}^2)^{1/2}, \tag{1}$$

where $\sigma_{lnx}$ and $\sigma_{lny}$ are the fractional measurement imprecisions of the respective NMHCs. Finally, we define $\sigma$ as the root-mean-square of the fractional uncertainty in the measurement of each NMHC, i.e.

$$\sigma = \sigma_{lnz} / (2)^{1/2}, \tag{2}$$

and take it as an indication of the imprecision of the NMHC measurements that constitute the ratio. If measurement imprecision dominates the variability of the determined ratio, then $\sigma$ is a good approximation; if true ambient variability contributes to the variability of the determined ratio, then $\sigma$ provides an overestimate of the measurement imprecision. However, note that measurement problems affecting each NMHC by the same factor will not affect their ratio. Thus $\sigma$ reflects the statistically uncorrelated measurement imprecision only; in some cases the true measurement imprecision could be larger. It should be emphasized that the measurement imprecision discussed here includes random errors or experimental variability from all sources including sampling technique, sample concentration and injection, chromatographic performance, and chromatography analysis.

Figure 3 presents the ratios of coincident measurements of the same NMHC from the two SOS aircraft data sets; thus ratios of unity are expected. The geometric mean ratios, given in the captions of Figure 3, are close to unity, indicating excellent systematic agreement between the two analytical systems. The $\sigma$ values are 11% and 13%. Since the analytical techniques are independent, their experimental random errors are uncorrelated, and $\sigma$ is an objective measure of their root-mean-square precision. The measurement precision varies with concentration; $\sigma$ averages 21% below 0.05 ppbv and 6.6% above 0.1 ppbv.

## 5. Ratios of Long-Lived NMHCs

### 5.1. Ratios of NMHCs of Similar Reactivity: Butane Isomers

The photochemical lifetimes of $i$-butane and $n$-butane are nearly equal. Atmospheric sources of the two isomers of butane are quite varied: fossil fuel and biomass combustion, natural gas emissions, petroleum production and refining, and other industrial processes [*Graedel et al.*, 1986; *Singh and Zimmerman*, 1992]. The ratio of the emitted isomers of butane
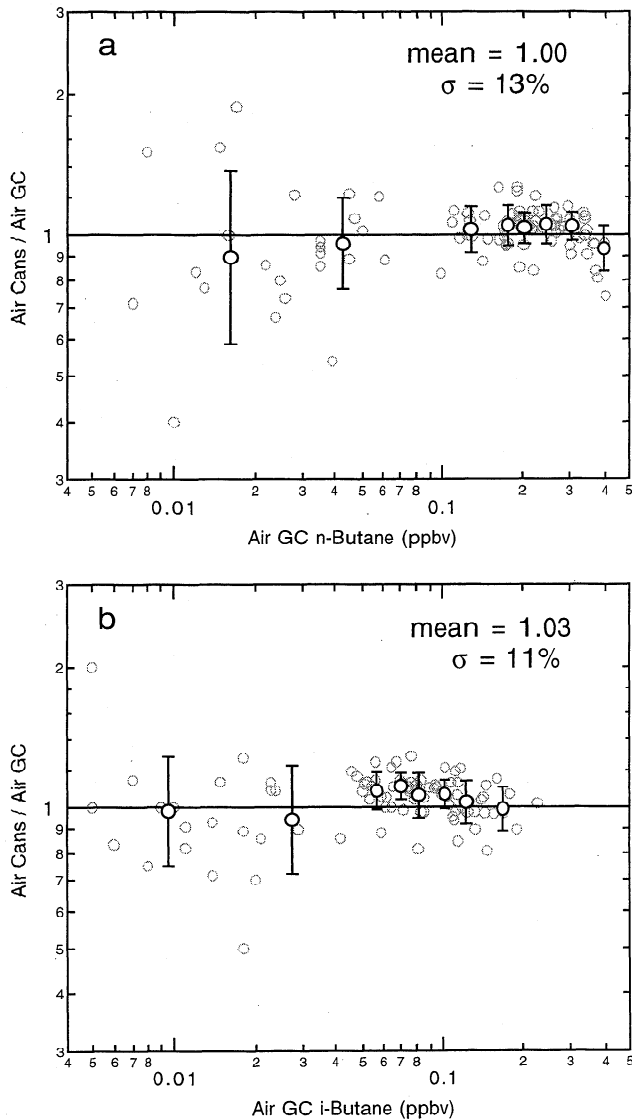
**Figure 3.** Log-log plots of the ratios of coincident measurements of (a) *n*-butane and (b) *i*-butane from the two SOS aircraft data sets as a function of the measured concentration. The geometric mean ratio and the root-mean-square of the fractional uncertainty in the measurement of each NMHC derived from the full data set are given in each caption. The thin-line circles indicate the individual measurements, and the thick-line circles and error bars give the geometric means and standard deviations of eight equal subsets of data in each panel.

reportedly vary fairly widely among these source classes and even among different emitters within a given class. However, data sets of ambient measurements show relatively constant ratios of the isomers in the troposphere. Evidently, emissions from distinct sources are mixed rapidly compared to the butane photochemical lifetime ($\approx 4$ days; see Figure 1) and transport time to the sampling locations. Even in urban areas, remarkably little variability is observed in the ratio of *i*-butane to *n*-butane. The four sites sampled by *Mayrsohn et al.* [1976] differed widely in their exposure to the manifold of urban sources in the Los Angeles urban area, yet the geometric mean ratio of the total data set was 0.46 with a $\sigma$ of 18%. The U.S. Urban data set of Table 2 is from 71 U.S. cities over five summers; the geometric mean ratio of the total data set is 0.40

with a $\sigma$ of 32%. A nearly constant ratio is expected for *i*- and *n*-butane across the continental United States.

Figure 4 compares the butane isomer ratio from the literature and SOS data sets to the *Seila et al.* [1989b] results. The literature data sets in Figure 4b show an excellent correlation ($r^2 = 0.98$ for the combined, logtransformed data) over nearly 4 orders of magnitude and approximately agree with the urban data. (The Los Angeles butane levels are predominately higher than the median urban levels of *Seila et al.* [1989b], perhaps reflecting the impact of emission controls over the decade of time between studies.) The few outliers represent a small fraction of more than 2000 observations. The SOS data in Figure 4a are in reasonable accord with the literature data, even though there is noticeably more scatter in the measurements ($r^2 = 0.88$). It should be noted that the scatter is primarily due to only two (SOS Cans and GC/MS A) of the five SOS data sets. The SOS data span a range of lower concentrations than the literature data since they include aircraft data from the free troposphere and only a small fraction of urban measurements.
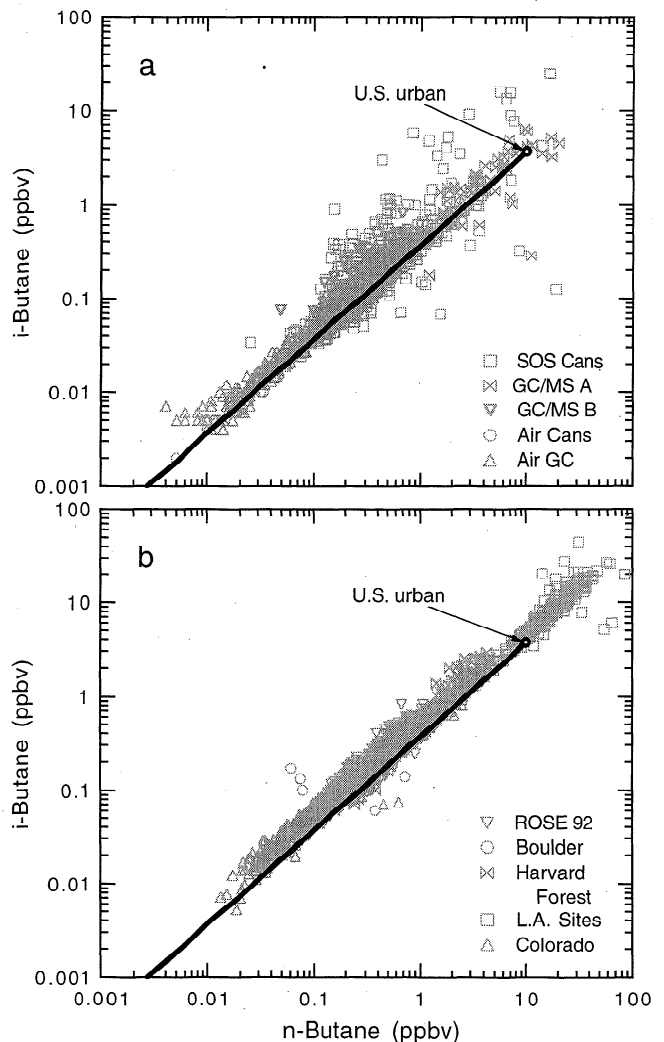


**Figure 4.** Log-log correlation plots for the butane isomers for (a) the SOS data sets and (b) the literature data sets. The symbols for the data sets are given in the legends. The median urban concentrations from Table 1 are given by the thick open circle, and the solid line indicates their constant ratio.
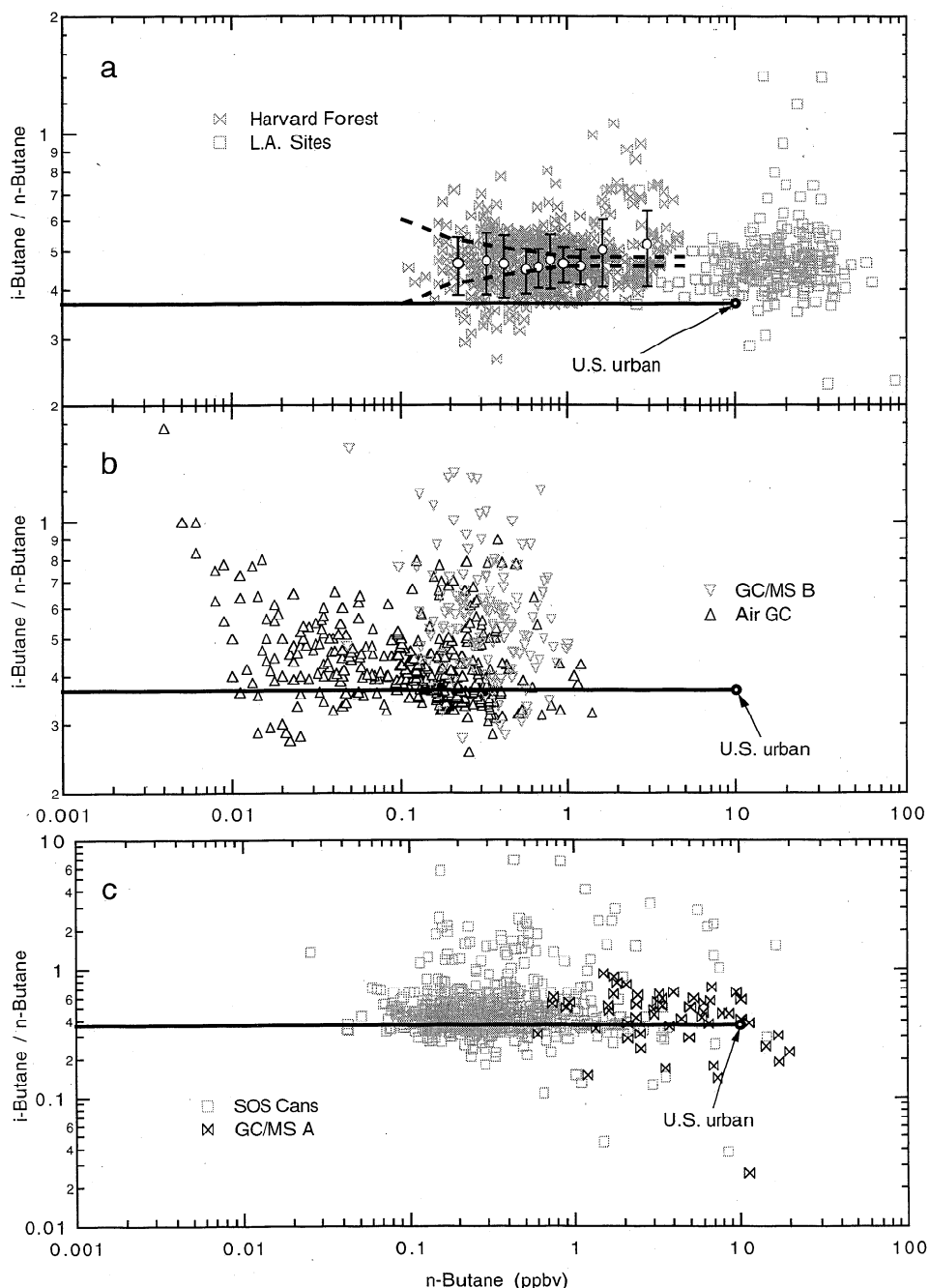
**Figure 5.** Log-log plots of the ratio of the butane isomers as a function of the $n$-butane concentration for six of the data sets. The median urban data from Table 1 are given by the thick open circle, and the solid line indicates their constant ratio. The range of the ordinate is expanded in Figure 5c. In Figure 5a the geometric means and standard deviations of 10% segments of the Harvard Forest data are shown by circles and error bars, and the dashed lines show the geometric standard deviations of the data expected from the reported precisions [*Goldstein et al.*, 1995].

