

Nonmethane hydrocarbons in surface waters, their sea-air fluxes and impact on OH in the marine boundary layer during the First Aerosol Characterization Experiment (ACE 1)

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Abstract. Concentrations of six abundant alkanes (propane, 2-methylpropane, butane, 2-methylbutane, pentane, cyclopentane) and three abundant alkenes (2-methylpropene, *cis*-2-butene, 1,3-butadiene) were determined in air equilibrated with surface seawater in real time during the International Global Atmospheric Chemistry First Aerosol Characterization Experiment (ACE 1) campaign to the Southern Ocean in November–December 1995. Concentrations in ocean surface water inferred from these measurements generally lay within the ranges observed by other investigators at other times in other regions of the global ocean. Concentrations tended to decrease with increasing latitude. Comparison with a limited number of dissolved organic carbon (DOC) data obtained during transit from Hawaii to Hobart, Tasmania, suggested that higher hydrocarbon concentrations were associated with higher DOC levels. During the ACE 1 intensive study period west and south of Tasmania the differences in NMHC concentrations among the three major water masses sampled, while frequently significant, were not related in a simple direct or inverse way to surface water temperature, concentrations of nitrate, chlorophyll *a*, or dimethylsulfide, or to calculated sea-to-air transfer velocity or solar radiation intensity. The only correlations that showed some consistency within water masses were with temperature (negative) and nitrate (positive), an essential nutrient for phytoplankton growth. Deduced sea-to-air fluxes indicated modest open-ocean emissions of C₃–C₅ NMHC in this part of the global ocean. Assuming that the deduced fluxes were balanced by reaction with hydroxyl radical, OH, we estimated that the nine measured NMHC together accounted for negligible removal of OH compared to that due to the dominant OH + CO reaction and about 5 times less than that due to the DMS + OH reaction in the region of the marine boundary layer studied during ACE 1.

1. Introduction

Nonmethane hydrocarbons (NMHC) are recognized as important participants in atmospheric chemistry. They serve chemically as precursors of tropospheric ozone in the presence of sufficient concentrations of NO_x [see, e.g., Liu *et al.*, 1989]. Also, their major sink in the troposphere is reaction with the hydroxyl free radical (OH), so that in sufficient abundance in the remote marine atmosphere they can play an important role in lowering levels of this dominant atmospheric oxidant [see, e.g., Donahue and Prinn, 1990]. The lifetimes of marine atmospheric NMHC range from a fraction of a day up to several months and their photochemical oxidation products form a complex mixture including carbon monoxide, aldehydes, ketones, organic acids, alcohols, and organic free radicals.

A number of measurements and studies of NMHC in the ocean and remote marine atmosphere have been carried out [see, e.g.,

Swinerton and Lamontagne, 1974; Rudolph and Ehhalt, 1981; Singh and Salas, 1982; Greenberg and Zimmerman, 1984; Bonsang and Lambert, 1985; Plass-Dülmer *et al.*, 1995]. These studies indicate that the ocean is a source of reactive NMHC to the remote marine boundary layer (MBL) because, in most cases, the ocean surface water was found to be supersaturated in NMHC with respect to the air above. The results of laboratory culture studies [e.g., Lee and Baker, 1992; Milne *et al.*, 1995; McKay *et al.*, 1996] and field work [e.g., Bonsang and Lambert, 1985; Plass-Dülmer *et al.*, 1995; Ratte *et al.*, 1995] suggest that NMHC are produced in oceanic surface waters biotically by living organisms or from organic matter exuded during growth, and abiotically by photochemical degradation of dead cells and dissolved organic matter (expressed as dissolved organic carbon (DOC)). Loss is thought to be governed by exchange into the atmosphere [Plass-Dülmer *et al.*, 1995; Ratte *et al.*, 1995]. The fate of the freshly emitted NMHC from the ocean is determined by photochemical destruction and transport to the free troposphere. Significant spatial and temporal variability in these production and loss processes leads to the large variability in atmospheric NMHC spatial and temporal behavior observed by many investigators [e.g., Bonsang *et al.*, 1988; Plass *et al.*, 1992; Donahue and Prinn, 1993; Atlas *et al.*, 1993], as critically reviewed by Singh and Zimmerman [1992].

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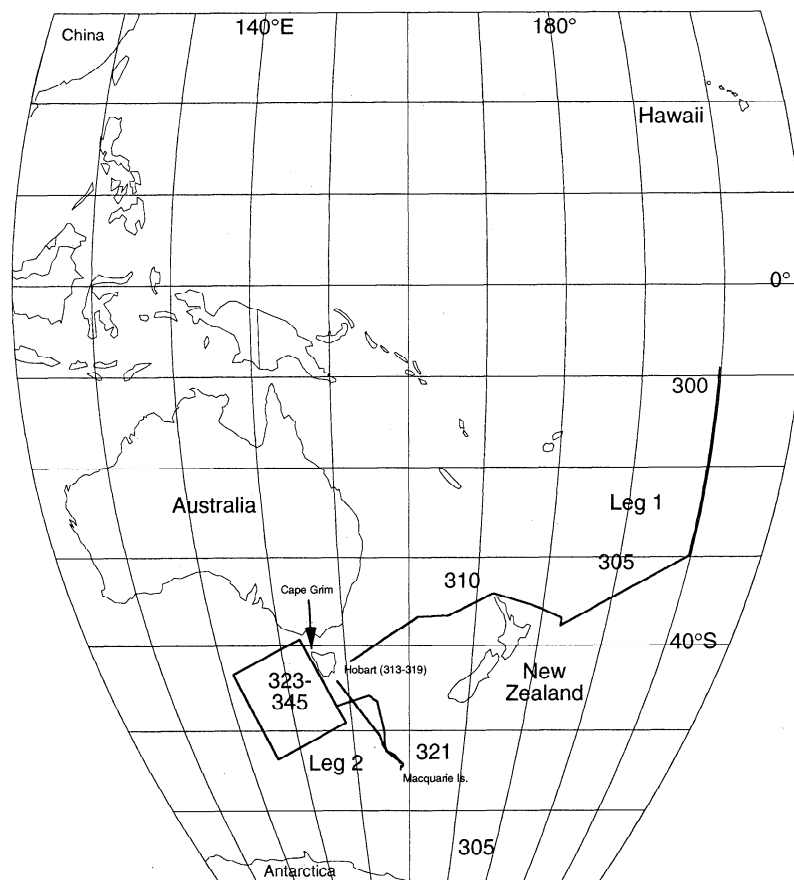


Figure 1. Map showing the portions of the ACE 1 cruise track of NOAA Ship *Discoverer* along which NMHC sampling was conducted. Approximate positions at the beginnings of selected Julian days are labeled.

In this paper, we report measurements of nine C_3 – C_5 NMHC made during the IGAC First Aerosol Characterization Experiment (ACE 1) aboard NOAA Ship *Discoverer* (November–December 1995) to characterize the distribution of NMHC in the surface waters of the remote Southern Ocean. We then combine these NMHC measurements with simultaneous measurements of wind speed to estimate sea-to-air fluxes of these compounds and assess their impact on OH in the MBL.

A meteorological and atmospheric chemical overview of ACE 1 is given by Hainsworth *et al.* [1998]. The oceanographic setting is discussed by Griffiths *et al.* [this issue]. Meteorological and chemical data sets from ACE 1, including ours, are available via <http://www.joss.ucar.edu>. The data we report from leg 1 (JD 300–JD 313) were obtained during transit from Hawaii to Hobart, Tasmania, through tropical, subtropical, and midlatitude South Pacific waters (see Figure 1). Leg 2 began with a transit from Hobart to Macquarie Island and part way back (JD 319–322) after which the ship moved westward and spent the rest of the available time (JD 323–345) south and west of Tasmania.

2. Experimental

2.1. Water Analysis

Seawater NMHC concentrations were measured by the method described by Donahue and Prinn [1993]. An acrylic Weiss-type equilibrator [Butler *et al.*, 1989] mounted on a weather deck was supplied continuously with a flow of 20 L min^{-1} of seawater from the ship's flow-through system. Ambient air in the 20-L headspace that is equilibrated with this flowing seawater was circu-

lated through copper tubing to the analytical system located in the ship's main laboratory and then back again using a Metal Bellows pump. The ambient air used to replace the headspace air consumed by sampling had much lower (factor of 100–1000) NMHC concentrations than the headspace air, as discussed later. An aliquot of 300 mL of the circulating gas was drawn at 30 mL min^{-1} through Nafion and a phosphorous pentoxide (Aquasorb) trap to absorb water followed by a sodium hydroxide (Ascarite) trap to absorb carbon dioxide, then into a 1.59 mm OD (0.762 mm ID) stainless steel collection loop, and finally exhausted through an electronic mass flow controller (Tylan, Inc.). Laboratory tests showed no losses at the 10^{-12} mole fraction level and mild contamination only for 2-methylpropene from Nafion [Donahue, 1991]. Also, standard analyses and standard addition experiments showed no significant loss or contamination due to Ascarite [Donahue, 1991]. The collection loop was cryogenically cooled with liquid N_2 vapor to a temperature between -150°C and -165°C monitored by an Omega thermocouple in direct contact with the loop. Immediately following collection, the NMHC samples were volatilized by immersion of the collection loop in water either at room temperature (before JD 335) or at about 80°C (after JD 335). The change on JD 335 failed to overcome difficulties with ethane and ethene determinations but did not produce noticeable changes in response to the compounds reported here. The volatilized gases were then sent directly to a 60-m PLOT column with Al_2O_3/KCl stationary phase (Chrompack) and then to a flame ionization detector (FID) in a Hewlett Packard 5890 Series II gas chromatograph.

