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MARINE TROPOSPHERIC HYDROCARBONS: AN INTERCOMPARISON EXERCISE

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MARINE TROPOSPHERIC HYDROCARBONS: AN INTERCOMPARISON EXERCISE

Thomas P. Carsey

Abstract. Results from an multi-laboratory intercomparison exercise for the determination of non-methane hydrocarbons in the North Pacific troposphere are presented.

Each of the ten participating laboratories analyzed marine air obtained on the NOAA ship R/V RESEARCHER and from a single large tank of Oregon coastal air for some or all of the following: ethane, ethylene, propane, propene, isobutane, n-butane, acetylene, 1-butene, isobutene (2-methyl-1-propene), cis-2-butene, trans-2-butene, iso- pentane, n-pentane, isopentene (2-methyl-1-butene), 1-pentene, benzene, toluene, methane, carbon dioxide, and methyl chloroform.

The following parameters were computed where data was sufficient for each laboratory and each analyte: mean mixing ratios, total (sampling plus analytical) precision, analytical precision, and sampling precision. Means were compared using a non-parametric procedure.

Mixing ratio vs time data for the various compounds indicated that diurnal changes were minimal or absent; however, slight decreases in mixing ratios were observed for C_2H_6, C_2H_2, CH_3CCl_3, CO and CH_4.

1. INTRODUCTION

Non-methane hydrocarbon (NMHC) gases are critical to the local and global production of a variety of significant trace tropospheric species such as ozone, carbon dioxide, aldehydes, organic acids, and nitrogen compounds (Duce et al., 1983, Warneck, 1988). They are produced by fossil fuel use, geochemical processes, certain types of vegetation and marine biota, and biomass burning (Stoiber et al., 1971; Robinson, 1978; Whelan et al., 1982; Wiesenburg et al., 1982; Zimmerman et al., 1988). NMHCs have been identified in marine air and water; many are suspected of having important marine sources (e.g. Lamontagne et al., 1974; Rudolph and Ehhalt, 1981; Kanakidou et al., 1988).

This paper describes an intercomparison exercise organized to evaluate intra-and inter-laboratory precision and relative accuracy in the determination of non-methane hydrocarbon concentrations in the marine boundary layer. Ten laboratories from the United Kingdom, the Federal Republic of Germany, France, and the United States participated (see Table I; order does not correspond to laboratory designation used below).

2. EXPERIMENTAL DESIGN

The exercise was conducted on the NOAA ship RESEARCHER, approximately 250 miles northwest of Honolulu, Hawaii. Sampling began at GMT 0400 28-May-87 (1800 27-May Local Time) and ended GMT 0000 29-May-87 (1400 28-May-87 Local Time), with the ship oriented with the bow into the wind for the duration of the exercise. Total distance traveled during the exercise was about 24.9 miles. Atmospheric samples were obtained from the bow of the ship, ~7 meters above the sea surface. Subsequent air trajectory plots (Harris, 1982) indicated that the sampled air had not passed over continental land masses for at least ten days, although transit over the Hawaiian Islands cannot be excluded (Figure 1).

Each participant was to obtain a sequence of eleven pairs of samples from the bow (hereafter denoted 'bow samples'), one pair obtained every two hours, using his/her own methodology. These procedures are described in Table II. Because a variety of sampling methods were employed, sampling time required to obtain a single sample varied from laboratory to laboratory (from a few seconds to several minutes).

In addition to the bow samples, six samples per laboratory were to be taken via direct connection from a 32-liter stainless steel tank filled at high pressure (450 psig) with coastal air from Cape Meares, Oregon (prepared by R. A. Rasmussen). These latter samples, denoted 'tank samples', were used to assess analytical precision.

The above experimental regimen was followed by all participants except for the following. Laboratory 3 performed on-board analysis and was not able to obtain duplicate bow samples or any tank samples for analysis. Laboratory 2 did not submit tank sample results. Laboratory 7 obtained three to four bow samples instead of two at each sampling time. The statistical treatment was able to accommodate those modifications.

The analytical procedures employed by the various laboratories are summarized in Table II. Except for Laboratory 3, which employed on-board analysis, all participants collected samples in stainless steel canisters for shipment and subsequent laboratory analysis. All laboratories employed gas chromatographic analysis.

3. RESULTS

3.1. Analytes

Results were reported for the following chemical analytes: ethane, ethylene, propane, propene, isobutane, n-butane, acetylene, 1-butene, isobutene (2-methylpropene), cis-2-butene, trans-2-butene, isopentane (2-methylbutane), n-pentane, isopentene (2-methyl-1-butene), 1-pentene, benzene, toluene, methane, carbon dioxide, and methyl chloroform; however, not all laboratories were able to measure all analytes. Additional hydrocarbon or non-NMHC results were reported by some laboratories; also, for some analytes only one laboratory reported data. For those analytes an intercomparison was precluded; however, these are reported herein for comparison purposes.

Outliers exceeding a single (5%) outlier Grubb's test (Barnett and Lewis, 1978) were deleted from the received data sets. A total of 29 out of 1942 data were deleted as outliers from the bow and 0 out of 462 from the tank sample data sets.

3.2. Inter-laboratory (relative) Accuracy

Because of the small changes in the mixing ratio with time in the bow sample data (see below), the mixing ratios were averaged across the 20-hour sampling period. Although this approach ignores small decreases in mixing ratio with time observed for some analytes, these changes were small compared to the spread in the data.

To accommodate a between-laboratory comparison of the sample means for each analyte, The Kruskal-Wallis (non-parametric) test as formulated by Conover (1971) was employed. The results of this test are shown by horizontal lines which connect laboratories whose means are not significantly different a the 5% confidence level. These results are given in Figure 2 for bow samples and Figure 3 for tank samples. Each figure also includes the maximum, minimum, and mean mixing ratio from each laboratory, ordered by increasing mean. The data as presented are subject to the atmospheric homogeneity observations noted above;

however, the plots provide a ready means for visual comparison of the data.

The mean values obtained for each analyte, for each laboratory and the overall average of all laboratories is given in Table III for both bow and tank samples.

The average mixing ratios as measured from the bow were similar to published levels for marine atmospheres, (e.g., Bonsang et al., 1988; Bonsang and Lambert, 1985; Cronn and Nutmagul, 1982; Greenberg and Zimmerman, 1984; Khalil and Rasmussen, 1988; Rudolph and Ehhalt, 1981; Singh et al., 1982), and did not change markedly during the 20 hours of the experiment (see below). Although models have predicted significant diurnal changes in the mixing ratios of some NMHC species (Graedel, 1979; Rudolph and Ehhalt, 1981), no diurnal changes were evident in the data reported here; (similar results were noted by Singh et al., 1988). Small but statistically significant decreases (a few ppt/hour or less) in the mixing ratios of C_2H_6, C_2H_2 and CH_3CCl_3 with time was observed (95% confidence interval); decreases were also noted for C_2H_4, C_3H_8, n-C_5H_{12}, C_6H_6, $CH_3C_6H_5$, CH_4, and CO, not statistically different from zero. These changes were quite gradual over the coarse of the experiment and would not have impacted negatively on the intercomparison exercise.