The experimentally determined ratios of the butane isomers are examined in Figure 5 and summarized in Table 3. The mean ratios are larger than the ratio of the urban medians from Table 1; this is the one significant disagreement that we find between the *Seila et al.* [1989b] data and the present data sets. Given the hypotheses that guide this discussion, this disagreement suggests a systematic error of about 20-25% in the determination of $n$-butane by *Seila et al.* [1989b], as will be discussed further below. The average geometric mean ratio of the first 10 data sets in Table 3 (0.48±0.02, 1 σ confidence limit) is in good agreement with other data sets from a variety

of sites (e.g., *Jobson et al.*, [1994b] report a ratio of 0.47±0.01).

The Harvard Forest data in Figure 5a provide an excellent example of the expected behavior of experimentally determined ratios in general. The overall variability in the determined ratios is small; the average, uncorrelated measurement precision of each butane isomer can be no worse than the 12% σ value to achieve such small scatter. The variability of the ratio determinations is indicated by the error bars in Figure 5a as a function of $n$-butane level. They indicate that at the lowest levels the variability is consistent with the

**Table 3.** Parameters for Butane Ratio Evaluation

| Data Set | Mean Ratio | ADL[a] | $\sigma$ |
|----------|-----------|--------|----------|
| Median urban[b] | 0.37 | --- | --- |
| SOS Cans | 0.48 | 85% | 41% |
| GC/MS A | 0.41 | 42% | 41% |
| GC/MS B | 0.57 | 100% | 25% |
| Air Cans | 0.42 | 99% | 14% |
| Air GC | 0.43 | 93% | 17% |
| ROSE 92 | 0.56 | 100% | 16% |
| Harvard Forest | 0.47 | 100% | 12% |
| Colorado | 0.53 | 98% | 16% |
| Boulder | 0.51 | 100% | 15% |
| L.A. Sites | 0.46 | 100% | 18% |
| U.S. Urban | 0.40 | $\geq$ 99% | 32% |

[a]Fraction of chromatograms with both butane isomers above the detection limit.

[b]Ratio of median urban concentrations from *Seila et al.* [1989b].

10% measurement precision reported for the instrumentation at 0.2 ppbv [*Goldstein et al.*, 1995], which is indicated by the dashed lines. A regionally averaged "background" ratio is observed; variability in this background cannot be discerned above the experimental imprecision. At concentrations near 1 ppbv the variability of the ratio is smaller. However, the observed variability would imply a measurement precision worse than the 2% quoted by *Goldstein et al.* [1995]. This suggests that atmospheric variability contributes to the variability of the determined ratios at these concentrations. Nearby sources evidently influence the regionally averaged ratios to the extent that the ambient variability competes with the measurement imprecision. At concentrations above 1 ppbv the variability increases. Here it is likely that atmospheric variability driven by local emissions dominates the scatter and instrumental imprecision contributes negligibly. At these higher levels the variability of the ratios approaches that found by *Mayrsohn et al.* [1976] at the four Los Angeles sites (see Figure 5a.)

The other literature data sets and the two SOS aircraft data sets exhibit variability of similar magnitude and similar dependence on absolute concentration. The $\sigma$ values of the two aircraft data sets, 14% and 17% shown in Table 3, approximate the average measurement precision of 12%, derived from the comparison of coincident measurements of the butane isomers shown in Figure 3. This agreement indicates that at least at low concentrations, $\sigma$ provides a reasonable estimate of the measurement precision. Figure 5b shows one of these aircraft data sets. The scatter in the Air GC data set is similar to that in the Harvard Forest data set at butane levels near 0.1 ppbv but increases dramatically at the lowest levels. The tailing up of the ratios at the lowest $n$-butane ratios is likely a statistical artifact; the lowest $n$-butane values give the highest ratios since $n$-butane is in the denominator of the ratio.

The ROSE 92 and Colorado data sets show a dependence of the observed ratio upon wind direction, which suggests different emission source ratios in different regions. In the ROSE 92 study the geometric mean ratios were 0.51 and 0.64 in the quadrants of wind direction centered on north and southwest, respectively. (This dependence was also observed in a 1990 study at the same site.) When this wind direction dependence is removed from the data, $\sigma$ drops from 16% to 13%. In the Colorado data set reported by the same research group [*Goldan et al.*, 1996], geometric mean ratios were 0.45 and 0.57 with $\sigma$ values of 8% and 14% under east and west

winds, respectively. The absolute concentrations in the west winds were much lower, which accounts for their higher $\sigma$. The variability observed in these data sets is well within expected source variability, which is indicated by the $\sigma$ value of 32% from the 71 city, U.S. Urban data set.

The butane isomers are in the top 10 most abundant NMHCs (Table 1) and they are relatively unreactive. Thus butanes should be above the detection limit whenever other NMHCs are quantified, particularly in samples taken within the U.S. continental boundary layer. The literature data sets and three of the SOS data sets report both butane isomers above the detection limit for nearly all samples, excepting a small fraction of the data collected in the free troposphere.

To summarize, three evaluative tests may be applied to measurements of the butane isomers in the continental United States:

1. The geometric mean ratio of the butane isomers should be in the range of 0.4 to 0.6.

2. The value of $\sigma$ should be below 20%, unless very different source regions are sampled.

3. The butanes should be above the detection limit when other NMHCs are quantifiable except perhaps in the free troposphere.

Data sets failing these tests are suspect, and the experimental procedures should be reviewed before seeking an atmospheric explanation.

The first two SOS data sets of Table 3 are shown in Figure 5c, where the ordinate scale is expanded by a factor of 100 over that of the top two panels. These two data sets pass the first test, but fail the second and third. A large fraction of samples report one or both butane isomers as below detection limit. A fraction of the SOS Cans samples were collected from aircraft, where very clean air might be encountered. However, the aircraft fraction only accounts for a representative fraction of the below detection limit data. It is noteworthy that 74% of the $n$-butane and 63% of the $i$-butane below detection limit data occurred in the 29% of the samples that reported ethane below detection limit. A single experimental problem may account for both data anomalies. The GC/MS A data report one or both butane isomers below detection limit in 58% of the samples, unexpected for a suburban Nashville site.

The SOS Cans and GC/MS A data sets also exhibit much larger scatter in the ratios than any of the other SOS or literature data sets, and the scatter of the GC/MS B data is also somewhat large. The variability of the other data sets, which cover a variety of sampling regions and conditions, suggests that the ambient variability of the ratio is not high. Although the SOS Cans data set includes eleven surface sites and two aircraft, systematic differences between different sites contribute negligibly to the overall scatter. The average ratios from the different sites were not significantly different statistically. In the absence of evidence for a particularly unusual set of sources at the two GC/MS and SOS Cans sites, measurement imprecision must be suspected as the predominant cause of this scatter.

The GC/MS B data set also reports a geometric mean ratio somewhat higher than the other SOS data sets. The median ratio of the samples of the SOS Cans data set collected at this site was between 0.37 and 0.49. (The geometric mean ratio of this site subset was 0.69, but this was strongly influenced by one sample reporting a ratio of 5.7.) Lacking evidence that the ratio was systematically high at this site, systematic error should be suspected.
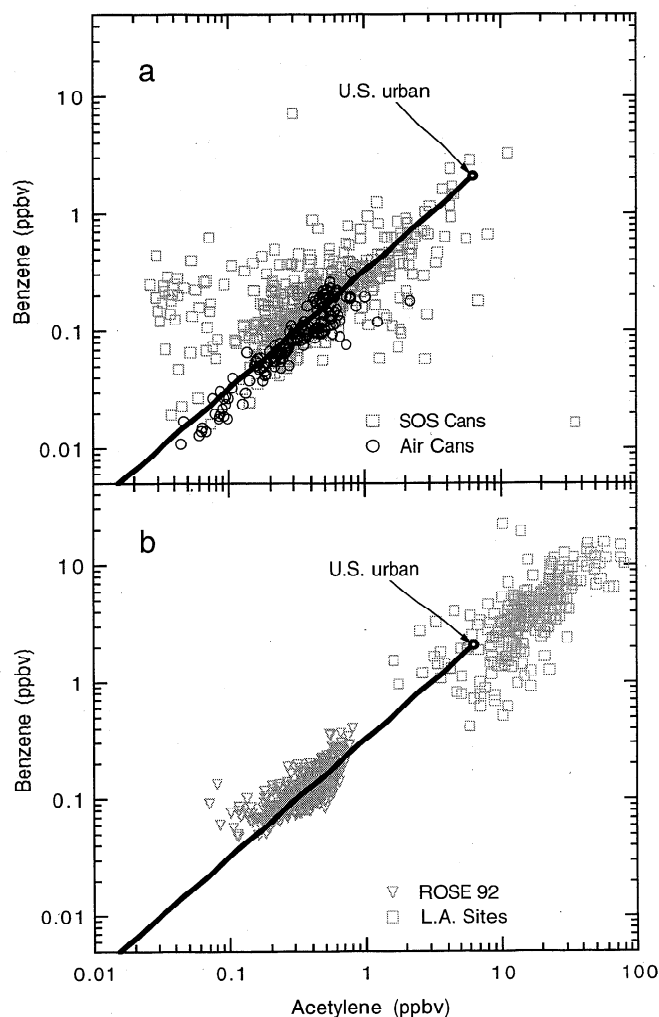
**Figure 6.** Log-log correlation plots of benzene versus acetylene for (a) the SOS data sets and (b) the literature data sets. The median urban concentrations from Table 1 are given by the thick open circle, and the solid line indicates their constant ratio.