The temperature program for analysis of the samples included

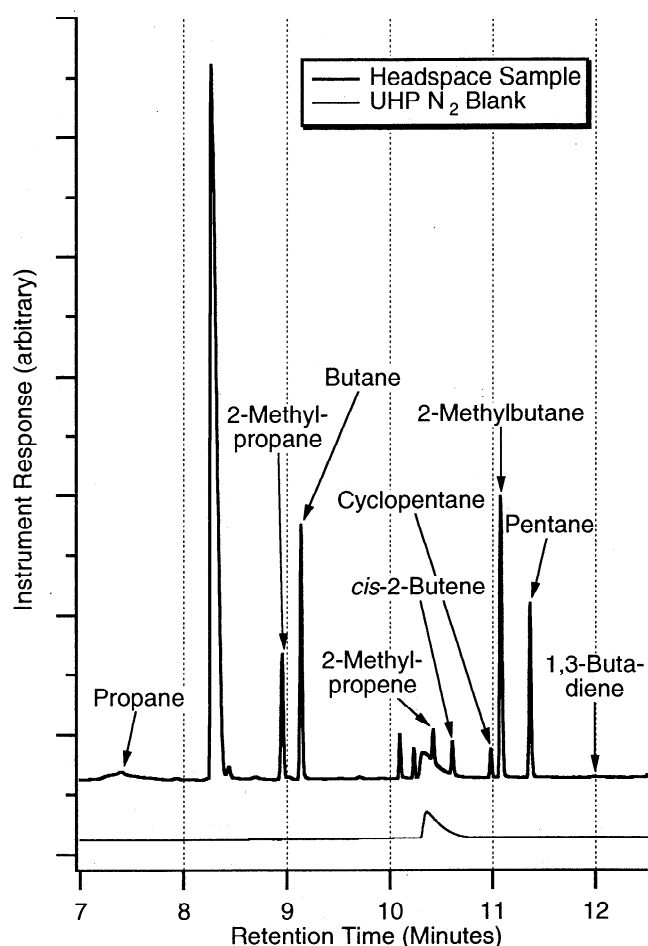


Figure 2. Chromatograms of an equilibrator headspace sample (heavy line) and trapping loop blank (light line) obtained aboard ship on November 20, 1995. The blank was collected by feeding UHP N_2 directly into the trapping loop after isolating the equilibrator and the ~ 30 m sampling and return-flow line which led from it to the analytical system in the ship's main laboratory.

an initial 3-min isothermal period at 60°C followed by heating at $10^\circ\text{C min}^{-1}$ to 135°C . After 5.5 min, heating resumed at $15^\circ\text{C min}^{-1}$ to a final temperature of 185°C where it was held for 15 min. After JD 321, the initial temperature was lowered from 60°

to 40°C to improve resolution of early-eluting compounds. The entire analysis of a sample of seawater-equilibrated gas required approximately 45 min from the beginning of the collection. Measurements were obtained nominally every other hour. An example chromatogram of seawater-equilibrated air is shown as the solid curve in Figure 2.

2.2. Calibration

An NMHC standard (5145) prepared at MIT using methods described by Donahue [1991] and Donahue and Prinn [1993] was analyzed once each day on most days. An onboard working standard was created by diluting 1 part of the 5145 standard into 100 parts of UHP nitrogen. The results reported here use our own absolute calibration scale [Donahue and Prinn, 1993] which has been intercompared with others, as discussed in the next section. A 75-mL sample (one quarter the volume of a normal equilibrator sample) of the diluted standard gas was collected using the same line and flow rate used for the equilibrator samples (specifically, the same traps, flow controllers, and collection loop). The chromatogram of each equilibrator sample was compared to the standard chromatogram which was obtained nearest to its collection time. Concentrations were then calculated assuming exact linearity of the FID with respect to its response per mole of each compound. For the equilibrator samples, this concentration represents the gas phase concentration which would be in equilibrium with the actual seawater concentration. To calculate the seawater concentration, we divided the measured equilibrator air concentration by the appropriate dimensionless Henry's law constant for the compound of interest (see Table 1).

2.3. Intercalibration

In order to relate our independent absolute calibrations for NMHC to those of other laboratories, we have participated in the IGAC Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE). Phases 1 and 2 of NOMHICE were described by Apel *et al.* [1994]. For phase 3, mixtures of more than 50 hydrocarbons and halocarbons were prepared by the National Institute of Standards and Technology (NIST). As in earlier phases, aliquots of mixtures were then put into canisters and analyzed by the NOMHICE coordinating laboratory at the National Center for Atmospheric Research (NCAR), sent to each participating laboratory for analysis, and then reanalyzed at NCAR after their return. In Table 2 we compare the mole fractions we determined in

Table 1. Reaction Rate Constants k Where Known for Reaction of Indicated NMHC and DMS With OH Radicals, Cl Atoms, and Ozone at 25°C [Atkinson, 1989; Atkinson and Carter, 1984]; Lifetimes τ During ACE 1 Due to Reaction With OH Radicals, Cl Atoms, and Ozone (Calculations Assume Diurnal Average $[\text{OH}] = 6 \times 10^5 \text{ cm}^{-3}$ [Wingenter *et al.*, this issue], $[\text{Cl}] = 7.2 \times 10^2 \text{ cm}^{-3}$ [Wingenter *et al.*, this issue], and $[\text{O}_3] = 2 \times 10^{11} \text{ cm}^{-3}$; and nondimensional Henry's law coefficients H from MacKay and Shiu [1981] and Donahue and Prinn [1990])

	$k(\text{OH})$	$\tau(\text{OH})$	$k(\text{Cl})$	$\tau(\text{Cl})$	$k(\text{O}_3)$	$\tau(\text{O}_3)$	τ_{overall}	H
Propane	1.2×10^{-12}	16.	1.6×10^{-10}	100.			14.	28.9
2-Methylpropane	2.3×10^{-12}	8.2	1.4×10^{-10}	115.			7.7	48.4
Butane	2.5×10^{-12}	7.6	2.3×10^{-10}	70.			6.8	38.7
2-Methylpropene	5.1×10^{-11}	0.4			1.2×10^{-17}	4.82	0.4	8.7
cis-2-Butene	5.6×10^{-11}	0.3			1.3×10^{-16}	0.45	0.3	5.8
Cyclopentane	5.2×10^{-12}	3.6					3.6	7.5
2-Methylbutane	3.9×10^{-12}	4.9	2.0×10^{-10}	80.			4.6	48.4
Pentane	3.9×10^{-12}	4.9	2.5×10^{-10}	64.			4.5	50.4
1,3-Butadiene	6.7×10^{-11}	0.3	5.6×10^{-10}	29.			0.3	74.6
DMS*	4.7×10^{-12}	4.0	3.3×10^{-10}	49.			3.7	2.1

Units: k , $\text{cm}^3 \text{ s}^{-1}$; τ , days. Reactions with Br atoms and NO_3 radicals may reduce overall lifetimes of some compounds.
* $k(\text{Cl})$ for DMS is from Sickel *et al.* [1992]; H for DMS is from Dacey *et al.* [1984].

Table 2. Comparison of NMHC Mole Fractions Determined in NOMHICE Canister CC111779AA by NCAR and MIT

Compound	NCAR		MIT	NCAR/MIT Ratio	
	Before	After		Before	After
Propane	25.3	25.5	32	0.80	0.81
2-Methylpropane	20.3	20.4	22	0.92	0.93
2-Methylbutene	9.95	10.1	11	0.91	0.92
Butane	30.9	31.2	36	0.86	0.86
cis-2-Butene	7.66	7.69	7.4	1.0	1.0
2-Methylbutane	15.2	15.3	20	0.78	0.78
Pentane	12.5	12.6	18	0.69	0.69
Cyclopentane	4.20	4.23	4.7	0.89	0.90
Mean				0.86	0.87
Standard deviation				0.11	0.11

Mole fractions in ppbv. Eight of the nine compounds for which we report results in this paper are included. The ninth, 1,3-butadiene, was not in the canister. NCAR data were provided by E. Apel (personal communication, 1995).

the NOMHICE phase 3 canister sent to us with those determined by NCAR. Our analyses were conducted in early January 1995. The ratios of NCAR's results to ours for these eight species ranged from 0.69 to 1.0 with a mean of 0.87 and a standard deviation (σ) of 0.11. For the full 23 NMHC we identified in the canister, the mean ratio was 0.96 ± 0.14 (1σ), so the differences appear not to be systematic overall but instead are likely to be methodological. These differences, together with similar differences among other independent laboratories [Apel *et al.*, 1994], indicate the magnitude of possible errors in absolute calibration. Multiplication of our reported concentrations by the ratios given in Table 2 converts them to the NCAR (NIST) scale.

2.4. Performance Checks

Some measurements were automatically rejected when a clear analytical problem was noted (e.g., collection flow rate was not maintained, damage to column discovered, etc.) or when they followed a significant system change (e.g., replacement of exhausted P_2O_5 traps). On occasion, analysis of the standard gas yielded statistically improbable ($>3\sigma$) responses. On these occasions the mean of the previous and subsequent calibration values was substituted for the rejected calibration.