3.3. Overall Precision

The total precision of a measurement was assumed to be the sum of within-laboratory, between-laboratory, and atmospheric variances. Within-laboratory variance included sampling and analytical variances. However, assuming both samples of a pair from one laboratory sampled the same atmosphere, only the sampling and analytical variances would contribute to the variance within a pair. Estimates of the overall within-laboratory (sampling plus analytical) precision were obtained by pooling the variances of each of eleven pairs of data from each laboratory (Lab 7: three or four data instead of two), as follows:

The mixing ratios were first converted to the natural log scale to facilitate pooling of variances. For the two mixing ratios C_{ikt1} and C_{ikt2} of a pair, Lab i, analyte k, time t, the standard deviation of the pair is given by ($\wedge$ denotes estimate):

$$\hat{\sigma}_{ikt} = \sqrt{\tfrac{1}{2}[(C_{ikt1}-C_{ikt2})^2]}. \qquad (1)$$

These values are then pooled to give the overall variance for lab i:

$$\hat{V}_{ik[overall]} = (\hat{\sigma}_{ik[overall]})^2 = \sum_{t=11}^{t=1} (\hat{\sigma}_{ikt})^2/11 \qquad (2)$$

for times t= 1 to t=11. Relative standard deviations were computed from the standard deviations (log scale):

$$\hat{RSD}_{ikt}[\text{linear scale}] \approx \hat{\sigma}_{ikt}[\ln \text{ scale}]. \qquad (3)$$

Relative standard deviation estimates are given in Table IV for all analytes.

3.4. Analytical precision

It was assumed that the mixing ratio data from the tank samples did not contain a contribution due to sampling variance or atmospheric inhomogeneity. Conse- quently, analytical precision estimates were obtained directly as follows:

$$\hat{\sigma}_{ik[analytical]} = \sqrt{\frac{\Sigma_n (C_{ikn}-\mu_{ik})^2}{N-1}} \qquad (4)$$

i = lab designation
N = 6 samples, n=1 to 6
k = analyte designation
μ_{ik} = mean mixing ratio value for the 6 samples

$$\text{and } \hat{RSD}_{ik[analytical]} = \frac{\hat{\sigma}_{ik}}{\mu_{ik}} \times 100. \qquad (5)$$

These results are given in Table IV for all analytes.

3.5. Sampling Precision

This was computed as the difference between the overall and analytical relative standard deviations described above; i.e.,

$$(\hat{RSD}_{[sampling]})^2 = (\hat{RSD}_{[overall]})^2 - (\hat{RSD}_{[analytical]})^2. \qquad (6)$$

This approach assumes an equivalence between tank and bow samples, i.e., that interferences are the same in both. For a few data sets the variance estimates

were not sufficiently accurate; viz.,

$$\hat{RSD}_{[overall]} < \hat{RSD}_{[analytical]}. \quad (7)$$

Except for those cases, the sampling precision estimates are listed in Table IV.

As noted in Table II, the participants employed a variety of sampling procedures, including previously evacuated canisters, canisters pumped with metal bellows pumps, and cryogenic pumping using liquid nitrogen. These procedures required various lengths of time to complete, from a few seconds to several minutes. Any changes in the ambient atmosphere during this interval would affect the measured mixing ratios; the spatial and temporal inhomogeneity of the atmosphere with respect to the analyte gas unavoidably contributed to sampling variance. This contribution may be roughly estimated as follows. A model relating inhomogeneity to tropospheric lifetime was developed by Junge (1974) for gases with lifetimes T of weeks or longer,

$$\text{Variability}[\sigma/\mu] = A \cdot T^{B} \quad (8)$$

where A and B are fitted varialbes. Equation 8 has been used by several investigators (e.g., Hamrud, 1983), and 8 has been recently rederived by Slinn (1988) to incorporate sampling intervals, viz., $A=\Delta S/\sqrt{12}$ and $B=-1$, where ΔS is the sampling time interval. With a sampling interval of 30 minutes, which exceeds that of any participant, the estimated atmospheric variability using equation 8 and tropospheric lifetimes from Warneck (1988) (n-C_4H_8 and 1-C_4H_8 lifetimes from Graedel, 1978) is only 1.2% for 2-pentene and is less for gases with longer lifetimes. Recognizing the limitations of the model (i.e., being derived for gases of longer lifetimes than NMHC species), a sizable contribution to the sampling precision from atmospheric inhomogeneity is not predicted.

4. SUMMARY AND CONCLUSIONS

The primary focus of the exercise was to determine the agreement of the participating laboratories in the measurement of the test NMHC gases. We may compare the laboratories via Figures 2 and 3 and Tables III and IV. In addition, the Friedman test has been employed (Conover, 1971) which generates a ranking of laboratories by analyte, low to high, from the set of eleven determinations (average of the two bow sample data per hour) made over the course of the exercise. As the ranking is performed separately with data from

each sampling time, the effects of changing atmospheric concentration are minimized. These results are given in Table V for the bow sample data. (Ranking for tank sample results can be gleaned directly from Figure 3.) A number of observations can be made from these results. Laboratory 1, using previously evacuated canisters, reported low concentrations for C_2H_6, C_2H_4, C_3H_8, i-C_4H_8 and C_2H_2, bow and tank samples, but high concentrations for i-C4H10 (bow) and i-C_5H_{12} (tank) compared to the other laboratories. Laboratory 2, which used cryogenically assisted pumping, was low for C_2H_6, C_2H_4, C_3H_6 and i-C_4H_{10} (bow samples only). Laboratory 3, which employed on-board analysis, was high for C_2H_6 (bow) and C_2H_4 (bow and tank), C_3H_6 (tank), and n-C_4H_{10} (tank samples). Laboratory 4 was high for C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_2H_2, i-C_5H_{12} and n-C_4H_{10} for the bow samples but, remarkably, not for tank samples. Laboratory 5 was somewhat eleveated for C_2H_6 (bow and tank), and for C_2H_2 and i-C_4H_8 (tank). Laboratory 6, which also used cryogenic pumping, was high for C_2H_6, C_3H_8, C_3H_6, C_2H_2 and n-C_4H_{10} (tank) but not bow samples. Laboratory 7 was intermediate in their reported values for both bow and tank samples. Laboratory 8 was somewhat high only for C_3H_8 (bow); Laboratory 9 was low for CH_4 (bow and tank) and high for C_2H_2 (bow) and n-C_4H_{10} (bow). Laboratory 10, which used a 3-column gas chromatographic system, obtained median values except for high values for C_2H_6 (bow) and CO (bow and tank), but low values for n-C_5H_{10} (bow).