In summary, experimental problems are indicated for the butane measurements in three of the SOS data sets. These included an unexpectedly large number of samples reporting one or both of the isomers below detection limit in two data sets, large measurement imprecision reflected in large scatter in the butane ratios, and possibly a systematic error indicated by a divergent mean ratio for one of the data sets. The two SOS aircraft data sets exhibited no experimental problems according to the diagnostics employed here.

## 5.2. Ratios of NMHCs of Different Reactivity: Benzene/Acetylene

Benzene and acetylene are abundant in urban emissions (Table 1). They have common sources, which should limit atmospheric variability of their ratio. (Both are primarily emitted by vehicle exhaust; the use of benzene as a solvent and its presence in unburned gasoline has been reduced over the last two to three decades due to toxicity concerns.) They are less reactive than the butane isomers (Figure 1), so emissions from sources with different ratios will be more well mixed in the continental boundary layer than the butane isomers.

Because of their long photochemical lifetimes the difference in their reactivity toward OH should only affect their ratio in remote areas. Finally, these two compounds have quite different chromatographic retention times, volatilities, and physicochemical behaviors with regard to canister or adsorbent materials; thus they may provide a stringent test of analysis procedures.

Figure 6 presents the correlation of benzene with acetylene. Only four of the ten SOS and literature data sets report both of these compounds due to the difficulty of analyzing both of these species by one system. The agreement of three of these data sets with the urban emission ratio is good, with few outliers. The SOS Cans data exhibit large scatter, indicating significant experimental problems.

Figure 7 and Table 4 present the distributions of the ratios. The L.A. Sites ratio is significantly lower than the median urban value; this difference may reflect measurement problems in the L.A. Sites data set or varying emission ratios over time (the Los Angeles data were collected about a decade earlier).

The mean ratio of the ROSE 92 data set agrees with the median urban value, while the Air Cans mean ratio is 20% lower. This lower ratio could possibly reflect the greater reactivity of benzene compared to acetylene that would gradually reduce the ratio in an air mass isolated from fresh emissions. The Air Cans data were collected from an aircraft, with many samples taken in the free troposphere. A concentration-weighted average residence time of 5 days at a typical summertime diurnally averaged OH concentration of 1 x $10^6$ cm$^{-3}$ would convert the median urban ratio to the Air Cans mean ratio. However, this scenario is not supported by the altitude dependence of the ratio; the Air Cans ratios show no significant difference when free troposphere (likely more aged) samples are compared to boundary layer (likely fresher) samples. Therefore a 20% systematic error is indicated in the determination of this ratio in the Air Cans data set. This error is apparently in the determination of benzene, since the Air Cans and AIR GC acetylene measurements agreed to within 1%, as will be discussed below.

The scatter in the Air Cans and the ROSE 92 data sets (both 20%) are somewhat larger than was found for the butane isomer ratio. Either there is poorer measurement precision for acetylene and/or benzene or the benzene to acetylene ratio shows more ambient variability than the butane isomer ratio despite the lesser reactivity of the former species. The greater ambient variability of the benzene to acetylene ratio is supported by the greater variability seen in the urban data; both the L.A. Sites and the U.S. Urban data sets have substantially greater variability in this ratio than in the butane isomer ratio (compare Tables 3 and 4).

Figure 8, which shows the intercomparison of coincident measurements of acetylene and benzene, provides additional information regarding the instrumental precision. The acetylene data are from the two SOS aircraft data sets. The benzene data are from a 1990 study at the same site by the same research group that produced the ROSE 92 literature data set. During the 1990 study a GC/FID system similar to that used in ROSE 92 was compared to a second GC/FID system with separate sample collection and different chromatography [Montzka et al., 1993]. The acetylene data in Figure 8a are consistent with a systematic difference of no more than 1% and a mean experimental precision for the Air Cans and Air GC data sets of 6%, while the benzene data indicate a systematic difference of 5% and a mean experimental precision of 21%. If
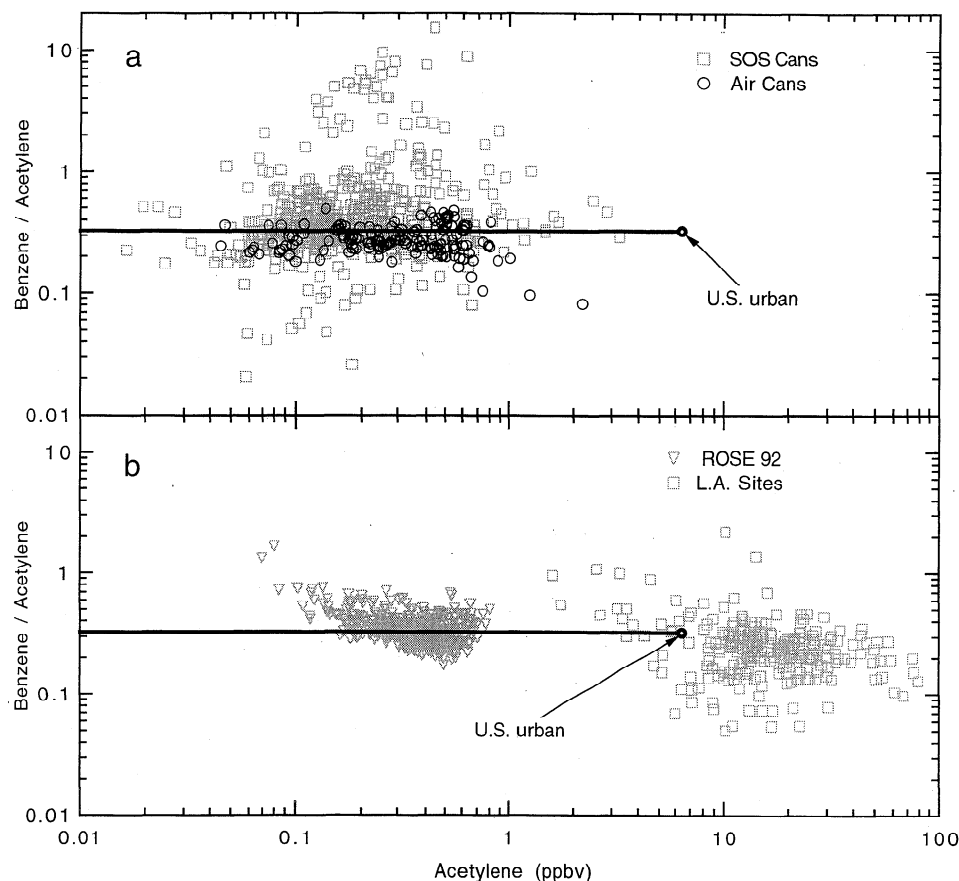
**Figure 7.** Log-log plots of the ratio of benzene to acetylene as a function of the acetylene concentration for (a) the SOS data sets and (b) the literature data sets. The median urban data from Table 1 are given by the thick open circle, and the solid line indicates their constant ratio.

these precisions can be taken as representative of the rural data sets presented in Figure 7 and Table 4, then a $\sigma$ value of 15% is expected for the benzene to acetylene ratio (the root-mean-square of the $\sigma$ value for the two constituent NMHCs) in the absence of ambient variability in this ratio. The $\sigma$ values of 20% found for the Air Cans and ROSE 92 data sets (which correspond to $\sigma_{lnz}$ values of 28%) implies that ambient variability of the benzene to acetylene ratio does contribute to the scatter in the observed ratios. This $\sigma_{lnz}$ value is consistent with the propagation of the 6% and 21% measurement precisions with an 18% ambient variability. Thus for this ratio, approximately equal contributions from ambient variability and instrumental imprecision to the variability of the observations are indicated for these two rural data sets.

**Table 4.** Parameters for Benzene to Acetylene Ratio Evaluation

| Data Set | Mean Ratio | ADL[a] | $\sigma$ |
|---|---|---|---|
| Median urban[b] | 0.33 | --- | --- |
| SOS Cans | 0.43 | 76% | 66% |
| Air Cans | 0.27 | 100% | 20% |
| ROSE 92 | 0.33 | 99% | 20% |
| L.A. Sites | 0.23 | 100% | 39% |
| U.S. Urban | 0.33 | $\geq 95\%$ | 44% |

[a]fraction of chromatograms with both benzene and acetylene above the detection limit.

[b]ratio of median urban concentrations from *Seila et al.* [1989b].

Three evaluative tests may be applied to measurements of acetylene and benzene from the continental United States:
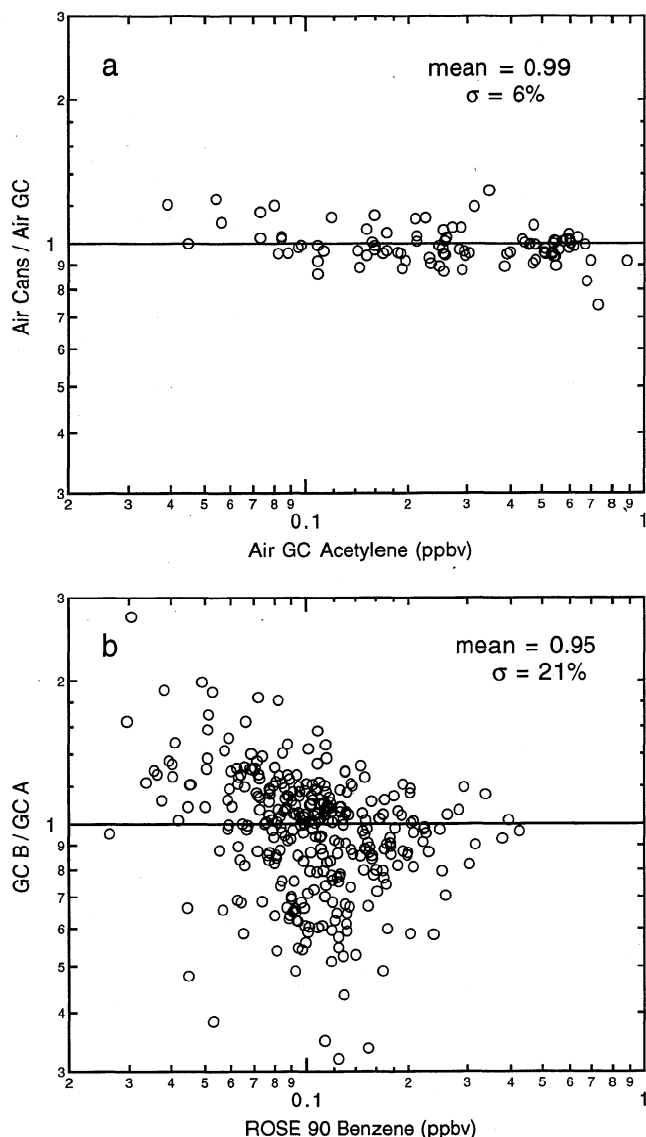
1. The geometric mean ratio of benzene to acetylene should be near the median urban ratio of 0.33.