The level of contamination was constrained using blank runs consisting of analyses of UHP nitrogen passed through the same analytical system with which the equilibrator headspace gas was analyzed. A blank chromatogram is shown as the dashed line in Figure 2. The only element of the analytical system which was not tested through this procedure was the equilibrator itself. In order to put an upper limit on the potential for contamination due to the equilibrator, we subsequently carried out laboratory experiments on the equilibrator used during ACE 1. These experiments involved blocking all openings in the equilibrator and purging it with UHP nitrogen at a low flow rate designed to simulate headspace conditions during routine operation on the ship. Figure 3 shows the results of a headspace analysis from one of these experiments. Ratios of concentrations in onboard blanks and subsequent laboratory headspace blanks to onboard equilibrator samples are shown in Table 3. To summarize, the onboard and subsequent laboratory experiments indicate that potential contamination is $\leq 3\%$ relative to the median value for each reported NMHC except for propane and 2-methylbutane for which it is $\leq 9-10\%$.

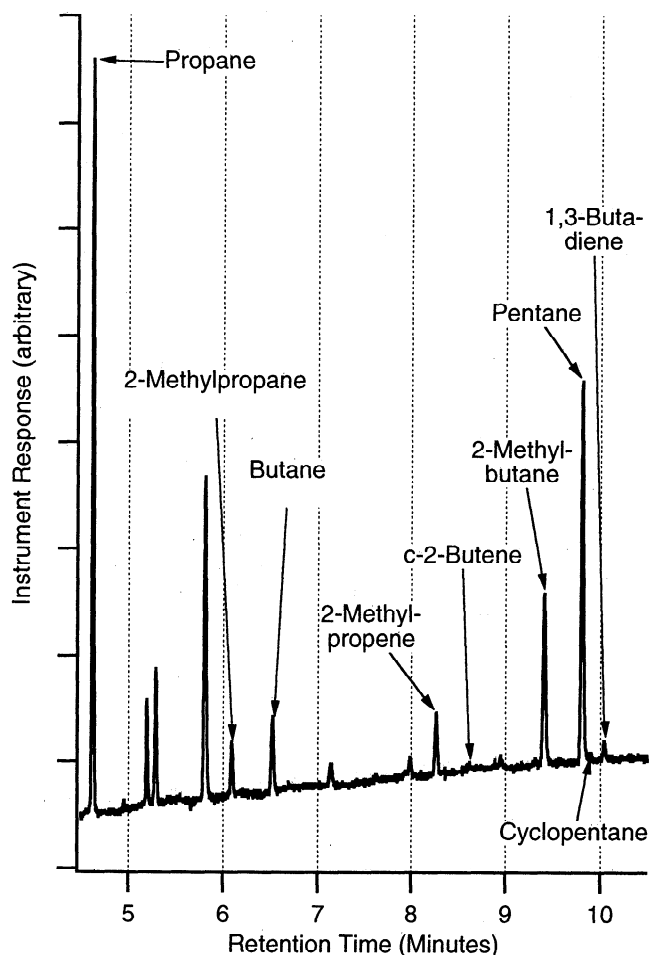


Figure 3. Chromatogram of a blank collected from the empty (no water) equilibrator in the laboratory at MIT on May 5, 1997. The device was sealed and flushed with UHP N_2 at about 40 mL min^{-1} for 5 hours to simulate ship headspace flushing during routine operation at sea before this sample was withdrawn for analysis. The analysis was performed on a different trapping and GC system from that used during the ACE 1 cruise, so the retention times are different, and the vertical scale is much expanded relative to Figure 2 to show detail. Calibrated concentrations are summarized in Table 3.

Table 3. Comparison of NMHC Mixing Ratios in Equilibrator Headspace Gas During Routine Operation With Those in a Trapping Loop Blank (UHP N₂) Taken During the Cruise on November 20, 1995, and an Empty Equilibrator Blank (UHP N₂) Taken in the Laboratory at MIT on May 5, 1997

	A Actual Sample, pptv	B Median of Samples, pptv	C Loop Blank, pptv	D Equilibrator Blank, pptv	D/A %	D/B %
Propane	7,921	2,189	<24	228	2.88	10.42
2-Methylpropane	18,094	5,163	<8.2	19	0.11	0.37
Butane	31,484	7,016	<8.2	30	0.1	0.43
2-Methylpropene	2,417	813	20	22	0.91	2.71
<i>cis</i> -2-Butene	3,772	590	<7.3	2	0.05	0.34
2-Methylbutane	2,389	519	<8.1	49	2.05	9.44
Pentane	21,279	6,057	<18	162	0.76	2.67
Cyclopentane	19,708	6,350	<2.1	9.6	0.05	0.15

We also attempted to measure NMHC in boundary layer air during ACE 1. Owing to suspected low level contamination for some species (e.g., ≈ 10 ppt) related to the traps used, we do not report these data here. However, they do provide upper limits to contamination since they were collected under identical circumstances to the equilibrator headspace samples in a parallel system. These measurements suggest that the maximum potential contamination levels from the traps used on our system were 1–3 orders of magnitude less than typical levels of NMHC species in the headspace of the equilibrator.

Summary statistics for measurements of all nine NMHC are provided in Table 4. Instrument precision was equated to the standard deviation in the instrument response to the onboard NMHC standard when the system was operating well during the cruise. The instrument precisions were much less than the relative standard deviations for the water measurements (see Table 4) implying that the variations in NMHC concentrations are real. Detection limits were determined by the integration software's ability to discern peaks from background noise as described by Donahue [1991].

2.5. Dimethylsulfide and Ancillary Measurements

Seawater dimethylsulfide (DMS) and atmospheric DMS concentrations were measured by automated gas chromatography with sulfur chemiluminescence detection [Bates *et al.*, 1998a].

Meteorological and solar radiation measurements made by other investigators are described by Bates *et al.* [1998b]. Seawater was sampled from the ship's clean seawater inlet, nominally 5 m below the sea surface at the bow, which also fed the equilibrator. Surface seawater temperature and salinity were measured with a Seabird SBE-21 thermosalinograph mounted in the ship's sea chest at the clean water inlet. Total nitrate was determined by standard autoanalyzer techniques [Parsons *et al.*, 1984]. Discrete samples for chlorophyll *a* measurements were collected every 4 hours while underway, preserved and then analyzed aboard ship with a fluorometer [Parsons *et al.*, 1984]. Further details on seawater analyses are given by Griffiths *et al.* [this issue].

3. Results

3.1. Water Concentrations and Ratios

Ideally, the equilibrator should achieve equilibrium between the flowing gaseous and aqueous phases. The actual partitioning of gases between the two phases depends on the Henry's law constant, the volume of the headspace, and the flow rates of headspace air and seawater, and can be conveniently expressed by a time constant for each gas. The shorter the time constant, the closer one should approach equilibrium between the two phases. This time constant is given by VH/Q [Butler *et al.*, 1989], where V is the volume of the head space (19 L) plus sampling–return

Table 4. Statistical Summary of Measured NMHC Mixing Ratios in Equilibrator Headspace Gas

	PRA*	MPA	BUA	MPE	BUE	CPE	MBE	PEA	BDE
N	290	309	309	309	282	298	311	312	177
Minimum	120	49	140	220	150	110	60	34	2
25th percentile	1,700	1,400	3,100	3,000	1,400	2,000	2,800	3,500	44
Median	3,000	3,500	6,100	4,400	3,300	3,400	4,800	5,600	76
75th percentile	5,400	8,300	10,000	8,900	5,600	6,400	7,200	9,900	110
Maximum	44,000	77,000	75,000	56,000	40,000	29,000	35,000	39,000	380
Mean	4,500	6,500	9,200	7,500	5,100	5,200	6,300	7,600	83
Standard deviation	5,100	9,000	10,000	8,200	6,000	5,000	5,800	6,200	55
R.S.D., %	110	140	110	110	120	97	91	81	67
Prec., %	8	11	9	5	7	6	12	5	26

Units are pptv except for number of measurements (N), relative standard deviation (R.S.D.) (%), and instrument precision (Prec.) (%). *PRA, propane; MPA, 2-methylpropane; BUA, butane; MPE, 2-methylpropene; BUE, *cis*-2-butene; CPE, cyclopentane; MBE, 2-methylbutene; PEA, pentane; BDE, 1,3-butadiene.

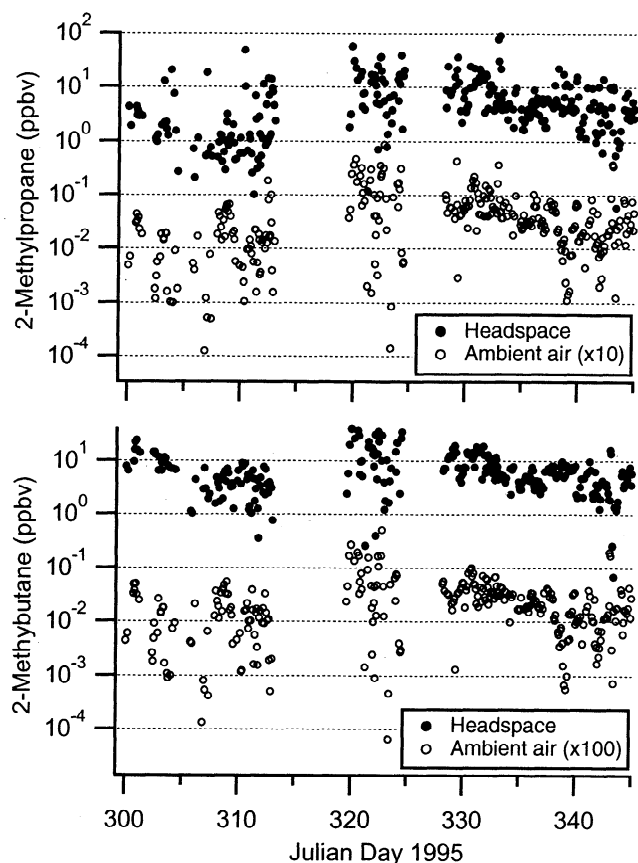


Figure 4. Mole fractions of 2-methylpropane (upper panel) and 2-methylbutane (lower panel) measured in the headspace of the seawater equilibrator (solid symbols) as a function of Julian time during the cruise. Also shown are upper limit estimates for mole fractions in MBL air (open symbols) inferred from equating sea-to-air fluxes with atmospheric destruction rates.

flow line (1 L), Q is the flow rate of the water (20 L min^{-1}), and H is the dimensionless Henry's law coefficient (see Table 1). Most light NMHC are sparsely soluble in water, and their resultant high Henry's law constants mean nonnegligible time constants (specifically, $H \text{ min}$ for the above values of V and Q) for the equilibrator to reach equilibrium. Accordingly, the NMHC concentrations in air samples from the equilibrator should represent concentrations in the water phase averaged over the preceding $H \text{ min}$ (or longer) after multiplying by the appropriate Henry's law constant (Table 1).