As expected, the variances for alkenes typically exceed that of the alkanes, due their higher reactivity; for example, overall precision for ethane averaged 11.3%, for ethene 48.53%. Analytes in higher concentration were measured with more precision: overall precision for methane was only 0.34%.

The different sampling procedures resulted in different sampling times per sample and different intervals between duplicate samples; e.g., laboratories 1 and 8 sampled for a few seconds with intervals of less than a minute. However, the sampling precision for labs 1 and 8 for most analytes was not significantly different when compared to the other laboratories.

Assuming the mean of all measurements of analyte in each sampling period define the actual atmospheric concentration of that analyte, the mixing ratios of most analytes did not change significantly during the day; for example, ethane mean values varied 10.4% (RSD), ethane varied 11.9% over the eleven hours of the exercise. There was no evidence for photochemically-driven changes in the concentration of any of the analytes.

5. ACKNOWLEDGMENTS

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Notes:
* Two laboratories withdrew after significant contamination of the samples was found (not listed in Table).

TABLE II

SAMPLING AND ANALYTICAL PROCEDURES
Listed in order of laboratory number

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1 Sampling was performed with 2-Liter stainless steel canisters previously evacuated under heating (100°C) for 12 hours. Preconcentration was performed on an enriched column (stainless steel, 15cm x 3.2mm OD) at -100°C. Analysis employed a Siemens Sichromat 2 double-oven gas chromatograph operated at subambient temperature. Separation used a 50m alumina PLOT column/WGA, with helium as carrier gas.

2 Sampling was done with 850 mL stainless steel cans internally electropolished and passivated. A Metal Bellows Model 158 pump was used to pressurize the canisters to 150-200 psig during the cryogenic-assisted fill cycle (liquid nitrogen). Analyses were made with Hewlett-Packard 5890 and 5790-A gas chromatographs with dual FIDs. The conditions of analyses were 500 mL sample, pre-concentrated via LOx freeze-out on glass beads, and hot water (85°C) release onto 3m x 3 mm Teflon columns packed with phenyl isocyanate/Porasil C operated at 45°C. Calibrations were made against SN0-12, OGC standard traceable to NBS-SRM propane.

3 Ambient air from ~7 m above the sea surface was sampled through 3/8"OD copper tubing. The air was dried through a column of anhydrous K_2CO_3. The hydrocarbons were trapped cryogenically with a 4 cm column of silicalite cooled to -90°C; the trap was then isolated and heated to 350°C. The contents were swept into a Shimadzu Mini-II gas chromatograph fitted with a phenyl isocyanate column and an flame ionization detector, and analyzed under isothermal conditions.

4 Ambient air samples collected through a stainless steel tube into 2-Liter stainless steel electropolished canisters. Preconcentration with trap filled with Tenax GC and cooled by liquid nitrogen. Analysis employed a Varian 3400 gas chromatograph equipped with a flame ionization detector, temperature controlled programming, and Al_2O_3/KCl porous layer open tubular column. The detection limit for a 1-Liter sample was about 2 pptv. The accuracy of the analysis was estimated between 5 and 10% for the measured range of concentrations.

5 Sampling employed 1.6-Liter stainless steel sample bottles pressurized to 60 psi with ambient air using two MB-158 metal bellows pumps in series. A 2-Liter aliquot of air was preconcentrated in a trap filled with silica wool cooled to 87.4°K with liquid argon. Capillary gas chromatography employed a 50m x 0.32mm PLOT Al_2O_3/KCl column, helium carrier and make-up gas, flame ionization detector, splitless injection, and temperature programming (253-263°K at 10°K/min, hold at 363°K).

6 Samples collected through a Teflon line into 1.6-Liter stainless steel bottles filled cryogenically by cooling with liquid nitrogen. Subsequent

analysis included drying with a Nafion dryer and preconcentration using a liquid argon trap. Analysis was performed on a HP Model 5890A gas chromatograph fitted with a 3m glass column packed with Durapack material, n-octane on Porosil C 80/100 mesh, and flame ionization detector. Five bow samples (every fourth bottle) were collected by drawing air through an ozone filter in a test to assess whether the presence of ozone in the bottles would reduce the concentration of unsaturated hydrocarbons in the samples.

7 Samples collected through a stainless steel line by metal bellows pump and collected in stainless steel canisters. Each sample was preconcentrated in a stainless steel precolumn packed with porous glass beads at about 80°K. Separation into heavy and light fractions by column 1 (Porapack QS, 100-120 mesh, 3m x 0.8 mm); the light fraction (≤C4) was separated on column 2 (Porapack QS, 100-120 mesh, 6m x 0.8mm), the ≥C5 fraction on column 3 (DB-1 capillary, 60m long), using nitrogen as carrier gas and temperature programming. Three detectors were used in series: photoionization, flame ionization, and electron capture.

8 Samples were collected in 2-Liter stainless steel canisters with metal bellows valves, pre-evacuated to 10^{-6} torr, within 15-30 seconds of each other. Samples were analyzed on an HP-5890a gas chromatograph fitted with two flame ionization detectors. To remove the water, sample canisters were cooled to -20°C for 20 minutes prior to analysis. Methane analysis employed 3'x1/8" stainless steel column packed with spherocarb (nitrogen carrier) while NMHC's were separated on a 15'x1.8" stainless steel OV-101 column (helium carrier). For the NMHC analysis, samples were preconcentrated on glass beads at liquid nitrogen temperature. The methane analysis was performed isothermally at 65°C while a temperature program of -80°C to 220°C was used for the NMHCs.

9 Samples were collected through a Teflon line via metal bellows pump into stainless steel canisters pressurized to ~15 psig. Preconcentrated used a 0.32cm x 15.24cm stainless steel tube packed with 60/80-mesh glass beads and maintained at -185°C with liquid oxygen; analysis was performed on an HP 5580 gas chromatograph. C2-C4 hydrocarbons were separated on a packed capillary column (610cm x 1.6mm) containing phenyl isocyanate/Porapil C at an oven temparature 50°C; higher organics (C5-C10) were separated on a DB-1 fused silica column (J&W Scientific) with helium as carrier gas (1 ml/min) and temparature programming (-50°C to 80°C at 4°C/min).