2. The value of $\sigma$ for rural areas should approach 20%, with values perhaps a factor of 2 higher in urban areas.

3. Benzene and acetylene should be above the detection limit when other NMHCs are quantifiable.

Data sets failing these tests are suspect, and experimental procedures should be reviewed before seeking an atmospheric explanation.

Each test suggests problems in the SOS Cans data set (Table 4 and Figure 7). The mean ratio is about 30% higher than expected; since acetylene (a light NMHC) is in the denominator, this deviation is consistent with the systematic undermeasurement of the light hydrocarbons, as suggested previously. As further indication of a light NMHC measurement problem, less than 1% of the samples reported acetylene but not benzene above the detection limit, while 76% of the samples with acetylene below the detection limit also reported ethane below the detection limit. The large scatter toward positive values for this data set probably arises from the same problem. The few outliers toward low ratios must have another cause.

## 6. Ratios of Short-Lived NMHCs

The ratios of slowly reacting NMHCs provide useful diagnostics of the measurement systems, but the more reactive

**Figure 8.** Log-log plots of the ratios of coincident measurements by two different techniques of (a) acetylene from the two SOS aircraft data sets and (b) benzene from two 1990 surface site data sets. The geometric mean ratio and the root-mean-square of the fractional uncertainty in the measurement of each NMHC are given in each caption.

NMHCs, the aromatics and the alkenes, are of greater interest with respect to photochemical production of ozone. Their measurement is challenging for three reasons. First, their urban ambient levels (Table 1) often are smaller than for the species investigated above, which reflects their smaller emission rates. Second, they are more reactive in the atmosphere (Figure 1), so their ambient levels drop rapidly during transport from emission sources and can reach sub-pptv levels. Third, their higher reactivity may well lead to measurement problems during the sample collection, concentration, and analysis processes.

## 6.1. Ratios of NMHCs of Similar Reactivity: Ethylbenzene/Toluene

Two relatively abundant aromatic NMHCs, ethylbenzene and toluene, have the same reactivity to within 20% (Figure 1).

With some notable exceptions the results in Figures 9 and 10 and Table 5 indicate that the ratio indeed does remain relatively constant over a wide range of ambient concentrations. The σ value for the U.S. Urban data set in Table 5 is smaller than found for the butane ratio and for benzene/acetylene. We take this to indicate that there is generally less variability in the emission ratios of these aromatic species compared to the two previous ratios. Despite these generally favorable conditions, the results in Figure 10 and Table 5 indicate experimental problems both in the literature and in the SOS data sets.

Two of the literature data sets report low mean ratios. The L.A. Sites value from 1975 measurements is nearly a factor of 3 lower than the median urban ratio from 1984 to 1986 measurements. This disagreement likely represents an experimental problem in the L.A. Sites data set. There is no evidence that emission ratios changed over the decade between the two measurement sets or that the emissions in Los Angeles have particularly low ethylbenzene to toluene ratios. For example, the ratio of the means from the 1979 measurements of *Singh et al.* [1981] in Los Angeles is 0.192, in reasonable agreement with the 0.153 median urban ratio. Because similar low ratios were found at each of the four sites included in the
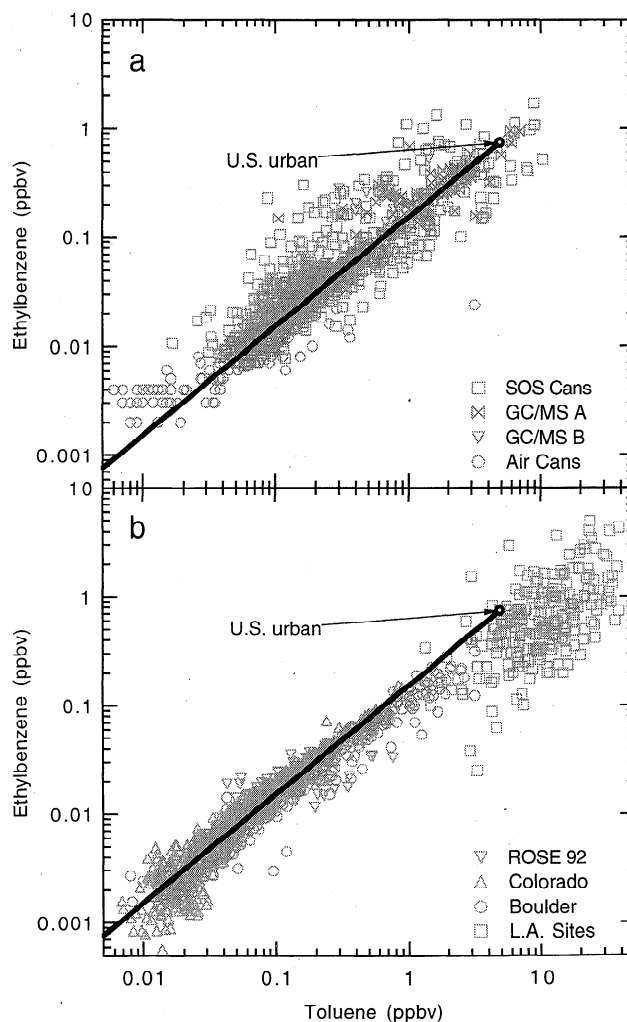


**Figure 9.** Log-log correlation plots of ethylbenzene versus toluene for (a) the SOS data sets and (b) the literature data sets. The median urban concentrations from Table 1 are given by the thick open circle, and the solid line indicates their constant ratio.
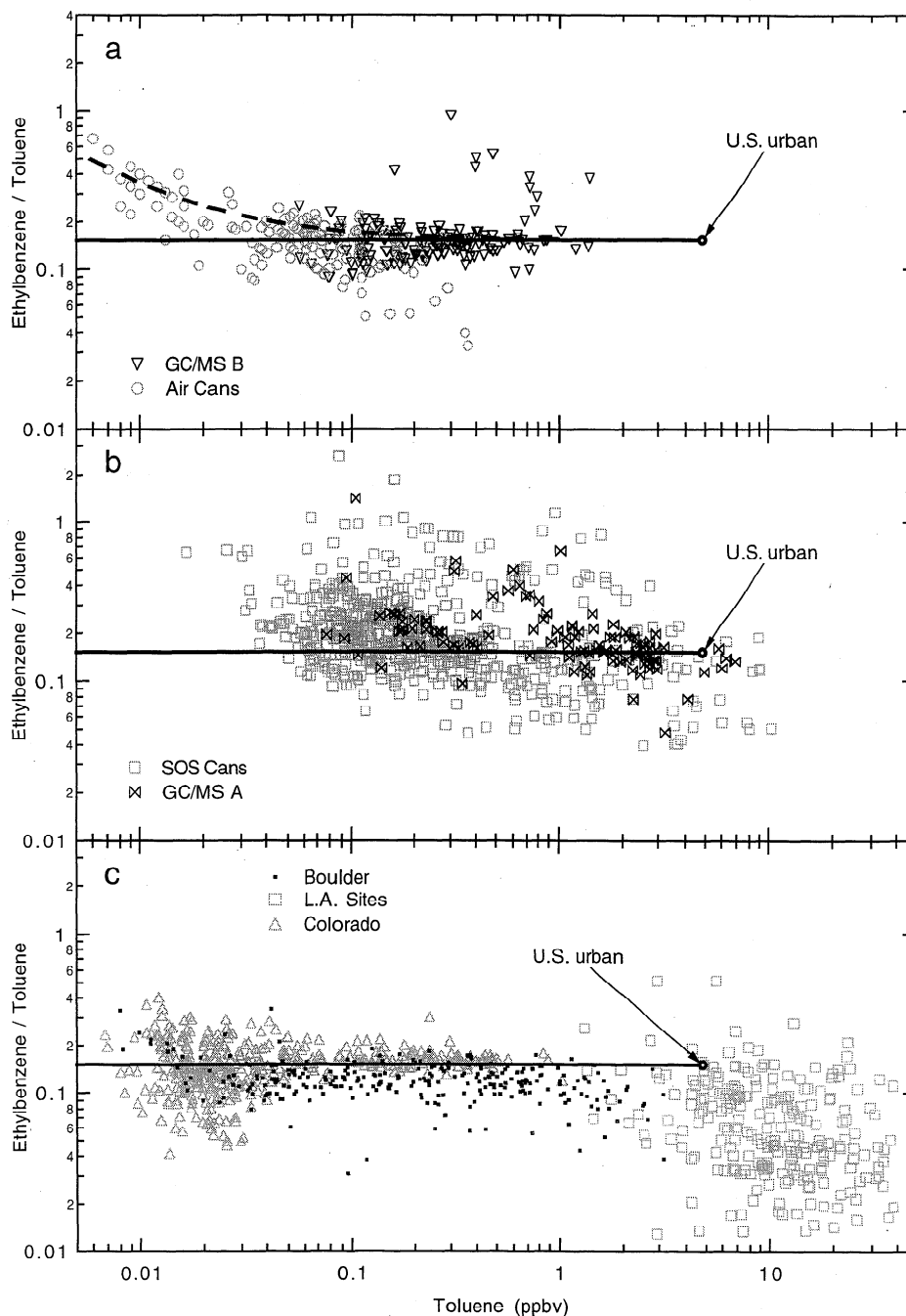
**Figure 10.** Log-log plots of the ratio of ethylbenzene to toluene as a function of (a) the toluene concentration for the SOS data sets and (b) the literature data sets. The median urban data from Table 1 are given by the thick open circle, and the solid line indicates their constant ratio.

L.A. Sites data set, the low ratios likely indicate a systematic instrumental problem rather than distortion by unrepresentative sources local to a particular sampling site. The Boulder mean ratio is 30% lower than the median urban ratio; this is likely due to the influence of local sources of toluene separate from the other aromatics that *Goldan et al.* [1995b] discussed. The other two literature data sets and the four SOS data sets agree with the median urban ratio to within 22% or better.

The ROSE 92 and Boulder data sets have $\sigma$ values significantly smaller than that of the U.S. Urban data set. This is reasonable for single-site studies versus the 71 cities

sampled in the U.S. Urban data set. In Figure 10c at the higher toluene levels, the Boulder data exhibit scatter primarily below the U.S. Urban median ratio, perhaps reflecting the sporadic influence of the local toluene source. The $\sigma$ value for the Colorado data set is similar to that of the U.S. Urban data set but is dominated by scatter at the low levels (Figure 10c), which must represent experimental imprecision. The root-mean-square imprecision of the toluene and ethylbenzene determinations (estimated as $\sigma$) is 6% for toluene > 100 pptv (ethylbenzene > $\approx$15 pptv) and 30% for toluene < 50 pptv (ethylbenzene < $\approx$7 pptv). The largest $\sigma$ value of any of the data sets is from the L.A. Sites, which likely reflects

**Table 5.** Parameters for Ethylbenzene to Toluene Ratio Evaluation

| Data Set | Mean Ratio | ADL[a] | $\sigma$ |
|---|---|---|---|
| Median urban[b] | 0.153 | --- | --- |
| SOS Cans | 0.187 | 86% | 44% |
| GC/MS A | 0.184 | 85% | 31% |
| GC/MS B | 0.153 | 100% | 25% |
| Air Cans | 0.156 | 94% | 38% |
| ROSE 92 | 0.168 | 95% | 17% |
| Colorado | 0.147 | 88% | 26% |
| Boulder | 0.118 | 96% | 21% |
| L.A. Sites | 0.059 | 99% | 51% |
| U.S. Urban | 0.144 | $\geq 99\%$ | 26% |

[a]fraction of chromatograms with both ethylbenzene and toluene above the detection limit.