We show in Figure 4 (solid symbols) the measured mole fractions in the equilibrator headspace, X_e , as a function of time during the cruise for two of the measured NMHC. The high variability in the measured values evident in Figure 4 is also evident for all other species measured, being least for 2-methylbutane and pentane, and most for 1,3-butadiene for which the fewest measurements are available (see Table 4). Generally, the variations in X_e for the various NMHC are strongly correlated with each other suggesting variations in the strength of a common oceanic source for them. In Figure 5 we show ratios of 2-methylpropane to butane (upper panel) and 2-methylbutane to pentane (lower panel). These ratios are comparatively steady (factor of ~ 2 variability versus factors of >10 variability in concentration for individual compounds) illustrating the above correlations.

3.2. Comparisons With Previous Surface Water NMHC Measurements

Figure 6 shows comparisons of the NMHC concentrations in near-surface seawater inferred from our equilibrator measurements with literature data. Similarly, Figure 7 shows the comparisons for the ratios of 2-methylpropane to butane and 2-methylbutane to pentane. The three rightmost boxes in each panel represent data obtained by our group during cruises in 1990 (SAGA 3) and 1992 (MAGE-92) and then ACE 1. Remaining boxes represent virtually all other open-ocean data obtained by other research groups for the compounds we report. Not included are the relative concentration data for propane, 2-methylpropane, and butane of *Brooks and Sackett* [1973] and *Brooks et al.* [1973]. Also excluded are inland sea samples and samples flagged as coastally influenced by *Swinnerton and Lamontagne* [1974]. Additional information about the data summarized in Figures 6 and 7 is given in Table 5.

This comparison suggests that concentrations of a particular NMHC in surface seawater vary by at least an order of magnitude between different ocean regions. Results of studies that included cruises to the same areas in different years (Beaufort Sea [*Macdonald*, 1976]; central North Atlantic [*Plass-Dülmer et al.*, 1993]) suggest that interannual variations can also be order of magnitude. However, as pointed out by *Plass-Dülmer et al.* [1995], even the relatively large combined data set for propane is inadequate to allow a systematic global analysis. Nevertheless, some

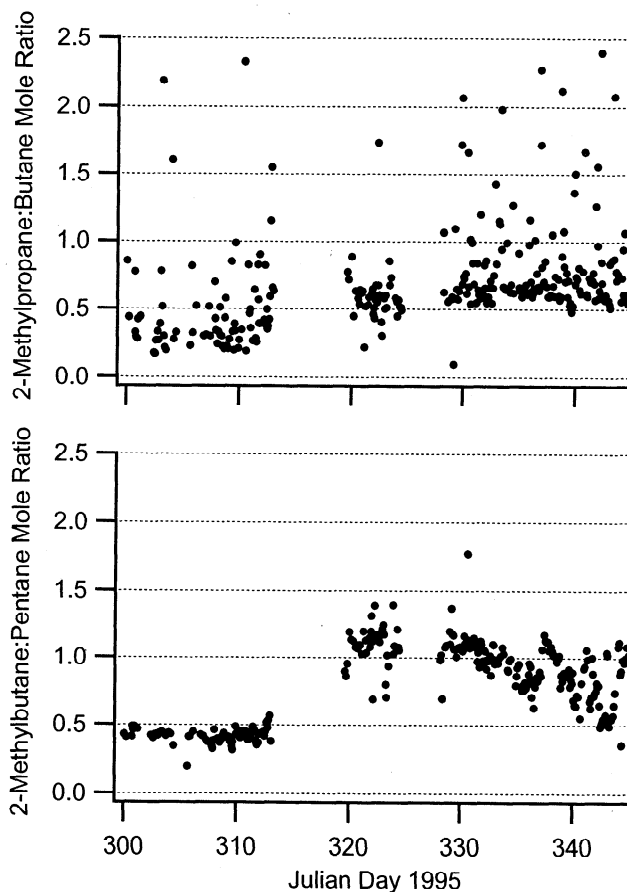


Figure 5. Ratios of 2-methylpropane to butane and 2-methylbutane to pentane measured in the headspace of the equilibrator during the cruise.

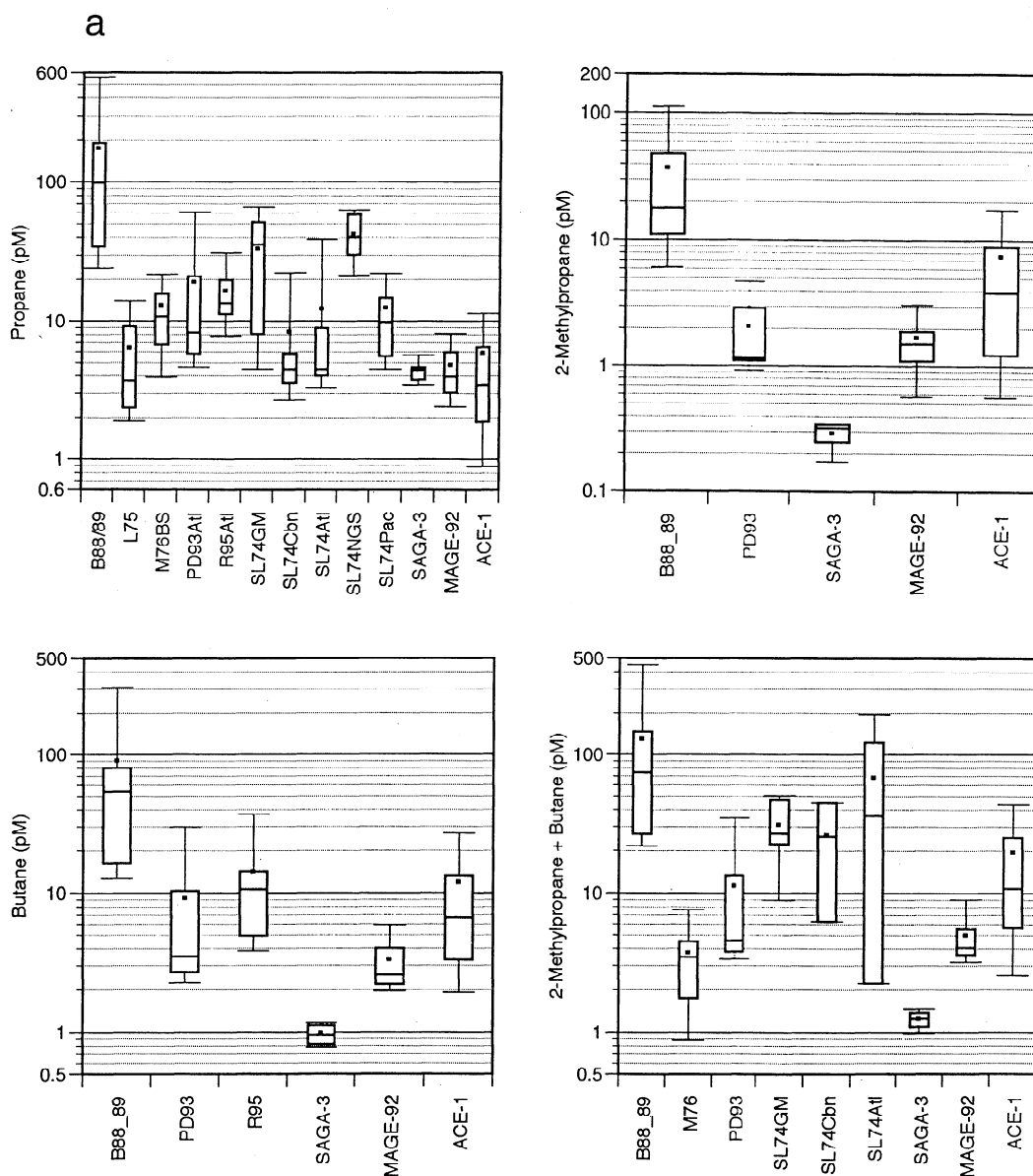


Figure 6. Comparison of measured NMHC concentrations in surface seawater at various places and times for (a) propane, 2-methylpropane, butane, and 2-methylpropane + butane; (b) 2-methylbutane, pentane, 2-methylpropene, and *cis*-2-butene. The top, bottom, and line through the middle of each box correspond to the 75th percentile, median, and 25th percentile, respectively. The whiskers on the top and bottom extend to the 90th and 10th percentiles, respectively. The dots indicate the means. Sources of data are B88_89, *Bonsang et al.* [1989]; L75, *Lamontagne et al.* [1975]; M76BS, *Macdonald* [1976]; PD93Atl, *Plass-Diilmer et al.* [1993]; R95, *Ratte et al.* [1995]; R96, *Riemer et al.* [1996]; SL74, *Swinerton and Lamontagne* [1974]; SAGA 3, *Donahue and Prinn* [1993]; MAGE-92, X. Shi and R.G. Prinn (unpublished manuscript, 1996); ACE 1, this study. See Table 5 for additional information about data sources.

general comments can be made. First, the mole fractions measured by *Bonsang et al.* [1989] are in general significantly higher than ours and all others. Putting their data aside, our ACE 1 measurements (see Figure 6) are comparable to others' for 2-methylpropane, butane, and *cis*-2-butene, higher than others' for 2-methylbutane and pentane, and lower than others' for 2-methylpropene and propene. Our ratios of 2-methylpropane to butane and 2-methylbutane to pentane (Figure 7) are higher and more variable than others', particularly in the region near and south of Tasmania where we sampled from JD 320 onward.