10 Samples were collected through a Teflon sampling line, each pair approximately 7 minute apart, into previously evacuated, electropolished, all stainless steel sample canisters with inlet and outlet stainless steel bellows valves pressurized to 60 psig by way of a two-stage all stainless steel metal bellows pump. All hydrocarbons and CO determined by gas chromatography with flame ionization detection. C_2-C_5 hydrocarbons were determined on two analytical columns: (1) packed column (610 cm x 0.076 cm ID stainless steel capillary) of n-octane on Porasil C 80/100 mesh, temperature program -50°C for 2 minutes, then raised to 100°C at 25°C/minute, helium carrier gas; (2) packed column (610 cm x 0.076 cm ID stainless steel capillary) of phenyl isocyanate on Porasil C, isothermal at 40°C, helium

carrier gas. C_5-C_{10} hydrocarbons were separated on a DB-1 fused silica capillary column (J&W Scientific) programmed from -50°C to 150°C at 4°C/minute with an initial hold of 2 minutes, hydrogen carrier gas. C_2-C_{10} hydrocarbons were preconcentrated from air samples in a stainless steel loop packed with glass beads (60/80 mesh) immersed in liquid argon. Methane and CO were separated on a packed column (183cm x 0.22 cm ID stainless steel) of molecular sieve 5A, nitrogen carrier; CO was converted to methane for detection.

TABLE IIIA. SAMPLE MEANS, BOW SAMPLES

LAB	Ethan C2H6	Ethen C2H4	Propa C3H8	Prope C3H6	iso-Butan iC4H10	n-Butan nC4H10	Acety C2H2	1-Buten 1C4H8	iso-Buten iC4H8	cis-2 Buten cC4H8	trns-2 Buten tC4H8	iso-Penta iC5H12	n-Penta nC5H12	iso-Pente iC5H10	1-Pente C5H10	Benz C6H6	Tolu C6H5Me	Meth CH4	CO CO	MeChlr CH3CCl3
1	0.778	0.083	0.032	0.072	0.055	0.072	0.081	0.037	0.046			0.038	0.075			0.014	0.025			
2	0.863	0.083	0.085	0.045	0.015	0.008	0.109											1.702	0.095	0.206
3	1.403	0.518	0.083	0.258																
4	1.392	1.981	0.292	1.419	0.033	0.112	0.123	0.293	0.396	0.050	0.055	0.298	0.074		0.140					
5	1.258	0.160	0.085	0.094	0.010	0.022	0.131	0.022	0.179	0.036		0.012	0.023		0.012					
6	1.100	0.084	0.074	0.125		0.053	0.108													
7	1.249	0.534	0.109	0.304	0.019	0.035	0.085					0.007								
8	1.152	0.275	0.195	0.261			0.095											1.704	0.098	
9	1.085	0.094	0.069	0.087	0.031	0.167	0.135											1.600		
10	1.353	0.279	0.137	0.221	0.016	0.034	0.099	0.058	0.060	0.060	0.019	0.014	0.017	0.019	0.039			1.699	0.174	
MN	1.154	0.414	0.118	0.298	0.027	0.056	0.105	0.122	0.176	0.049	0.045	0.064	0.056	0.019	0.101	0.014	0.025	1.676	0.121	0.206
LM	1.163	0.409	0.116	0.289	0.025	0.063	0.107	0.102	0.170	0.048	0.037	0.074	0.047	0.019	0.064	0.014	0.025	1.676	0.122	
%R	18.37	141.5	65.31	141.2	60.58	84.44	18.01	124.7	95.01	24.77	68.80	170.6	66.80	-	106.0	-	-	3.040	36.60	-
NL	10	10	10	10	7	8	9	4	4	3	2	5	4	1	3	1	1	4	3	1
NS	220	206	210	210	125	133	206	65	82	25	30	96	64	7	33	22	22	87	65	22

TABLE IIIB. SAMPLE MEANS, TANK SAMPLES

LAB	Ethan C2H6	Ethen C2H4	Propa C3H8	Prope C3H6	iso-Butan iC4H10	n-Butan nC4H10	Acety C2H2	1-Buten 1C4H8	iso-Buten iC4H8	cis-2 Buten cC4H8	trns-2 Buten tC4H8	iso-Penta iC5H12	n-Penta nC5H12	iso-Pente iC5H10	1-Pente C5H10	Benz C6H6	Tolu C6H5Me	Meth CH4	CO CO	MeChlr CH3CCl3
1	1.347	0.047	0.069	0.012	0.040	0.061	0.148	0.012	0.015			0.067	0.084			0.038	0.023			
2																				
3	2.220	1.130	0.400	0.330		0.250														
4	1.984	0.116	0.445	0.127	0.048	0.108	0.412	0.042	0.079	0.004	0.004	0.045	0.028		0.028					
5	2.537	0.143	0.478	0.083	0.057	0.077	0.532	0.025	0.475	0.018	0.019	0.014								
6	3.059	0.151	0.601	0.180		0.154	0.529													
7	2.218	0.093	0.400	0.044	0.052	0.130	0.364					0.020								
8	2.032	0.180	0.460	0.132			0.290											1.743	0.157	
9	1.954	0.053	0.360	0.031	0.052	0.090	0.293					0.015	0.010					1.585		
10	2.068	0.063	0.442	0.043	0.048	0.102	0.425					0.017	0.018					1.754	0.251	
MN	2.132	0.128	0.403	0.086	0.050	0.105	0.371	0.027	0.190	0.006	0.006	0.033	0.039		0.028	0.038	0.023	1.694	0.204	
LM	2.158	0.220	0.406	0.109	0.050	0.121	0.374	0.026	0.190	0.011	0.011	0.030	0.035		0.028	0.038	0.023	1.694	0.204	
%R	21.47	156.9	35.3	91.35	11.55	49.02	34.68	57.13	131.4	90.00	92.23	72.97	95.68		-	-	-	5.580	32.58	
NL	9	9	9	9	6	8	8	3	3	2	2	6	4	0	1	1	1	3	2	0
NS	48	47	48	47	36	42	47	16	18	7	7	30	21	0	6	6	6	18	12	0

Notes:

Mixing Ratio units ppbv (except for CH4 and CO, units ppmv)

MN: Mean of all samples

LM: Mean of laboratory means

%R: Relative standard deviation (%) of laboratory means

NL: Number of laboratories reporting results for an analyte

NS: Total number of valid samples

Data from Laboratories 2 and 8 were received subsequent to a preliminary presentation of the results (Carsey, 1987).

TABLE IVA. TOTAL PRECISION
(Units: % Relative Standard Deviation)

LAB	Ethan C2H6	Ethen C2H4	Propa C3H8	Prope C3H6	iso-Butan iC4H10	n-Butan nC4H10	Acety C2H2	1-Buten 1C4H8	iso-Buten iC4H8	cis-2 Buten cC4H8	trns-2 Buten tC4H8	iso-Penta iC5H12	n-Penta nC5H12	iso-Pente iC5H10	1-Pente C5H10	Benz C6H6	Tolu C6H5Me	Meth CH4	CO CO	MeChlr CH3CCl3
1	42.7	48.43	58.42	33.66	33.68	29.43	16.51	16.80	28.51			13.50	9.33			25.97	31.89			
2	3.76	11.14	8.39	13.50	15.13	25.92	13.32											0.10	1.78	0.60
3																				
4	8.30	52.31	19.79	19.82	31.75	26.17	13.95	18.61	14.30	13.01	14.04	13.94	29.17	21.51						
5	3.63	53.40	14.47	65.66			40.57	28.80	140.2			47.45								
6	4.79	34.77	27.87	33.53			31.62													
7	8.08	98.32	24.82	88.52	53.04	43.60	12.71					53.66								
8	4.24	11.11	21.90	16.30			17.71											0.13		
9	9.13	52.08	32.48	66.73			24.46											0.69		
10	17.3	75.17	45.89	94.17	37.04	63.53	21.49	45.69	44.99		0.0	34.65	32.45	34.65	52.45			0.45	11.16	
Ave	11.3	48.53	28.23	47.99	34.13	37.73	21.37	27.48	56.98	13.01	7.02	32.65	23.65	28.08	52.45	25.97	31.89	0.34	6.47	0.60