[b]ratio of median urban concentrations from *Seila et al.* [1989b].

experimental imprecision associated with the systematic instrumental error identified above.

Because of its low emissions and high reactivity, ethylbenzene may fall to or below pptv levels. However, the ROSE 92, Colorado, and Boulder data sets each found at least 88% of samples above the detection limit.

Three evaluative tests may be applied to measurements of ethylbenzene and toluene from the continental United States:

1. The geometric mean ratio of ethylbenzene to toluene should be within about 20% of the median urban ratio of 0.153.

2. The value of $\sigma$ for rural areas should approach 20%, with values below 30% in urban areas.

3. With due regard for instrumentation and site locale, the data generally should be above the detection limit, with the exception of a significant fraction of the cleanest air samples.

Data sets failing these tests are suspect, and experimental procedures should be reviewed before seeking an atmospheric explanation.

Of the SOS data sets, only the GC/MS B data set has a $\sigma$ value comparable to that of the U.S. Urban data set. The scatter in this data set (Figure 10a) primarily arises from outliers at high ratios that constitute less than 7% of the data set; if these outliers are excluded, $\sigma$ drops to 14%. It would be worthwhile to examine these outliers in detail to determine if there were any particular experimental conditions associated with them. The Air Cans data set has a high $\sigma$ value that arises partially from outliers at low ratios and relatively high toluene levels but primarily from large ratios at the lowest toluene levels. These large ratios in this data set may arise from a systematic offset in the ethylbenzene measurements; the dashed line in Figure 10a shows the effect that a constant 2 pptv ethylbenzene offset would have on an otherwise constant ethylbenzene to toluene ratio. The SOS Cans and GC/MS A data sets (Figure 10b) have $\sigma$ values higher than the U.S. Urban data set with scatter at all toluene levels, which likely reflects experimental imprecision.

This is the first ratio for the Air Cans data set with a significant fraction (6%) of the measurements of at least one of the species below the detection limit. These data represent the cleanest air parcels encountered in the aircraft sampling. The GC/MS B data set found 100% of the data above the detection limit for all three of the ratios discussed (butanes, benzene/acetylene, ethylbenzene/toluene); this reflects the more polluted rural surface location of this measurement site. In contrast, the SOS Cans and the GC/MS A data sets found a greater proportion of both of these aromatic species above the detection limit than in the previous two ratios. This is again consistent with a light NMHC measurement problem in the SOS Cans data set. For the GC/MS A data set, this feature must provide useful diagnostic information.

## 6.2. Ratios of NMHCs of Different Reactivity: Xylenes, Toluene, and Benzene

Most ratios of NMHCs are expected to change due to differential reactivity as the NMHCs are removed from the atmosphere by reaction with OH. If all of the NMHCs in a sampled air parcel were emitted simultaneously, and the time between emission and measurement is known, then the evolution of the ratios can provide information regarding the average OH concentration [e.g., *Roberts et al.*, 1984, and references cited therein]. However, this simple picture is not met in practice, and the inevitable mixing of NMHCs from different sources emitted at different times complicates the interpretation [*McKeen and Liu*, 1993].

Comparison of two NMHC ratios at least allows limits to be placed upon expected NMHC ratio evolution. Figure 11 shows ratios derived from the three most abundant aromatic NMHCs from Table 1. (Metaxylene and paraxylene are usually reported together since they are difficult to separate in the GC analysis process; an effective OH rate constant of $2 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ is assumed for the xylene mixture.) The ratios of the urban median concentrations are indicated by the small, thick open circle. If all of the NMHCs reacted with OH at the same rate, all measurements would scatter closely about this point. Two limits can be placed upon the evolution of the ratios, given the reactivity differences. In the absence of mixing, the ratios would be expected to evolve according to the respective OH kinetics. *Roberts et al.* [1984] show that on log-log plots of the ratios, the initial emission ratios would evolve along the "aging" line in Figure 11, whose slope is given by $(k_{m,p-xylene}-k_{benzene})/(k_{toluene}-k_{benzene})$. In the absence of reaction, mixing of polluted air parcels with pristine air would not affect the ratio. However, if fresh emissions are mixed with air that has been aged to the extent that the xylenes and toluene have been reduced to negligible levels, but significant levels of the less reactive benzene remain, then mixing would reduce each ratio proportionately. Then the ratios would move along the "mixing" line with a slope of unity. In reality, aging and mixing occur simultaneously, and the measurements should fall into the sector between the "mixing" and the "aging" lines.

The literature data sets in Figure 11b meet these expectations. (The L.A. Sites data are not included and will not be used further since the aromatic data from this set is suspect.) The full U.S. Urban data set represents urban measurements; the data scatter above and below the ratio of the medians, predominately along the mixing line. The three suburban and rural literature data sets span relatively wide ranges of values and fall primarily within the "allowed" region between the two solid lines as expected. The points at the highest ratios in the Boulder data set, which lie to the right of the ratio of urban medians, correspond to the distinct toluene sources identified by *Goldan et al.* [1995b]. The data from all three sets fall generally near the "mixing" line. Evidently, the sampled air parcels generally represent mixtures of relatively fresh emissions superimposed upon a more aged NMHC mixture.

The SOS data sets in Figure 11a present a similar picture except that greater scatter is obvious, particularly in the SOS
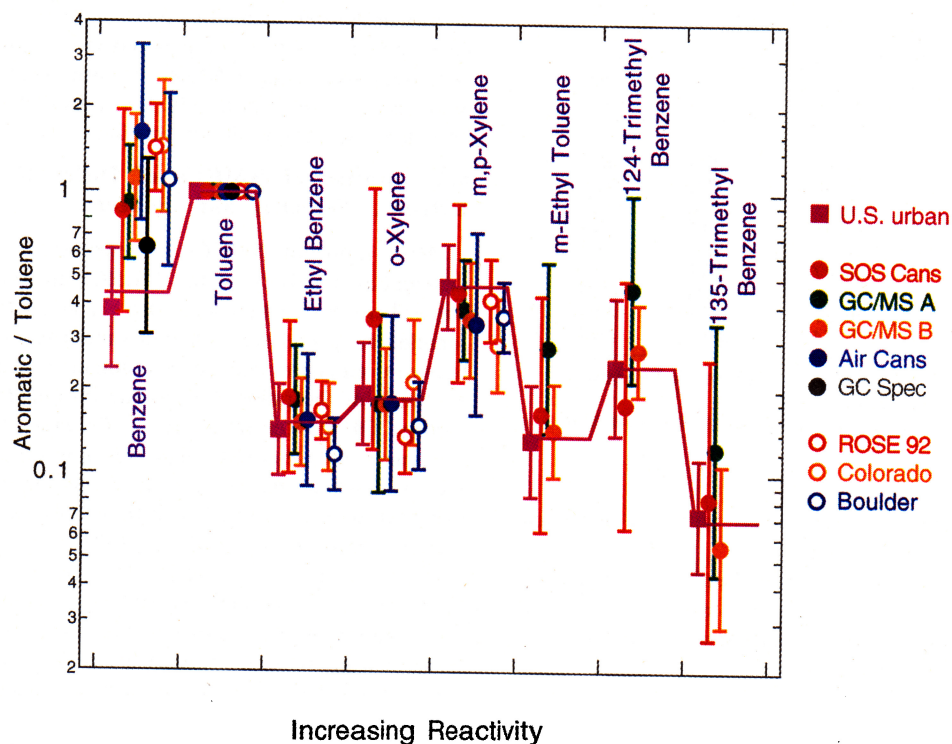
**Plate 1.** Log plot of ratios of aromatic NMHCs to toluene in order of increasing OH reactivity of the aromatic. Each symbol and error bar give the geometric mean and standard deviation for the labeled ratio. The color key for the data sets is on the right; solid and open symbols indicate the SOS and literature data sets, respectively. The ratios of the urban medians are indicated by the solid line through the data.
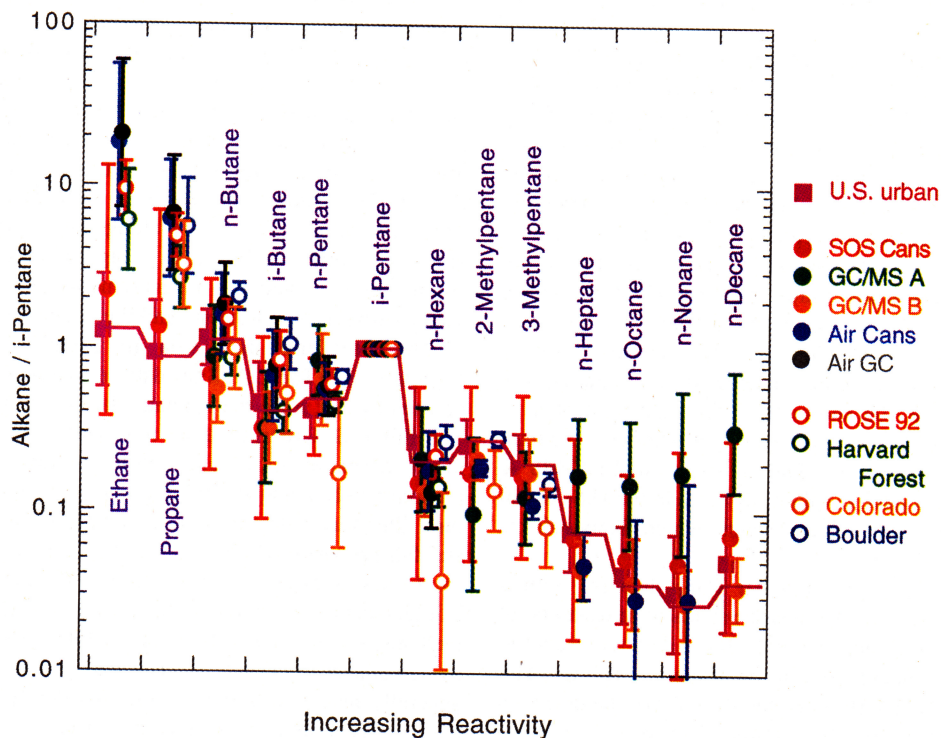