3.3. Surface Oceanic NMHC Distributions During ACE 1

Among parameters measured during ACE 1 that may aid interpretation of NMHC distributions are surface water temperature (T), salinity (S), concentrations of nitrate, chlorophyll *a*, and dimethylsulfide (DMS), transfer velocity (W), and solar radiation (I). For our analysis we used 30-min averages of T, S, nitrate, I, and DMS data from the ACE 1 data archive. We estimated values at 30-min intervals for chlorophyll *a* by interpolation (smoothing spline) of data for discrete samples collected nominally every 4

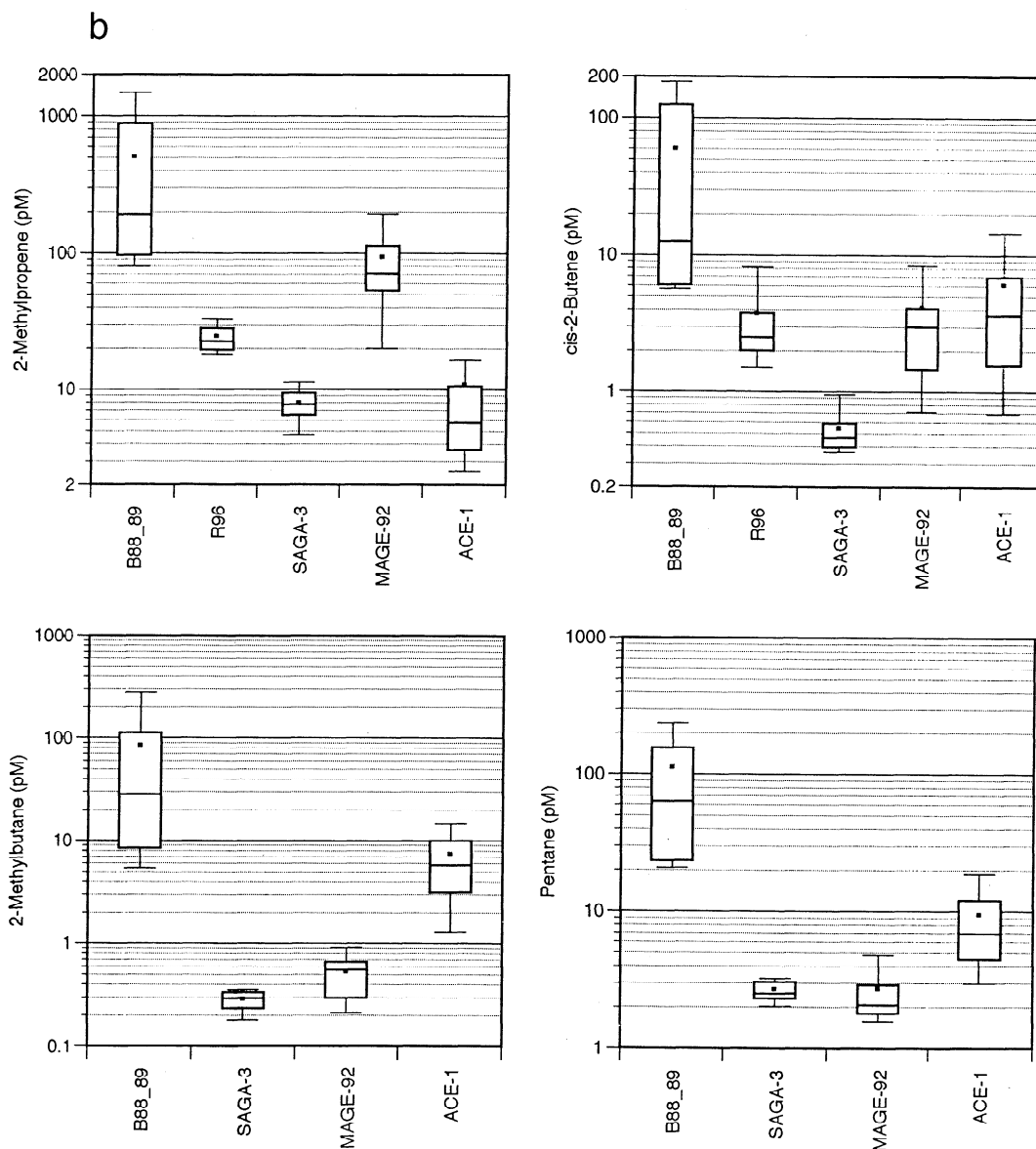


Figure 6. (continued)

hours. We describe calculation of W in section 3.4. We then associated the 30-min average values of these parameters to the NMHC samples collected closest in time.

3.3.1. Synopsis of surface water hydrography. Inspection of time series plots (not shown) of the NMHC data along with position, T , and S data suggests that the leg 1 data set may be divided into three periods. Period 1 (JD 300.1-304.4) is the southward transit from 9°S to 31°S along 160°W (see Figure 1). T decreased from 28.9°C to 18.4°C , while S varied between 35.00 and 35.85 psu. No NMHC data were acquired 1 day (JD 301.245-302.249) during this period due to instrument problems. Period 2 (JD 305.8-310.6) is the westward transit from $\sim 31^{\circ}\text{S}$, 160°W to $\sim 36^{\circ}\text{S}$, 168°E during which T and S fluctuated relatively little within the ranges of $16.5^{\circ}\text{--}17.5^{\circ}\text{C}$ and 35.40-35.50 psu, respectively. Period 3 (JD 310.8-313.1) is the remainder of leg 1 from $\sim 36^{\circ}\text{S}$, 168°E to Hobart. T varied from $13^{\circ}\text{--}17^{\circ}\text{C}$ and S varied from 35.15-35.50 psu.

Leg 2 began on JD 319 with a southeastward transit from Hobart to Macquarie Island, approximately 1 day close offshore

Macquarie, and then a transit northwestward to $\sim 47^{\circ}\text{S}$, 150°E in the main ACE 1 working area where operations continued for the remainder of the cruise (JD 346). A detailed analysis of the oceanographic setting during leg 2 is given by Griffiths *et al.* [this issue] based on data obtained aboard the *Discoverer* combined with those obtained on the Australian R/V *Southern Surveyor* which operated in the same region from JD 319 to 341. In accordance with their definitions of the major surface water masses based on salinity, we divide our leg 2 data into subsets for Subtropical Convergence Zone (STCZ) water ($34.8 < S \leq 35.2$ psu), Subantarctic and Subantarctic Front (SA/SAF) water ($34.2 \leq S \leq 34.8$ psu), and Polar and Polar Front (P/PF) water ($S < 34.2$ psu). We obtained only two samples representing Subtropical (ST) water ($S > 35.2$ psu) and do not consider those samples further here. No NMHC data were acquired between JD 324.5 and 328.2 due to instrument problems.

3.3.2. NMHC spatial distributions and trends during leg 1.

The concentrations of all nine compounds were highest during period 1. However, not all compounds decreased in concert. The

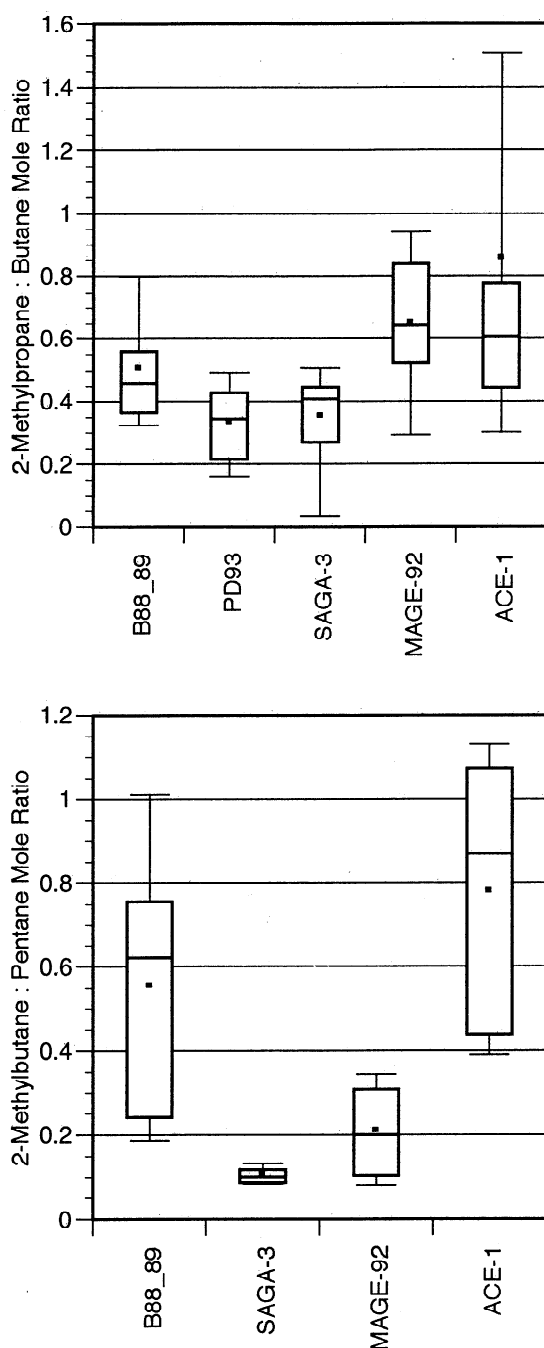


Figure 7. Comparison of 2-methylpropane to butane and 2-methylbutane to pentane ratios in surface seawater at various places and times. See caption to Figure 6 for explanation of symbols and data sources.

three C_3 compounds decreased monotonically from period 1 to period 3. Butane, 2-methylpropene, and *cis*-2-butene decreased rapidly from period 1 to period 2 and then stayed about the same through period 3. 2-Methylpropane and 1,3-butadiene decreased rapidly from period 1 to period 2 but then increased during period 3. Propane also showed signs of a monotonic decrease, although the differences in median concentrations were not significant. Surface water DOC concentrations also decreased from 75–85 μM during period 1 to 60–70 μM during period 2 to 50–60 μM during period 3 (data of Y. Suzuki on <http://www.joss.ucar.edu>), consistent with the hypothesis that NMHC result from degradation of

DOC. Only eight DOC measurements are available for comparison, so a more detailed analysis is not warranted.