TABLE IVB. ANALYTICAL PRECISION
(Units: % Relative Standard Deviation)

LAB	Ethan C2H6	Ethen C2H4	Propa C3H8	Prope C3H6	iso-Butan iC4H10	n-Butan nC4H10	Acety C2H2	1-Buten 1C4H8	iso-Buten iC4H8	cis-2 Buten cC4H8	trns-2 Buten tC4H8	iso-Penta iC5H12	n-Penta nC5H12	iso-Pente iC5H10	1-Pente C5H10	Benz C6H6	Tolu C6H5Me	Meth CH4	CO CO	MeChlr CH3CCl3
1	20.58	160.7	54.85	28.44	10.13	15.10	42.00	29.81	25.31			25.27	13.32			36.20	142.67			
2																				
3																				
4	4.39	18.56	3.25	33.75	3.11	2.34	3.02	18.46	29.93	15.81	22.35	36.09	17.95	47.95						
5	1.83	31.10	5.36	27.60	6.88	15.60	13.05	28.26	104.1			29.05								
6	10.38	16.10	22.99	58.62		23.71	9.27													
7	2.82	41.13	3.95	50.26	3.65	3.43	3.55					3.19								
8	2.38	9.94	7.14	15.50			6.17											0.19		
9	1.78	38.29	5.74	44.35	8.66	7.50	6.16					43.83	40.00					1.53		
10	1.08	32.61	2.65	27.95	8.45	4.02	4.40					30.98	22.27					0.33	19.01	
Ave	5.59	43.47	13.19	35.78	6.77	10.23	10.91	25.47	53.07	15.80	22.30	28.00	23.35	47.95	-	36.20	142.7	0.49	19.01	

TABLE IVC. SAMPLING PRECISION
(units: % Relative Standard Deviation)

LAB	Ethan C2H6	Ethen C2H4	Propa C3H8	Prope C3H6	iso-Butan iC4H10	n-Butan nC4H10	Acety C2H2	1-Buten 1C4H8	iso-Buten iC4H8	cis-2 Buten cC4H8	trns-2 Buten tC4H8	iso-Penta iC5H12	n-Penta nC5H12	iso-Pente iC5H10	1-Pente C5H10	Benz C6H6	Tolu C6H5Me	Meth CH4	CO CO	MeChlr CH3CCl3
1	37.43		20.09	18.00	32.12	25.27		13.11												
2																				
3																				
4	7.05	48.90	19.52		31.60	26.07	13.61	2.39					23.00							
5	3.14	43.42	13.44	59.58			38.41	5.53	93.88			37.52								
6	30.81	15.75				30.23														
7	7.57	85.31	24.50	72.87	52.92	43.46	12.20					53.57								
8	3.51	4.96	20.70	5.03			16.44													
9	8.96	35.39	31.95	49.58			23.57													
10	17.26	67.72	45.81	89.93	36.06	63.40	21.03					15.51	23.60					0.32		
Ave	14.4	40.15	24.83	51.47	36.43	40.75	20.85	6.97	93.88			35.50	23.30					0.32		

TABLE V

FRIEDMAN'S RANK TEST RESULTS

LAB	C2H6	C2H4	C3H8	C3H6	C2H2	NC4H10	IC4H10	1C4H8	IC4H8	NC5H10	IC5H12	CH4	CO
1	2.10	2.50	1.13	3.83	2.10	5.67	5.83	1.50	1.55	4.00	4.00		
2	1.70	2.88	5.69	1.42	6.20	1.00	1.83					3.09	1.50
3	7.85	8.38	4.50	6.50									
4	8.35	9.63	9.50	10.00	5.80	6.00	3.83	3.00	3.73	3.00	5.00		
5	7.40	5.38	5.63	3.67	6.70				3.00	2.00	2.75		
6	4.45	2.44	3.00	5.50	5.50	4.00							
7	7.30	7.63	7.00	7.50	3.00	2.33	2.58				1.13		
8	5.15	7.13	9.13	7.83	3.75							3.32	1.50
9	3.70	2.94	2.19	3.58	7.70	5.33	4.50					1.00	
10	7.00	6.13	7.25	5.17	4.25	3.67	2.24	1.50	1.73	1.00	2.13	2.59	3.00
x^2	58.05	56.45	62.72	37.50	36.06	13.14	19.45	15.00	21.54	6.00	14.95	21.63	16.50
Sig	0.000	0.000	0.000	0.000	0.000	0.041	0.002	.0006	.0001	.1116	.0048	.0001	.0003

FIGURE 1

Isobaric back-trajectories for 1200, 28-May-1987 GMT. Sampling period was 0400 28-May-1987 GMT (1800 local) to 0000 29-May-1987 GMT (1400 28-May-1987 local). Solid: 850mb; dot: 700 mb; dash: 500 mb. Trajectories computed by NOAA/GMCC/ ATP (Harris 1982).