**Plate 2.** Log plot of ratios of alkanes to *i*-pentane in order of increasing reactivity of the alkane with OH. The format of the plot is described in the caption to Plate 1.
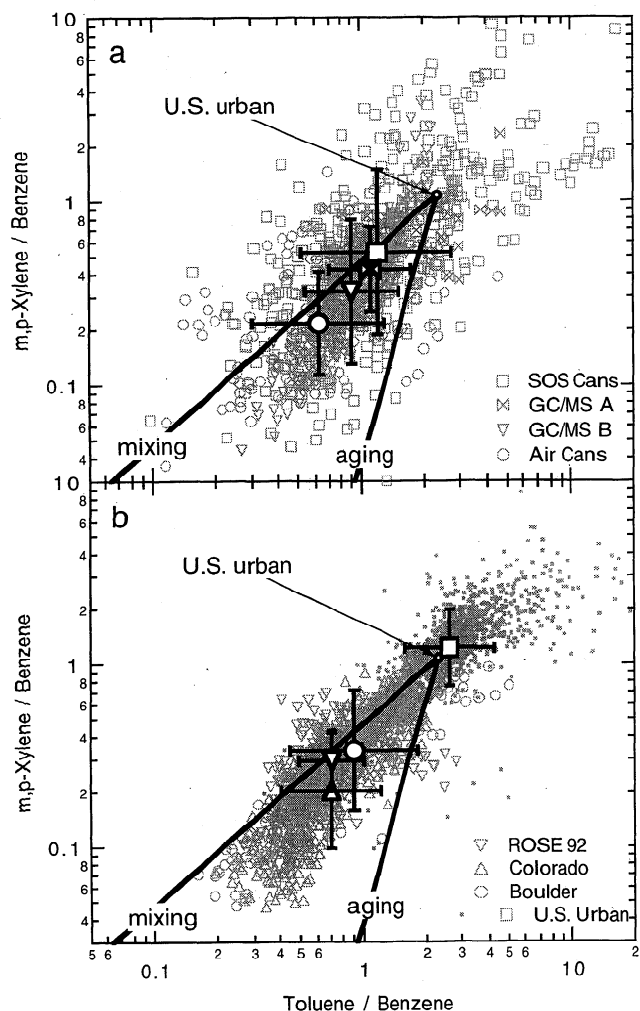
**Figure 11.** Log-log plots for the ratios of m,p-xylene to benzene versus toluene to benzene for (a) the SOS data sets and (b) the literature data sets. The ratios of the median urban concentrations from Table 1 are given by the small, thick open circles. The solid line labeled "mixing" indicates the proportional reduction of the emission ratios with a slope of unity. The "aging" line shows the evolution of the ratio for reaction with OH. The geometric means and standard deviations for the ratios from the data sets are indicated by the respective large symbols and error bars.

Cans data set. Large imprecision in the SOS Cans data set has been identified repeatedly in this work. The ratios of the Air Cans data are lower, corresponding to the generally more aged air found in the aircraft samples. The Air Cans data also exhibit substantially greater scatter at small ratios than the literature data sets, including a significant fraction of points outside the allowed sector. The scatter may indicate the difficulty of obtaining reliable measurements of aromatic NMHCs below a few tenths of a ppbv in canister samples.

The larger symbols with error bars in Figure 11 give the geometric mean and standard deviations for each ratio and thus provide a summary of the distribution of the ratios in each data set. The deviation of the mean from the U.S. Urban median ratio gives a measure of some weighted average age of the NMHC mixture, where the aging process includes reaction of freshly emitted NMHC with OH and the mixing of fresh

emissions with more aged "background" air. In the discussion below, we use these geometric means and standard deviations to examine the behavior of many ratios in the data sets; however it must be kept in mind that the magnitude of the geometric standard deviations reflects three factors: variation in ratios of emissions, the range of "ages" of sampled air parcels, and any imprecision of the measurements.

## 7. Concentration Patterns

### 7.1. Aromatics

Plate 1 presents the geometric means and standard deviations of the ratios of the aromatic NMHCs to toluene for all data sets. These symbols are thus analogous to the symbols with error bars in Figure 11, except that a different aromatic NMHC has been selected for the denominator. Data from urban areas should lie near the U.S. Urban median ratios indicated by the connected horizontal line segments, much as do the squares, the symbols for the complete U.S. Urban data set. Data from sites more isolated from sources should show two effects of the aging that must occur during transport from the sources to the sampling site. First, the benzene to toluene ratio is expected to be higher than the urban ratio since the less reactive NMHC is in the numerator. Second, the geometric mean ratios to the right of toluene should lie below the U.S. Urban line due to the faster removal of the more reactive NMHC in the ratio numerator. These ratios are expected to fall progressively farther below the line as the reactivity of the aromatic increases to the right in Plate 1.

The literature data sets (open circles) qualitatively follow these expectations. The benzene to toluene ratios are factors of 2.5 to 3.3 above the urban ratios, and the xylene ratios usually lie below the urban median ratios. Higher aromatics are not reported in any of the literature data sets.

The SOS data sets present a less clear picture. In all cases the benzene to toluene ratio is well above the urban ratio. Included here is an additional data set (GC Spec) of benzene and toluene measurements (P. Shepson, private communication, 1997) collected at the same site as the GC/MS B data set; there is a significant disagreement in the geometric mean benzene to toluene ratio from these two data sets (0.64 versus 1.11). It would be informative to investigate the cause of this difference. Apart from this discrepancy, the benzene ratios from all of the SOS data sets are in approximate agreement with the literature data sets. The Air Cans ratio is the highest, in accord with the greater degree of aging expected for the aircraft samples.

A remarkable feature of the SOS data sets in Plate 1 is that there is no apparent decrease in the ratios as the reactivity of the aromatics increases to the right of toluene. The GC/MS B data set is in agreement with the urban median ratios for all of the more reactive aromatics. However, the SOS Cans and the GC/MS A data sets present no coherent aging pattern; some ratios agree with the urban ratios, but some seem to be enriched in the more reactive aromatics, a feature that must indicate experimental problems. For example, in the SOS Cans data, one xylene ratio indicates enrichment of that NMHC, while the other xylene ratio agrees with the urban pattern, and in the GC/MS A data set the xylenes fit the urban pattern, but the three most reactive aromatics are enriched with respect to toluene. (Some such effects could arise from greater fractions of the more reactive NMHCs falling below the detection limit and leaving only relatively unaged samples

available for calculating ratios; however, that is not the case in these examples since the median, including below detection limit data, ratios show the same trends.) This disagreement with expected patterns must indicate experimental problems. Problems with the Air Cans data set are indicated by the very large standard deviations of the ratios regardless of the degree of aging, although the aging patterns agree with the literature data sets.

## 7.2.    Alkanes

Plate 2 is a plot for the alkanes similar to Plate 1 for the aromatics. This figure is very similar to that presented by *Jobson et al.* [1994b]. Here *i*-pentane has been selected for the denominator of each ratio. Aging is expected to increase the ratios of the less reactive alkanes (ethane, propane and the butanes) from the ratio of urban medians and to decrease the ratios of the alkanes that are more reactive than *i*-pentane.

The light alkanes in the literature and SOS data sets generally behave as expected. The reactivity of *n*-pentane and *i*-pentane is very nearly equal; thus their ratio should remain nearly constant. The ratio is generally consistent between data sets and shows low variability within data sets. The two exceptions are the GC/MS A and Colorado data sets; their systematic deviation suggests systematic errors. (The cause of the deviation in the Colorado data set is discussed below.) The ratios for the butane isomers from several of the data sets are above the urban ratio, the expected result of aging. However, *i*-butane is apparently consistently more aged than *n*-butane despite their similar reactivity; this supports the hypothesis that *n*-butane is overestimated in the U.S. Urban data set. All data sets exhibit aging in the propane and ethane measurements; but the SOS Cans data are outliers, again indicating a systematic problem in the light NMHC measurements. The two SOS aircraft data sets show the greatest degree of aging, again consistent with sampling at higher altitude. Perhaps surprisingly, the one wintertime data set, Boulder, shows a high degree of aging of the light alkanes. This is due to the superposition of relatively fresh emissions upon the elevated, hemisphere-wide background levels of the light alkanes [*Jobson et al.*, 1994b; *Goldstein et al.*, 1995].

Similar to the aromatics shown in Plate 1, the difference between the data set ratios and the urban ratio does not consistently increase with reactivity of the NMHCs in these data sets. The heavy alkanes in three of the data sets (GC/MS B, Air Cans, and Boulder) closely follow the U.S. Urban pattern. The SOS Cans and especially the GC/MS A data rise above the U.S. Urban pattern at the heaviest alkanes, suggesting systematic problems in these measurements. A second concern is the large variability of the measured ratios in the SOS Cans for all alkanes, and in the Air Cans for the heaviest NMHCs. The SOS Cans data set must have significant problems with experimental imprecision. The Air Cans data set seems to have a similar problem with the most reactive alkanes that are found at the lowest levels.

The Colorado data set is clearly an outlier in Plate 2. This problem has been traced the coelution of ethanol with *i*-pentane, which falsely increases the denominator of all of the ratios. Also, *n*-pentane and *n*-hexane were poorly resolved from acetone and methylvinyl ketone, respectively. The procedure for integrating these two alkanes underestimated concentrations below about 0.1 ppbv in particular, leading to
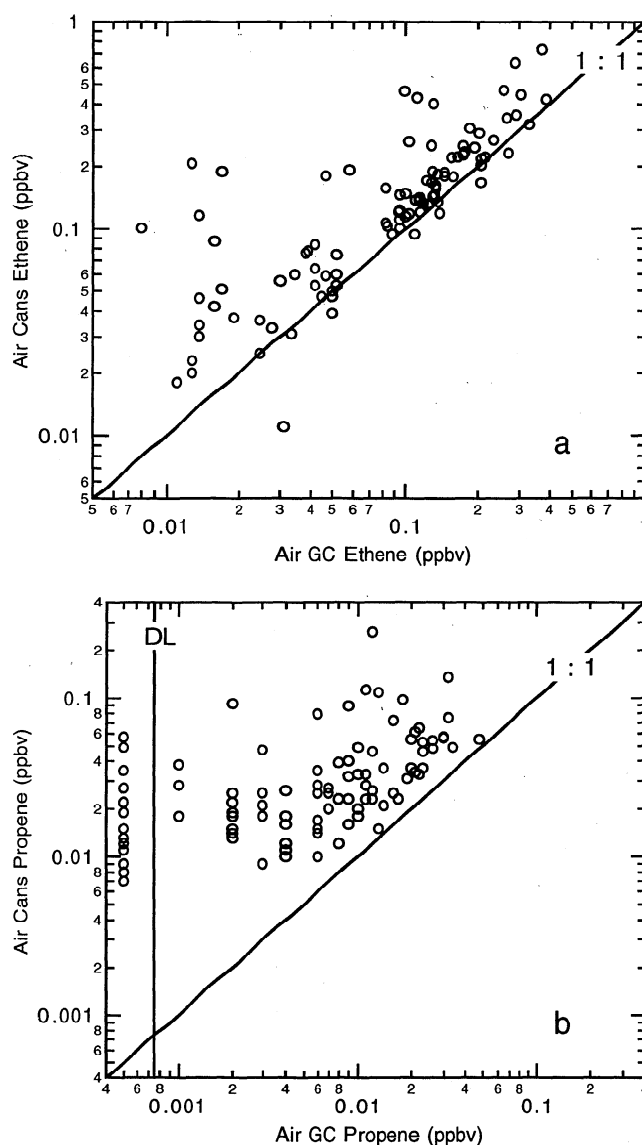


**Figure 12.** Log-log correlation plots of the simultaneous measurements of (a) ethene and (b) propene from the two SOS aircraft data sets. The 1:1 line in each panel indicates where points in good agreement would lie and the DL line in Figure 12b separates the Air GC measurements of propene above from those below the detection limit; the points reported as below the detection limit are plotted here as 0.0005 ppbv.

highly variable ratios systematically below the U.S. Urban pattern.