Propane showed no significant trend with latitude during period 1. 2-Methylpropane and *cis*-2-butene appeared to show secular decreases. With a few outliers ignored, linear regressions yielded significant slopes of -0.097 ± 0.020 and -0.072 ± 0.020 pM deg^{-1} , respectively. Cyclopentane, 2-methylbutane, and pentane appeared to increase slowly to 16°S , then decreased rapidly and significantly southward to 22°S . Linear regression slopes for the downtrend portions were -1.45 ± 0.28 , -0.62 ± 0.16 , and -1.44 ± 0.36 pM deg^{-1} , respectively. 2-Methylpropene decreased comparatively very rapidly and nonlinearly with latitude to 16°S then ceased to trend.

During period 2, significant increases from east to west were apparent for butane (0.18 ± 0.08 pM deg^{-1}), cyclopentane (0.22 ± 0.10 pM deg^{-1}), 2-methylbutane (0.22 ± 0.06 pM deg^{-1}), and pentane (0.43 ± 0.13 pM deg^{-1}). 2-Methylpropane appeared to increase as well, but not significantly. Propane showed no trend. Too few *cis*-2-butene and 1,3-butadiene data were acquired during this period to allow trends to be discerned.

There were hints of continued increases in 2-methylpropane, butane, and 1,3-butadiene concentrations east to west during period 3, but none were significant. Trends were not evident for the other compounds.

3.3.3. NMHC variations among and within water masses during leg 2. First, we consider differences in NMHC concentrations among the major water masses described by *Griffiths et al.* [this issue]. Figure 8 shows summary box-whisker plots of T, nitrate, chlorophyll *a*, W, DMS, and I data for STCZ, SA/SAF, and P/PF water. Each water mass had a distinct signature with respect to T, chlorophyll *a*, DMS, and nitrate, (e.g., warm, high chlorophyll, high DMS, low nitrate for STCZ water). DMS was lower in P/PF water than in the other two water masses. W was higher when P/PF water was sampled reflecting generally higher wind speeds at those times. The extrinsic parameter I was not dependent on the nature of the underlying water, as one might expect.

Inspection of Figure 9 suggests that eight of the nine compounds measured (all except 1,3-butadiene) were generally present at higher concentrations in STCZ water relative to SA/SAF and P/PF water. A comparison of Figures 8 and 9 indicates that the differences in NMHC concentrations among water masses were not systematically related in a simple direct or inverse way to any of the six ancillary physical and chemical variables.

Correlations of the measured NMHC with T, W, I, chlorophyll *a*, nitrate, and DMS within each water mass are summarized in Table 6. The only correlations that show some consistency during the entire leg are with T and nitrate, an essential nutrient for phytoplankton growth. Specifically, most measured NMHC showed significant negative correlations with T within all three water masses, while correlations with nitrate were positive for eight of nine NMHC in SA/SAF water and five of eight NMHC in P/PF water. *Griffiths et al.* [this issue] noted that nitrate south of the STCZ region was relatively constant with depth reflecting deep winter mixing. Elevated NMHC concentrations in waters associated with upwelling have been observed elsewhere [e.g., *Lamontagne et al.*, 1975; *Plass-Dülmer et al.*, 1993]. Together these observations suggest that NMHC in surface water may be related to communication with deep water. This is difficult to verify, however, because almost no data are available for NMHC in deep water, or even into the thermocline. *Swinnerton and Lamontagne* [1974] observed subsurface ethene maxima in some (but not all) locations in various ocean basins. They did not report

Table 5. Sources of Data Plotted in Figures 6 and 7

Source	Sampling Location	Sampling Dates	Number of Samples (Total)	Remarks
<i>Bonsang et al.</i> [1988]	Western tropical Indian Ocean	April 1985	8	label = "B88_89" in figures [this and next entry combined]
<i>Bonsang et al.</i> [1989]	Northeast of Hawaii [$\sim 24^\circ\text{N}$, $\sim 154^\circ\text{W}$]; Hao Atoll [$\sim 18^\circ\text{S}$, $\sim 141^\circ\text{W}$]	May 1987	2	
<i>Lamontagne et al.</i> [1975]	Panama-Tahiti-Hawaii-Ecuador	June 1987	4	lagoon sample excluded
<i>Macdonald</i> [1976]	Beaufort Sea, $130^\circ\text{--}139^\circ\text{W}$, shoreward of 100 m depth contour	March–April 1974	41	label = "L75" in figures
<i>Plass-Dülmer et al.</i> [1993]	Bremerhaven, Germany- 30°N , 30°W - 30°S , 30°W -Rio Grande, Brazil	August 1974	35	label = "M76" in figures; only samples from ≤ 10 m depth included
		August 1975	52	
<i>Ratte et al.</i> [1995]	Bremerhaven, Germany- 0° , 18°W -Puerto Madryn, Argentina 25×25 km "stations" at 42°N , 5°E ; 37°N , 13°W ; 57°N , 15°W ; and 56°N , 5°E plus transits between	September–October 1988	65	label = "PD93" in figures; individual sample data not presented; used tabulated means for three latitude bands for each cruise
		August–September 1989	~ 110	
<i>Rierner et al.</i> [1996]	Gulf of Mexico, Shark River, and Florida Bay	April–May 1991	124 for propane; 138 for other compounds	label = "R95" in figures; individual sample data not presented; used tabulated means for each station and transit
		not given	12	label = "R96" in figures
<i>Swinerton and Lamontagne</i> [1974]	Gulf of Mexico	October 1966, June 1971, October 1971, June 1973	15	label = "SL74GM" in figures; samples flagged contaminated not included
		Caribbean Sea	April 1969, May 1970, May 1971, October 1971, July 1973	40
<i>Donahue and Prinn</i> [1993]	Atlantic Ocean	May 1966, June 1968, April 1969, December 1969, May 1971, January–June 1972, July 1973	93	label = "SL74Atl" in figures; mostly western margin from Norfolk, VA [USA] to Barbados; 1 station at $\sim 52^\circ\text{N}$, $\sim 20^\circ\text{W}$
		Norwegian-Greenland Sea transit	August 1971	95
<i>Donahue and Prinn</i> [1993]	Pacific Ocean, Panama-Hawaii transit and Los Angeles, CA [USA]-McMurdo, Antarctica transit	May–June 1971	95	label = "SL74Pac" in figures
		November–December 1972	63	
<i>X. Shi and R.G. Prinn</i> (unpublished manuscript, 1996)	tropical Pacific region bordered by 20°N , 15°S , 145°W , and 170°W	February–March 1990	15	label = "SAGA 3" in figures
		Los Angeles, CA [USA]- 10°N , 140°W - 10°S , 140°W - 12°S , 135°W and return along approximately the same track	February–March 1992	28
This study	see Figure 1	November–December 1995	315	label = "ACE I" in figures

temperature data though, so it is not clear where the maxima occurred relative to the thermocline. *Bonsang et al.* [1992] found maxima for ethane, ethene, and isoprene at or slightly below the thermocline in two profiles down to 1000 m in the Mediterranean ($43^\circ 36' \text{N}$, $7^\circ 29' \text{E}$) and one in the South Pacific ($15^\circ 08' \text{S}$, $148^\circ 15' \text{W}$). Concentrations at greater depths were similar to or lower than near-surface concentrations. They noted that NMHC maxima were not coincident with fluorescence maxima. *Milne et al.* [1995] also found subsurface isoprene maxima offset from fluorescence maxima at several stations in the Florida Strait near 24.5°N , 81.5°W . Like *Swinerton and Lamontagne* [1974], these authors reported no temperature data, so it is not possible to determine where the isoprene maxima occurred relative to the

thermocline. Finally, *Plass-Dülmer et al.* [1993] obtained one profile through the mixed layer into the thermocline in the Bay of Biscaye and two more on the equator at 18°W . Five of six compounds for which data are given (ethane, ethene, propane, propene, 1-butene) showed surface maxima. Acetylene showed a maximum within the mixed layer in both equatorial profiles.