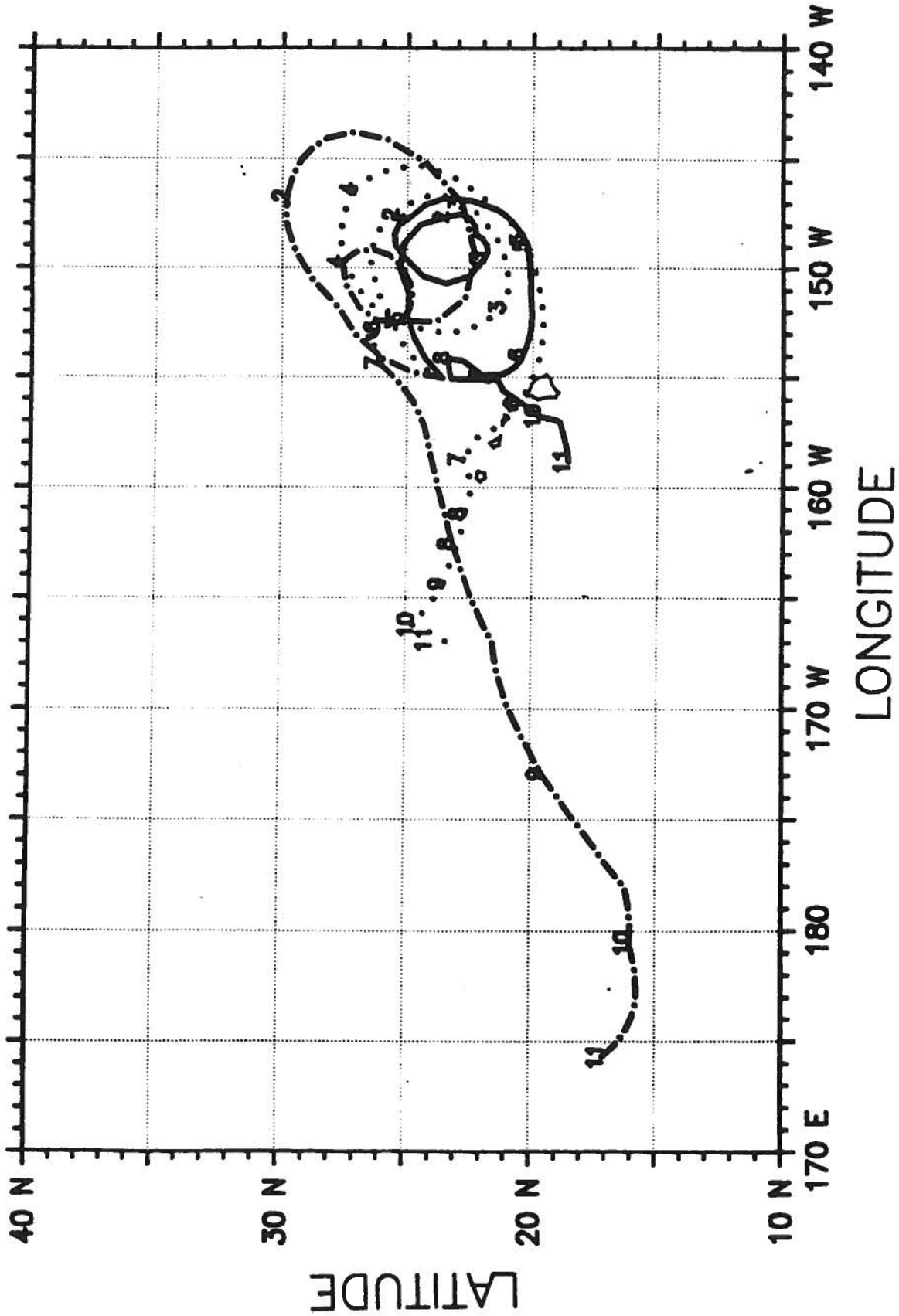
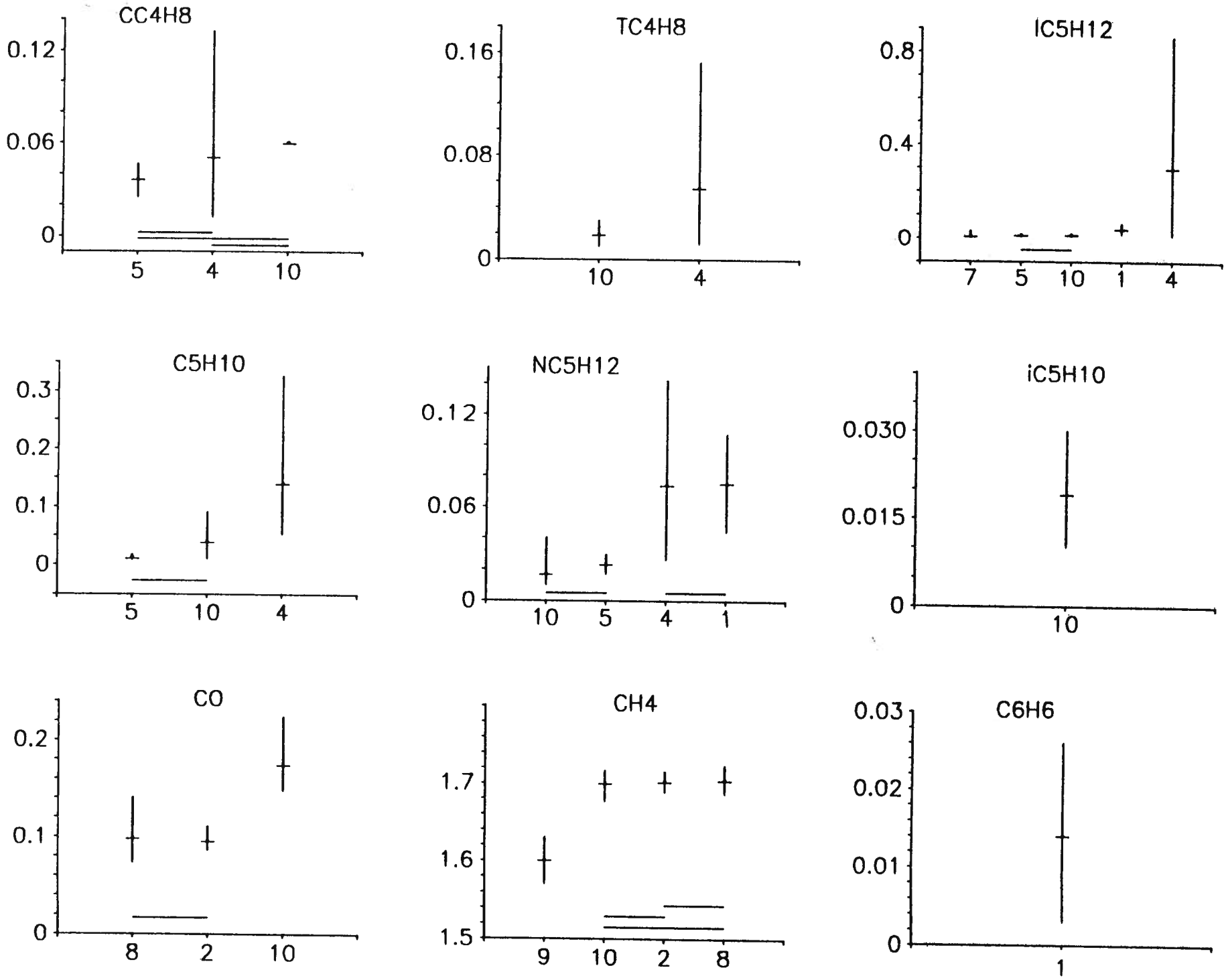

40 N
30 N
20 N
10 N
LATITUDE
170 E
180
170 W
160 W
150 W
140 W
LONGITUDE

FIGURE 2

Range and mean of mixing ratios for most analytes and laboratories, bow sample data. Individual laboratories are placed along the horizontal axis of each plot in order of increasing mean. Vertical axis is mixing ratio in ppbv (except for CH_4 and CO, ppmv). For each laboratory, the horizontal bar marks the mean for that analyte and the vertical bar connects the maximum and minimum mixing ratio value. Horizontal bars between laboratories connect data sets that are statistically similar according to a Kruskal-Wallis test (see text).