## 7.3.    Alkenes

Figure 12 compares coincident measurements of two alkenes from the two SOS aircraft data sets; significant systematic errors are obvious. The canister-based measurements (Air Cans) are generally significantly higher, often by a factor of 10 or more, than those from the in situ GC system (Air GC). Other comparisons between canister and in situ GC measurements [*Donahue and Prinn*, 1993; *Greenberg et al.*, 1996] also found substantially higher alkene levels in the canisters. Although Figure 12 shows clear disagreement between the two data sets, it does not establish which, if either, is correct.
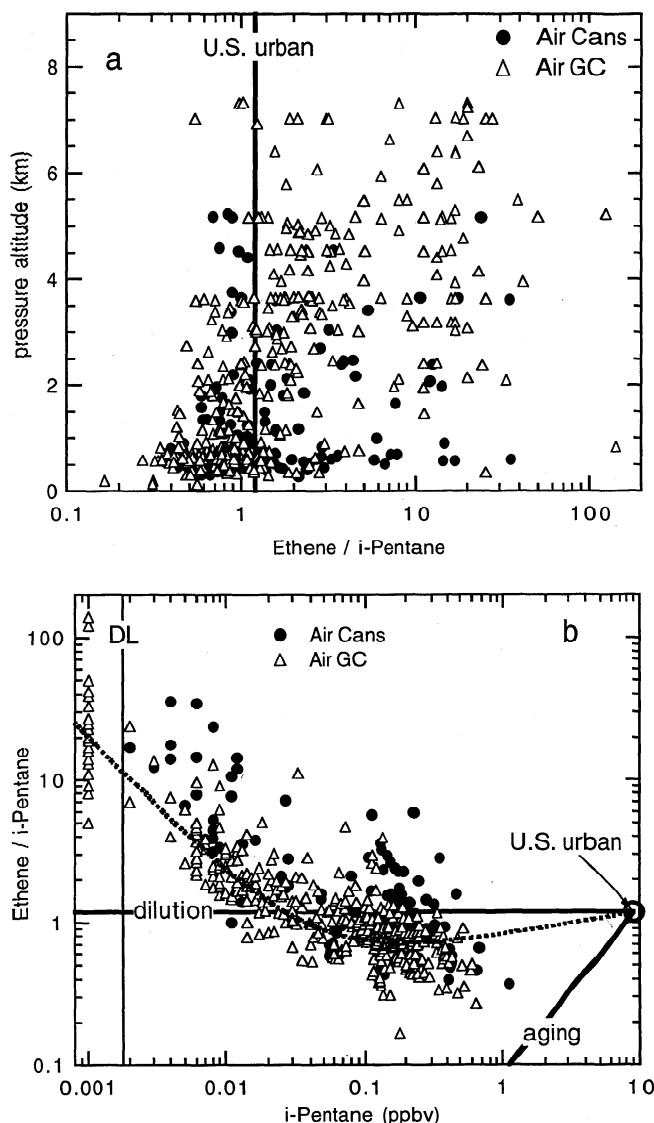
**Figure 13.** Ethene to *i*-pentane ratio for the two SOS aircraft data sets as a function of (a) altitude and (b) *i*-pentane mixing ratio. The solid line in Figure 13a and the open circle and the line labeled "dilution" in Figure 13b give the urban median data. The solid "aging" line in Figure 13b shows the evolution of the ratio expected from reaction with OH. The curved dotted line is discussed in the text. The DL line in Figure 13b separates the Air GC measurements of *i*-pentane above from those below the detection limit; the points reported as below the detection limit are plotted in both panels as 0.001 ppbv.

Examining the ratio of ethene to *i*-pentane (Figure 13) provides an indication of the cause and magnitude of the systematic errors. *I*-pentane is the most reactive of the alkanes consistently above the detection limit in the aircraft samples. Ethene is about a factor of 2 more reactive, so the ratio of ethene to *i*-pentane should decrease as air samples age. Figure 13a presents the altitude dependence of this ratio. More aged air is expected at higher altitudes, particularly above the boundary layer height of 1 to 2 km; thus the points should lie progressively further to the left of the U.S. Urban line with increasing altitude. Clearly, this expectation is not met in either of the data sets, since the data are predominately to the right at high altitudes, often by 1 to 2 orders of magnitude.

Figure 13b shows the dependence of the ethene to *i*-pentane ratio upon the *i*-pentane concentration. Analogous to previous discussion, the data should lie predominately in the sector between the "aging" and the "dilution" lines. However, in both data sets the ratio increases as the *i*-pentane levels decrease.

Assuming that the *i*-pentane measurements are accurate, as was generally indicated by the investigation of the alkane measurements in the previous section, the behavior in Figure 13 definitely indicates that the ethene measurements are too high, not only in one but in both data sets. At the lowest levels of *i*-pentane, i.e., presumably the most aged air, the ethene to *i*-pentane ratio is an order of magnitude or more larger than in fresh urban emissions, which implies at least an order of magnitude error in the ethene measurements.

A simple model illuminates the source of this systematic error in the Air GC data set. Imagine an urban mixture of ethene and *i*-pentane subject to aging according to the OH reactivity of Figure 1 and exponential dilution by pristine air (time constant of 0.5 days). Then subject ethene (but not *i*-pentane) to a constant measurement offset of 0.02 ppbv. The evolution of the two NMHC mixing ratios is described by

$$\text{ethene} = 10.7 \text{ ppbv } e^{-t/0.5} \, e^{-0.736 \, t} + 0.02 \text{ ppbv} \qquad (3)$$

$$\text{i-pentane} = 9.06 \text{ ppbv } e^{-t/0.5} \, e^{-0.337 \, t}. \qquad (4)$$

The dotted line in Figure 13b shows the results of this model and fits the trend of the data well. A small offset could result from an experimental artifact or the coelution of another ambient compound that exists at low levels in the atmosphere or has only a small sensitivity to the FID detector. Subsequent to this analysis, the operation of the Air GC system has been reviewed, and an artifact of the correct magnitude has been found (P.D. Goldan, private communication, 1997). This artifact was caused by ethene generation during the sample concentration process; its magnitude depended upon ambient ozone concentration and altitude. It should be emphasized that Figure 12 implies that the Air Cans data set must overestimate the amount of ethene to an even greater extent.

Figure 14 examines the correlation between propene and ethene in the six data sets reporting both compounds. Two of the data sets follow the expected behavior for urban emissions affected by reaction and dilution. The U.S. Urban data points show remarkably little scatter for these two species, and at the lowest ethene levels, the propene values begin to drop below the line. Data below the line at lower ethene levels is the behavior expected when reaction with OH begins to become important in the urban samples. Of the other five data sets, only the Air GC data show similar aging indications, and only these data exhibit the very low levels expected for a reactive species like propene (lifetime ≈ 10 hours) for samples collected at sites isolated from nearby sources. The other four data sets do not exhibit the expected behavior. The Harvard Forest and Air Cans data largely scatter about the emission ratio, while the SOS Cans and the ROSE 92 data lie predominately above the line. The intercomparison in Figure 12 established that the Air Cans data are definitely too high. They are higher than the Air GC data, which in turn are too high. The large scatter and the predominance of points above the emission line indicate experimental problems in the SOS Cans data; this problem is probably associated with the problems in the measurement of the light NMHCs, which were
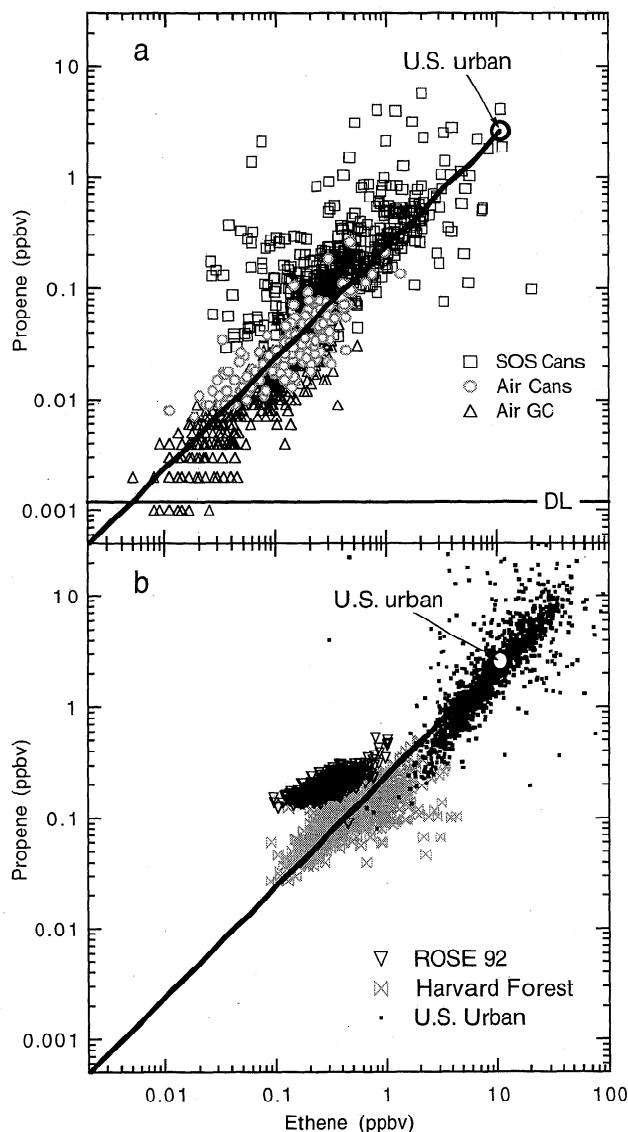
**Figure 14.** Log-log correlation plots of propene versus ethene for (a) the SOS data sets and (b) the literature data sets. The median urban concentrations from Table 1 are given by the thick open circle, and the solid line indicates their constant ratio. The DL line in Figure 14a separates the Air GC measurements of propene above from those below the detection limit; the points reported as below the detection limit are plotted here as 0.0005 ppbv.

discussed in earlier sections. The Harvard Forest and ROSE 92 data may be affected by errors similar to those identified in the other data sets; however, another interpretations is possible. *Goldstein et al.* [1996] report emissions of alkenes from the forests surrounding the Harvard Forest site; the ROSE 92 data also were collected at a forested site. The patterns in these two data sets may be due to the biogenic emissions rather than the urban patterns that we are relying upon in this work.

Plate 3 compares the ratio of each alkene to $i$-pentane in all of the data sets; $i$-pentane rather than one of the alkenes is chosen for the denominator because it is reported in all data sets. All of the alkenes are more reactive than $i$-pentane by a factor of 2 or more, so we expect the data to lie at or below the U.S. Urban ratios and to fall progressively farther below as the reactivity of the alkenes increase. There are some

inconsistencies between the two U.S. urban data sets. Some of the alkenes appear in one of the data sets but not in the other. When the alkene appears in both data sets, the horizontal line segment, which gives the ratio of the urban medians listed in Table 1 for the 1984-1986 data, is generally in close agreement with the square symbol, which gives the geometric mean ratios for the complete 1984-1988 data set. The one exception is c-2-pentene. Evidently, a bookkeeping error was made in the medians published by *Seila et al.* [1989b]. Recalculation of the median gives a value of 1.7 ppbC rather than the listed value of 3.6 ppbC; this correction eliminates the one large disagreement between the two data sets and brings the ratio of medians into better agreement with three of the four SOS data sets.