Previous work suggests that the main loss process for NMHC is exchange to the atmosphere [*Plass et al.*, 1992; *Plass-Dülmer et al.*, 1995; *Ratte et al.*, 1995]. Negative correlations of NMHC concentrations with W might therefore be expected. Only one or two compounds were significantly correlated with W within each water mass we sampled (see Table 6). Negative correlation with W was apparent for pentane in STCZ and SA/SAF water and for

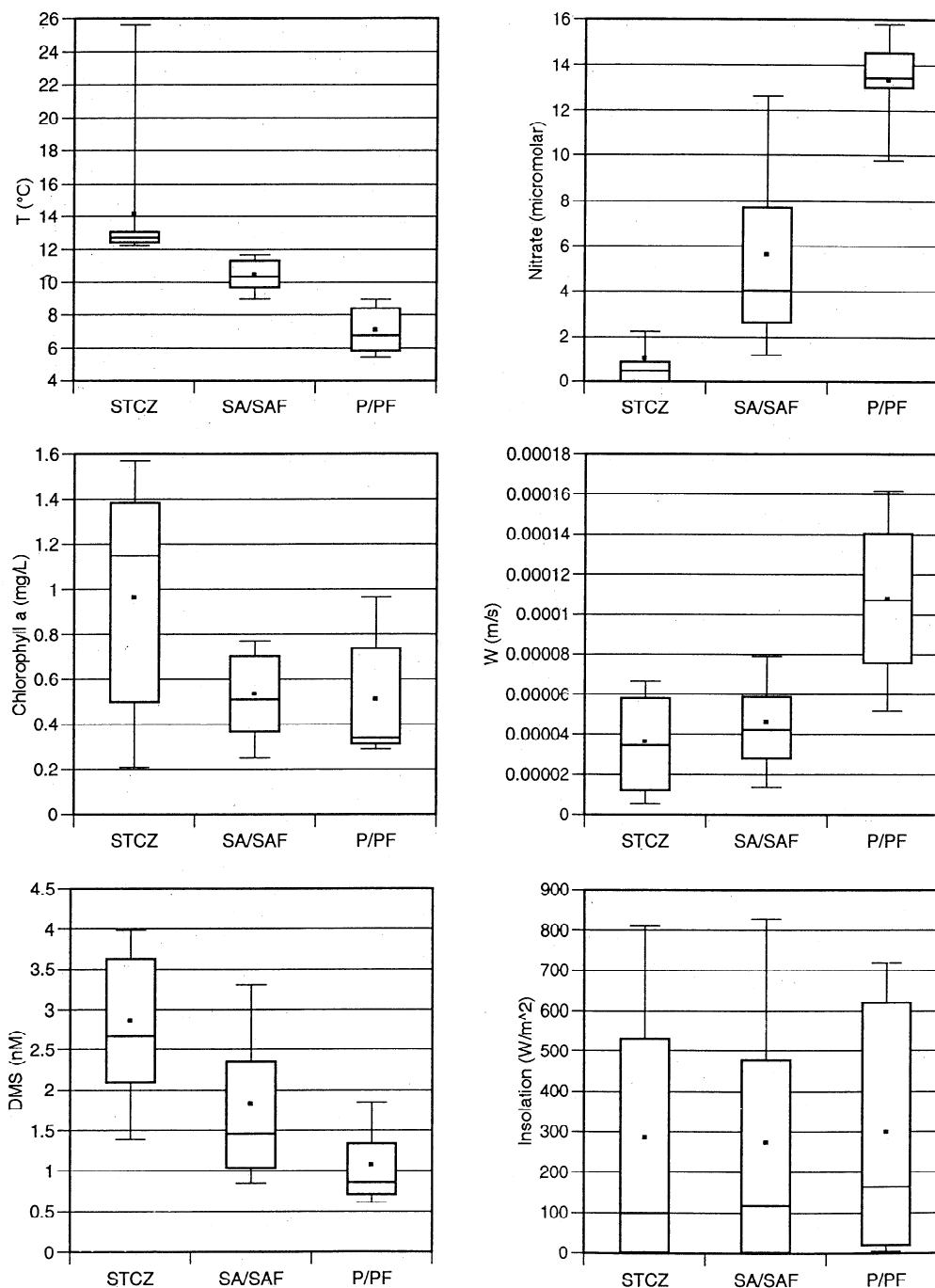


Figure 8. Comparison of data for (clockwise from upper left) sea surface temperature, nitrate, transfer velocity, solar radiation, DMS concentration in surface water, and chlorophyll *a* in STCZ, SA/SAF, and P/PF water. See caption to Figure 6 for explanation of symbols.

propane and 2-methylpropane in P/PF water; 1,3-butadiene was positively correlated with *W* in STCZ water. Many other correlations with *W*, though not significant at the $P = 0.05$ level, were also negative. In their analysis of a global dataset of oceanic NMHC based on in situ analysis ($n=75$) assembled from the literature, Plass-Dülmer *et al.* [1995] found a negative correlation of ethene and but no correlation of ethane with *W*. Ratte *et al.* [1995] selected eight time periods ≥ 48 hours with fairly constant wind velocity at one location and found five of six NMHC to be negatively correlated with *W*. However, none of the correlations

was significant at the $P = 0.05$ level. Lack of consistent and significant negative correlations with transfer velocity in any of these studies, including ours, suggests that surface water NMHC concentrations generally may be only weakly affected by loss to the atmosphere.

Laboratory studies [e.g., Wilson *et al.*, 1970; Lee and Baker, 1992] have demonstrated that NMHC production in seawater from degradation of organic matter increases with increasing illumination. However, field observations have not confirmed this effect in the open ocean [e.g., Plass-Dülmer *et al.*, 1995]. Our

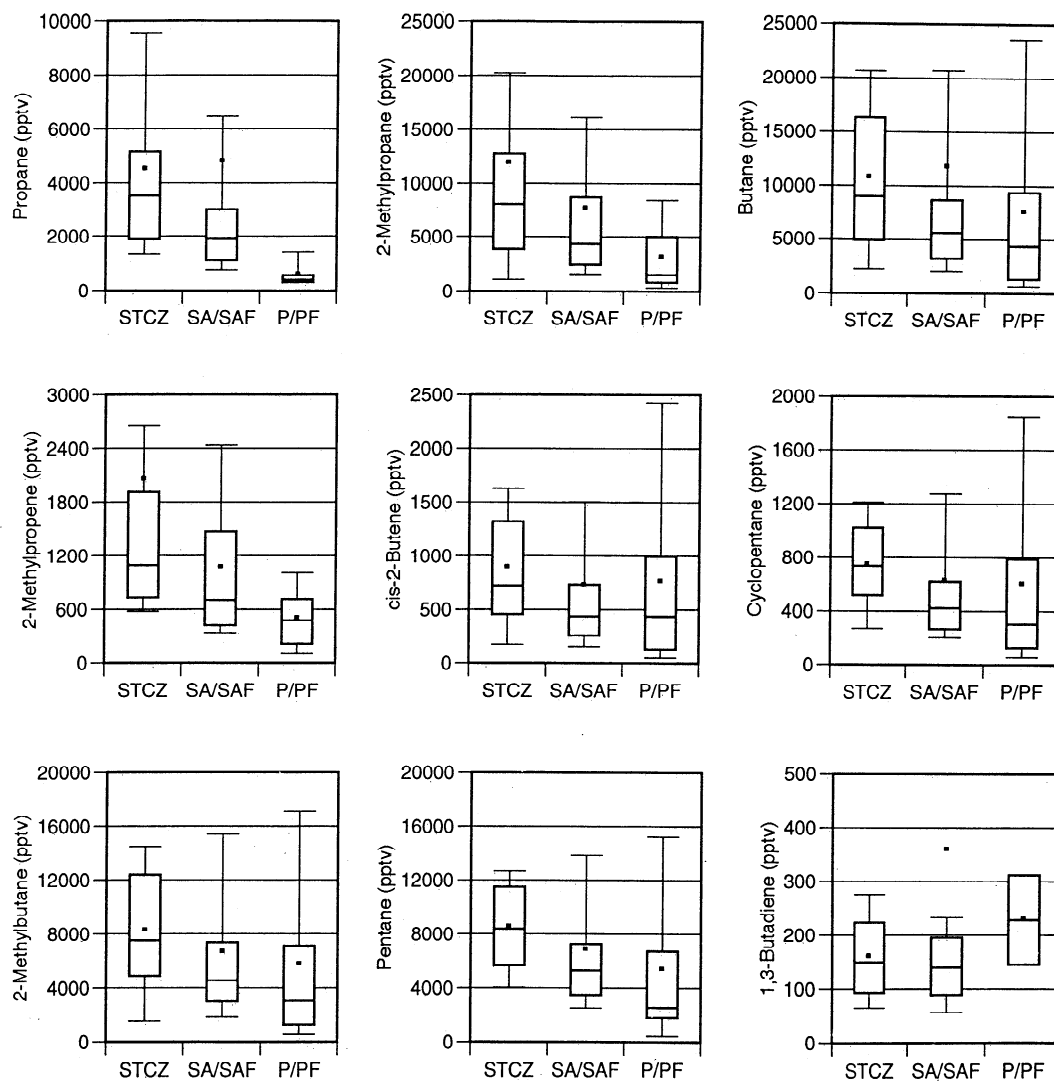


Figure 9. Comparison of data for measured NMHC in STCZ, SA/SAF, and P/PF water. See caption to Figure 6 for explanation of symbols.

results were that only three NMHC in STCZ water and one in SA/SAF water showed significant positive correlations with solar radiation, I (see Table 6).

Significant positive correlations with chlorophyll a were evident only for butane in STCZ and SA/SAF water and for propane and 2-methylpropene in P/PF water. Numerous previous studies [e.g., Swinnerton and Lamontagne, 1974; Bonsang et al., 1992; Milne et al., 1995; Plass-Dülmer et al., 1993] noted approximate but not exact coincidence of NMHC maxima with either chlorophyll a or in situ fluorescence in vertical profiles, as noted above.