CC4H8
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0.06
0
5
4
10
TC4H8
0.16
0.08
0
10
4
IC5H12
0.8
0.4
0
7
5
10
1
4
C5H10
0.3
0.2
0.1
0
5
10
4
NC5H12
0.12
0.06
0
10
5
4
1
iC5H10
0.030
0.015
0
10
CO
0.2
0.1
0
8
2
10
CH4
1.7
1.6
1.5
9
10
2
8
C6H6
0.03
0.02
0.01
0
1

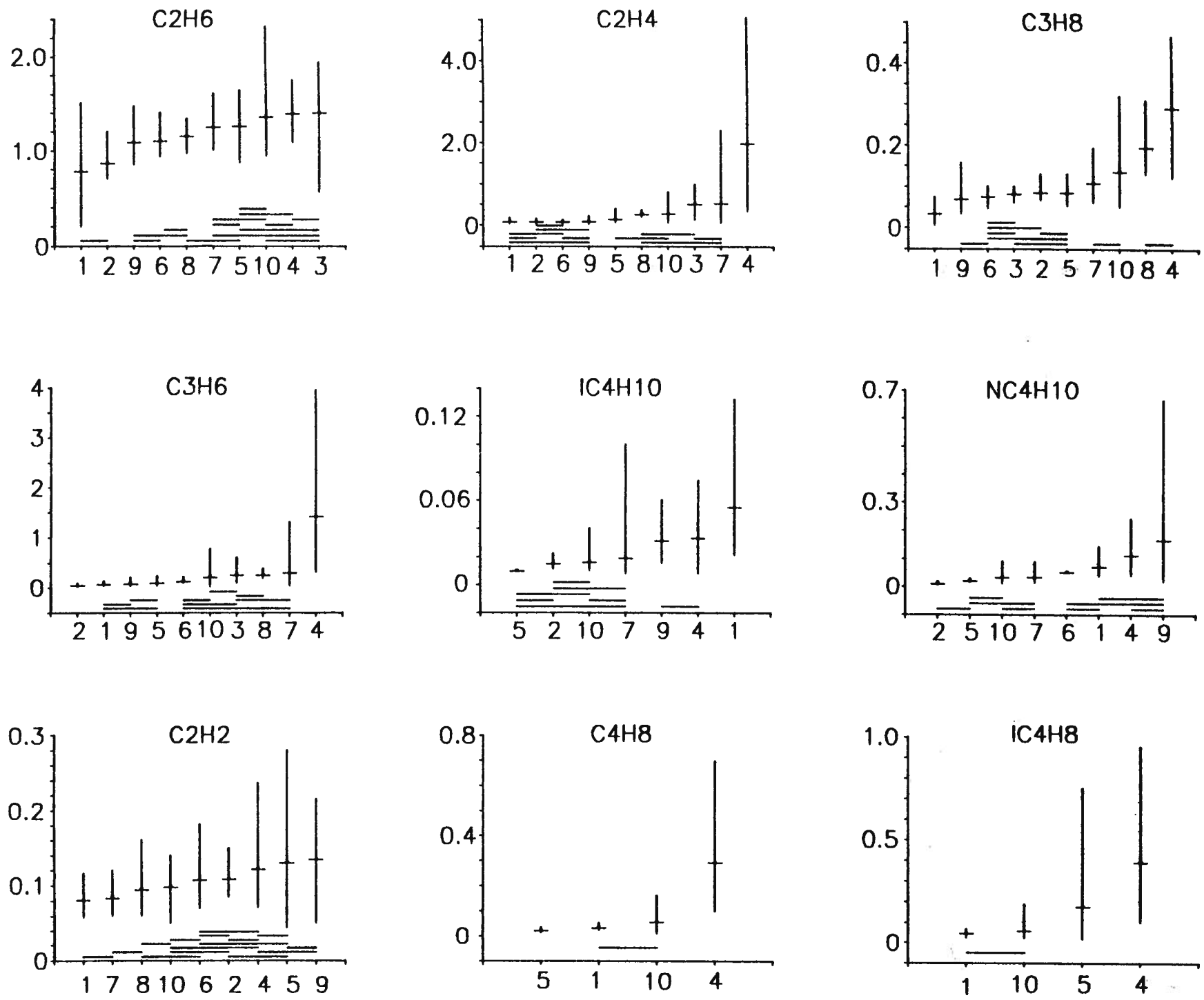
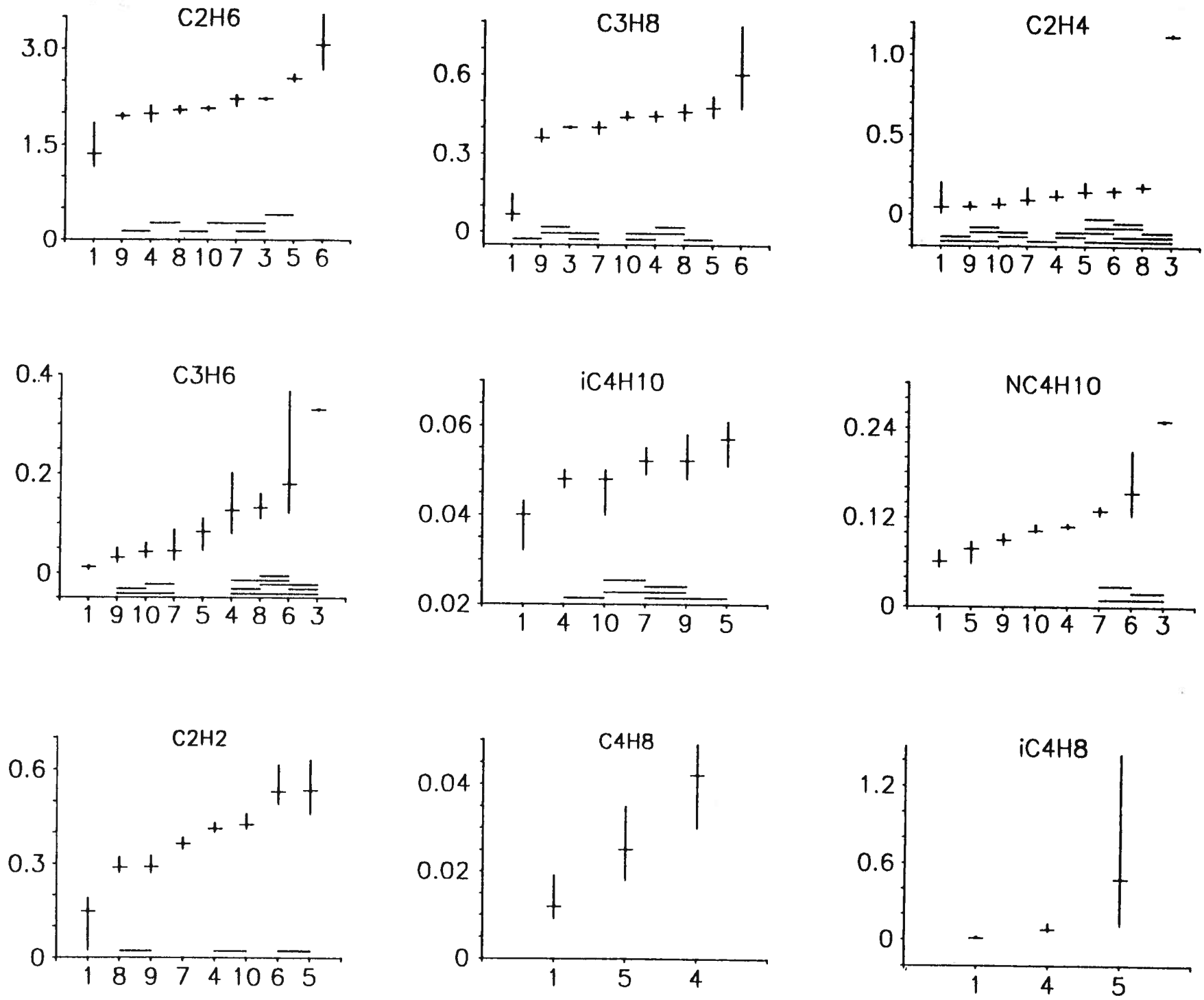