The literature data sets of Plate 3 define no consistent pattern; each data set reports different alkenes, and there is no clear indication of progressively greater alkene depletion with greater alkene reactivity. Harvard Forest reports the most alkenes of the literature data sets; compared to the urban pattern, two of the ratios are higher (ethene and propene), one is lower (t-2-pentene), and two are in close agreement (1-butene and 3-methyl-1-butene). It is possible that these ratios may reflect a balance between the aging of anthropogenic emissions and the contribution of the reported biogenic emissions [*Goldstein et al.*, 1996], so no conclusions regarding the validity of the Harvard Forest data can be reached. The ethene and propene ratios from the forested ROSE 92 site are not consistent with either an aged urban pattern or the Harvard Forest pattern; these data must represent very different biogenic emission patterns or the propene measurements must be affected by a relatively large (approximately a factor of 3 at median concentrations) systematic error. The one Boulder ratio is in agreement with fresh urban emissions as may be expected for this wintertime suburban data set.

The SOS data sets seem to reflect significant experimental errors. Despite the errors pointed out in the discussion of Figures 12 and 13, the Air GC data approximate the expected aged urban pattern; the ethene ratio is close to the urban value and the propene ratio is significantly lower than the urban value, consistent with its greater reactivity. The more reactive alkenes are not included in this data set; they are reportedly usually below the detection limit of a few pptv. However, in general, the ratios of the SOS Cans, Air Cans, and GC/MS B data sets closely follow the urban pattern with no apparent aging, even for the alkenes with lifetimes approaching an hour at midday. This lack of evidence of aging is not understood and deserves further study. The ratios of the GC/MS A data set are usually above the urban ratios, which must reflect substantial systematic errors. The variability of the reported ratios in the SOS Cans and Air Cans data sets is very large, much larger than the urban variability and generally larger than any of the other data sets. Such large variability could conceivably arise from a wide range in the degree of aging in the sampled air parcels; however, given that the mean ratios indicate a lack of aging, the large variability must reflect experimental problems in these canister measurements for all of the alkenes.

## 8. Conclusions

The hypotheses that have guided this discussion are supported by the eleven data sets that we have investigated. In
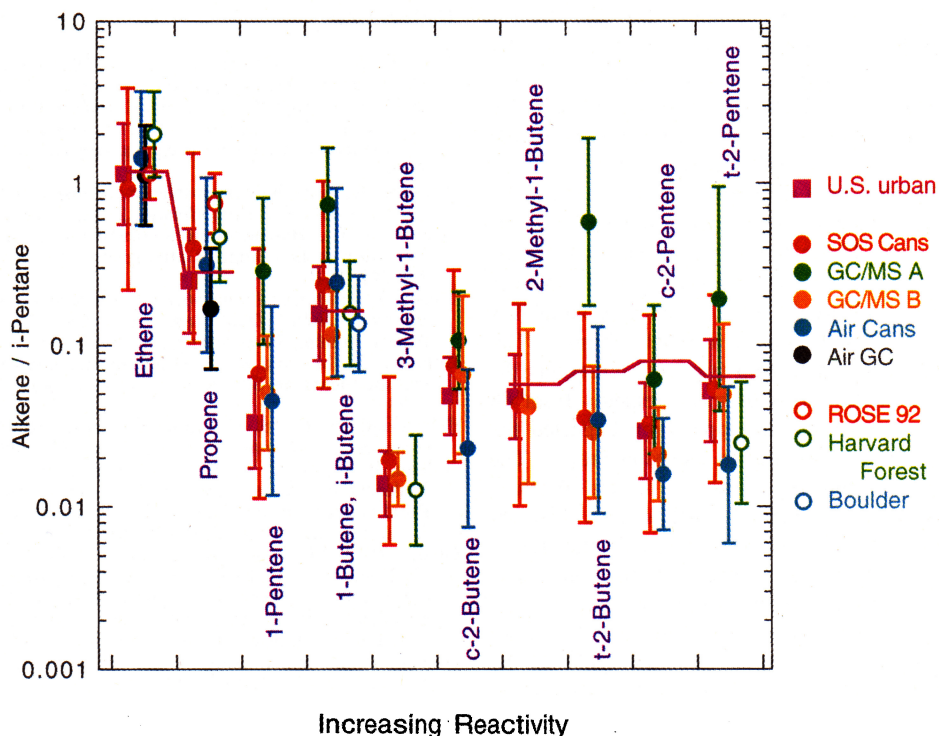
**Plate 3.** Log plot of ratios of alkenes to *i*-pentane in order of increasing reactivity of the alkene with OH. The format of the plot is described in the caption to Plate 1. The gaps in the ratios of the urban medians occur at alkenes not listed in the top 48 most abundant NMHCs by *Seila et al.* [1989b].

general, the patterns of the NMHCs approximately agree with the urban emission pattern of Table 1, modified by the expected photochemical removal processes and dilution. The NMHC patterns for the aromatics, alkanes, and alkenes are illustrated in Plates 1 through 3, respectively. Exceptions to this agreement are attributed to plausible systematic errors; in some cases the errors have been independently verified and the specific causes identified. The tests presented here should provide useful diagnostics for all anthropogenic NMHC measurements collected in North America. Similar tests, based upon the perhaps different emission patterns of other regions, presumably could be developed.

One caveat applies: the data sets we examined were collected in 1984-1995 (with the exception of one in 1975). In general over this time and over a wide region of the United States, the consistency of the observed NMHC patterns is remarkable. However, since 1995 or in the future, these patterns may change as emission control technology evolves. In that case, a contrast with the patterns presented here will be one possible means of documenting those changes.

Of the tests developed, only one could be applied quantitatively to the absolute concentrations: all measurements of ethane should find concentrations above 0.3 ppbv. A second, more qualitative test suggests that if any NMHCs are measured in a sample, then the more prevalent and less reactive compounds in Table 1 should be among those found above the detection limit.

The other quantitative tests rely upon selected ratios of NMHCs. The ambient concentrations of the anthropogenic NMHCs are likely to approximately define a lognormal distribution. This implies that the ratios of NMHCs will also approximately define a lognormal distribution. Thus the geometric mean ratio and the standard deviation of the

logarithms of the ratios are taken as the bases of the tests. The mean ratio of longer-lived NMHCs with similar lifetimes should remain constant at the urban emission ratio during dilution and photochemical removal. Three such ratios are investigated: *i*-butane:*n*-butane, acetylene:benzene, and
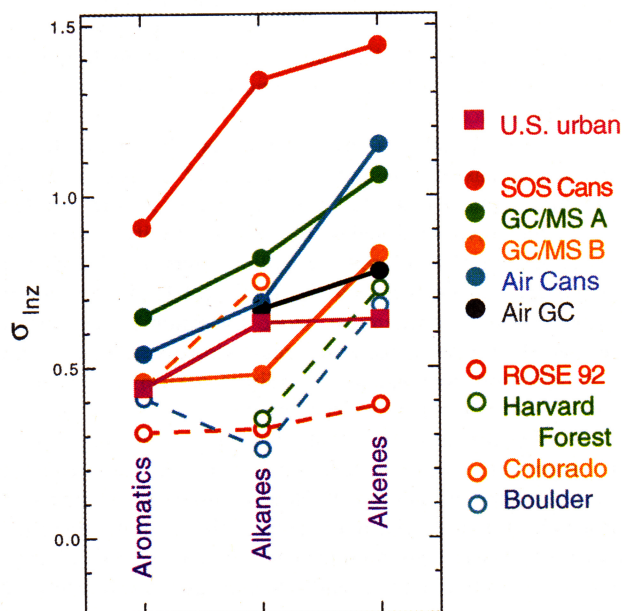


**Plate 4.** Average standard deviation of the logarithms of the ratios for each NMHC family in Plates 1 through 3. The color key for the data sets is on the right; solid and open symbols indicate the SOS and literature data sets, respectively.

ethylbenzene:toluene. Data sets giving ratios that diverge from the ratios of Table 1 are assumed to be affected by systematic errors. It is also argued that the ambient variability of these ratios is small enough that the standard deviation of the logarithms of the reported ratios can provide a test of the experimental imprecision for NMHC data sets.

The ratios of NMHCs with different lifetimes can also be used to test for experimental problems. Several specific examples are discussed. Plates 1 through 3 each shows ratios of a family of NMHCs to a selected reference NMHC with a lifetime of 2 to 4 days. Plate 4 shows the average variability of the logarithms of the ratios for each NMHC family. The average $\sigma_{lnz}$ for the U.S. Urban data (squares) represents the variability observed in the ratios of measurements from 88 sites in 71 cities; it is taken as the upper limit expected for ambient variability due to variation in emission ratios. The variability in data from suburban to rural to remote locations should be reduced due to mixing of NMHCs from different sources and increased due to variability in ratios that result from photochemical removal of NMHCs at different rates. However, the patterns in Plates 1 through 3 are quite close to the urban emission patterns, which suggests that this latter contribution to the variability is minor. The variability of the literature data sets (dashed lines with open symbols) are usually similar or smaller than the urban variability; the exceptions are attributed to specific effects or errors that are discussed: systematic errors in the Colorado alkanes and biogenic emissions in the Harvard Forest alkenes.

Many experimental problems were identified in the SOS data sets. The measurements of the light NMHCs in two data sets were often too low, as indicated by below detection limit data reported for ethane and other abundant NMHCs of low reactivity. As indicated by their large variability evident in Plate 4, two of the data sets had extensive problems with measurement precision in each of the families of NMHCs, and one had problems with the alkene precision. Specific systematic problems were identified in the SOS data sets as well as the literature data sets. The alkene measurements seem to suffer from experimental problems in many of the data sets, although the tests relied upon patterns of anthropogenic emissions, and alkenes are reported to have important biogenic sources.

A crucial question is how important are the errors? It is not possible to answer this question outside of the context of how the measurements are to be used. Some of the problems identified involve species of low reactivity and/or low concentration. Therefore the resulting errors may be of minor importance in determining the total NMHC loading or the potential for photochemical ozone formation in the sampled air parcel. However, the errors could strongly influence source reconciliation conclusions or indirect determinations of air mass history or radical concentrations.

Finally, the most important conclusion of this paper is that a rigorous field intercomparison of simultaneous measurements of ambient NMHCs by different techniques and researchers is of crucial importance to the field of atmospheric chemistry. The tests presented here are suggestive of errors but not definitive; only a field intercomparison can resolve the uncertainties.

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C.T. Farmer, D.D. Riemer, and R.D. Zika, University of Miami, Rosenstiel School of Marine and Atmospheric Science, Miami, FL 33149.

F.C. Fehsenfeld, P.D. Goldan, B.T. Jobson, W.C. Kuster, D.D. Parrish, and M. Trainer, NOAA Aeronomy Laboratory, R/E/AL7, 325 Broadway, Boulder, CO 80303. (e-mail: parrish@al.noaa.gov)

W.A. Lonneman, Senior Environmental Employment Program, National Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

M.O. Rodgers, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332.

V. Young, Department of Chemical Engineering, Ohio University, Athens, OH 45701.