C2H6
2.0
1.0
0
1 2 9 6 8 7 5 10 4 3
C2H4
4.0
2.0
0
1 2 6 9 5 8 10 3 7 4
C3H8
0.4
0.2
0
1 9 6 3 2 5 7 10 8 4
C3H6
4
3
2
1
0
2 1 9 5 6 10 3 8 7 4
IC4H10
0.12
0.06
0
5 2 10 7 9 4 1
NC4H10
0.7
0.3
0
2 5 10 7 6 1 4 9
C2H2
0.3
0.2
0.1
0
1 7 8 10 6 2 4 5 9
C4H8
0.8
0.4
0
5 1 10 4
IC4H8
1.0
0.5
0
1 10 5 4

FIGURE 3

Range and mean of mixing ratios for most analytes and laboratories, tank sample data. Details similar to Figure 2.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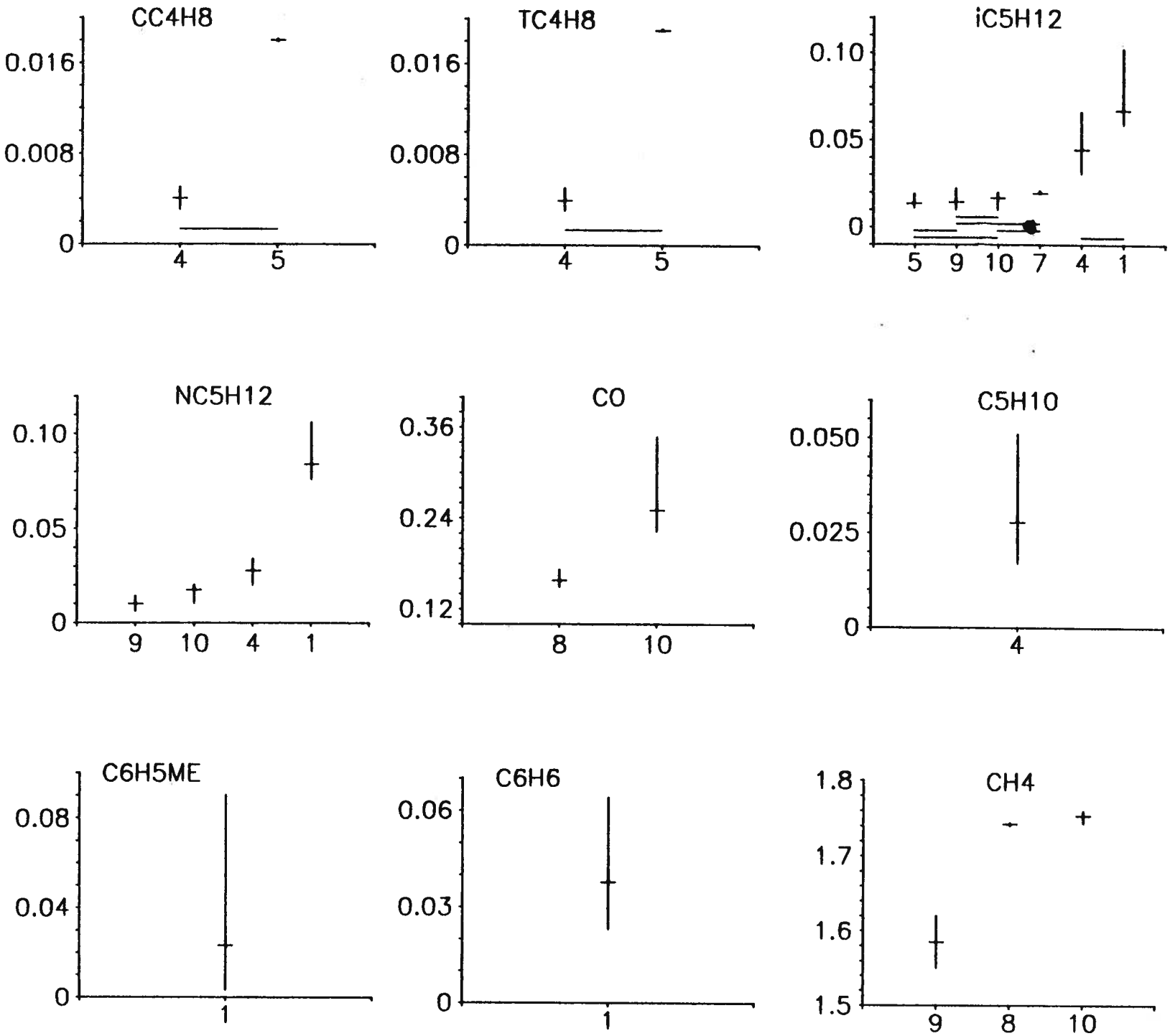
1.5
0
1 9 4 8 10 7 3 5 6
C3H8
0.6
0.3
0
1 9 3 7 10 4 8 5 6
C2H4
1.0
0.5
0
1 9 10 7 4 5 6 8 3
C3H6
0.4
0.2
0
1 9 10 7 5 4 8 6 3
iC4H10
0.06
0.04
0.02
1 4 10 7 9 5
NC4H10
0.24
0.12
0
1 5 9 10 4 7 6 3
C2H2
0.6
0.3
0
1 8 9 7 4 10 6 5
C4H8
0.04
0.02
0
1 5 4
iC4H8
1.2
0.6
0
1 4 5



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