There have been no previous reports of relationships between NMHC and DMS in seawater to our knowledge. Correlations of NMHC with DMS were mostly negative in STCZ and SA/SAF water, although only two and four of nine were significant in these respective water masses. Propane was positively correlated with DMS in P/PF water. The lack of correlations with DMS may reflect the fact that DMS originates almost exclusively from degradation of a single compound (dimethylsulfoniopropionate) produced mainly by a few phytoplankton species [see, e.g., Jones et al., 1998], while NMHC derive from the complex mixture of

carbon-containing compounds that make up the DOC pool or from direct biological origin.

Finally, we note that only four surface water DOC measurements were made on days that we sampled during leg 2 (data of Y. Suzuki on <http://www.joss.ucar.edu>). DOC concentrations in STCZ water (58 and 72 $\mu\text{M C}$) were similar to those SA/SAF water (62 and 56 $\mu\text{M C}$). As for leg 1, a detailed discussion of NMHC–DOC relationships is not warranted.

3.4. Sea-to-Air Fluxes of NMHC

The sea-to-air flux (Φ) of a compound is proportional to the difference between the concentration (mol m^{-3}) measured in the equilibrator headspace gases ($[e]$) and in the atmosphere over the ocean ($[a]$): specifically $\Phi = W([e] - [a])/H$ [Liss and Slater, 1974]. As noted earlier, for all the NMHC reported here, $[e]$ typically exceeds $[a]$ by factors of 10–1000; the same is true for DMS. Hence Φ can be estimated without significant bias using values of $[e]$ alone. Using the work of Liss and Merlivat [1986] and Roether [1986], the proportionality constant W (transfer velocity) can be calculated from the wind speed [see, e.g., Donahue

Table 6a. Correlations of Measured NMHC With Surface Water Chlorophyll *a*, Transfer Velocity, and Temperature Within STCZ, SA/SAF, and P/PF Surface Waters Sampled During Leg 2

	Chlorophyll <i>a</i>			Transfer Velocity			Temperature		
	n	ρ	P	n	ρ	P	n	ρ	P
STCZ									
Propane	47	0.015	0.4595	48	0.019	0.4482	51	-0.003	0.4915
2-Methylpropane	47	0.019	0.4487	48	-0.065	0.3279	50	-0.132	0.1777
Butane	47	0.102	0.2445	48	-0.215	0.0702	51	-0.283	(0.0227)
2-Methylpropene	47	0.279	(0.0292)	48	0.048	0.3711	51	-0.301	(0.0167)
cis-2-Butene	47	0.119	0.2098	48	-0.170	0.1219	51	-0.313	(0.0134)
Cyclopentane	47	0.024	0.4353	48	-0.206	0.0789	51	-0.289	(0.0205)
2-Methylbutene	47	0.065	0.3297	48	-0.229	0.0582	51	-0.320	(0.0118)
Pentane	47	0.016	0.4568	48	-0.240	(0.0499)	51	-0.275	(0.0259)
1,3-Butadiene	27	-0.133	0.2488	28	0.346	(0.0361)	31	-0.109	0.2752
SA/SAF									
Propane	106	0.054	0.2900	107	-0.020	0.4184	122	0.063	0.2442
2-Methylpropane	110	-0.108	0.1298	110	-0.096	0.1581	125	-0.203	(0.0119)
Butane	110	-0.089	0.1764	110	-0.128	0.0907	125	-0.356	(<0.0001)
2-Methylpropene	110	0.365	(0.0001)	110	0.117	0.1109	125	-0.380	(<0.0001)
cis-2-Butene	109	0.038	0.3465	109	-0.054	0.2873	124	-0.465	(<0.0001)
Cyclopentane	109	-0.040	0.3388	109	-0.068	0.2399	125	-0.372	(<0.0001)
2-Methylbutene	110	-0.001	0.4958	110	-0.109	0.1276	125	-0.372	(<0.0001)
Pentane	110	-0.146	0.0637	110	-0.198	(0.0194)	125	-0.272	(0.0012)
1,3-Butadiene	74	0.074	0.2636	74	0.139	0.1175	85	0.251	(0.0107)
P/PF									
Propane	20	0.581	(0.0057)	22	-0.478	(0.0142)	20	-0.770	(0.0004)
2-Methylpropane	20	0.382	(0.0479)	22	-0.372	0.0441	20	-0.612	(0.0038)
Butane	21	0.185	0.2040	22	-0.221	0.1556	21	-0.275	0.1094
2-Methylpropene	18	0.180	0.2290	20	-0.197	0.1953	18	-0.407	(0.0467)
cis-2-Butene	19	0.222	0.1731	21	-0.223	0.1593	19	-0.458	(0.0260)
Cyclopentane	17	0.209	0.2016	19	-0.174	0.2302	17	-0.419	(0.0469)
2-Methylbutene	19	0.230	0.1646	21	-0.210	0.1738	19	-0.457	(0.0263)
Pentane	20	0.219	0.1699	22	-0.186	0.1970	20	-0.425	(0.0320)
1,3-Butadiene		too few data			too few data			too few data	

For each compound, n = number of data pairs available for calculation, ρ = value of Spearman's rank correlation statistic, and P = significance level for statistic (probability of erring by rejecting a null hypothesis of no correlation). Correlations significant at the P < 0.05 level are in parentheses.

and Prinn, 1993]. Using the above sea-air flux formula and H values from Table 1, we thus computed the fluxes of NMHC and DMS throughout the cruise and the results are shown in Figure 10. The calculated W values are also shown in Figure 10. Standard errors in W and H are large and lead to uncertainties in calculated fluxes of 50–100% [Donahue and Prinn, 1993]. Our instrumental uncertainties would add significantly to the overall uncertainty only for 1,3-butadiene (see Table 4). The large variations in X_a (Figure 4 and Table 4) and W (Figure 10) are reflected in the factor of 100–1000 variations in calculated fluxes.

3.5. Estimated Concentrations of NMHC in Surface Air and the Impact of NMHC and DMS on the OH Budget

The concentrations of NMHC in the atmospheric boundary layer can be estimated from our calculated sea-to-air fluxes, rates of reactions with OH, ozone, and chlorine atoms (see Table 1), and atmospheric transport. The dominant initial step in the oxidation of most NMHC is attack by OH that is formed locally from reaction of water vapor with $O(^1D)$ or HO_2 with nitric oxide. The tropospheric ozone precursor to $O(^1D)$ in clean MBL air could come from transport from regions of higher ozone mixing ratio or be formed locally through the oxidation of CO and NMHC in the presence of sufficient NO_x . If the ratio of the concentration of NO to O_3 is lower than a critical value (about 2×10^{-4}), the chemistry results in destruction rather than production of tropospheric ozone

([Levy, 1971; Finlayson-Pitts and Pitts, 1986]). For unsaturated NMHC, attack by O_3 can also be significant but still secondary to attack by OH ((see Table 1)). The role of Cl atoms is also likely to be minor in view of its low estimated concentrations during ACE-1 ([Wingenter et al., this issue]).

By combining the sea-to-air fluxes calculated in the preceding section with estimates of the height ($h = 1.5$ km)) of the mixing layer and of OH concentrations ($[OH]$) in the MBL, we can estimate upper limits for the molmolec fractions ($[X_a]$) of short-lived NMHC in the MBL. We achieve this by equating Φ to the NMHC column destruction rate due to OH:

$$\Phi = \int_0^h k[OH][X_a] dz \approx k[OH][M]hX_a$$

where $[M]$ is the total molecular density, z is altitude, and the overbars denote altitude averages. Estimates of $X_a = \Phi / (k[OH]h[M])$ so obtained are illustrated in Figures 4a and 4b for two compounds. We assumed $[OH]$ equivalent to estimated diurnal average $[OH] = 6.1 \times 10^5 \text{ cm}^{-3}$ for the MBL [Wingenter et al., this issue] which are consistent with OH measurements made during ACE 1 [Mauldin et al., 1998]. Slightly lower X_a values would result if reactions with Cl and O_3 given in Table 1 were to be considered. These estimates are generally consistent with atmospheric NMHC measurements obtained from aircraft during the ACE 1 intensive period [Blake et al., 1996] as

Table 6b. Correlations of Measured NMHC With Surface Water Nitrate and Dimethylsulfide and With Solar Radiation Intensity Within STCZ, SA/SAF, and P/PF Surface Waters Sampled During Leg 2

	Nitrate			Dimethylsulfide			Solar Radiation		
	n	ρ	P	n	ρ	P	n	ρ	P
STCZ									
Propane	52	-0.172	0.1097	55	0.124	0.1811	55	0.389	(0.0021)
2-Methylpropane	51	0.049	0.3645	54	-0.194	0.0789	54	0.234	(0.0442)
Butane	52	0.141	0.1570	55	-0.278	(0.0205)	55	0.055	0.3430
2-Methylpropene	52	0.020	0.4432	55	-0.024	0.4300	55	0.120	0.1889
cis-2-Butene	52	0.155	0.1342	55	-0.323	(0.0088)	55	-0.003	0.4912
Cyclopentane	52	0.222	0.0564	55	-0.095	0.2426	55	-0.001	0.4971
2-Methylbutene	52	0.197	0.0797	55	-0.205	0.0660	55	-0.010	0.4707
Pentane	52	0.236	(0.0460)	55	-0.123	0.1830	55	0.021	0.4387
1,3-Butadiene	32	0.172	0.1691	34	-0.196	0.1301	34	0.323	(0.0318)
SA/SAF									
Propane	112	-0.047	0.3102	131	-0.068	0.2191	130	0.116	0.0938
2-Methylpropane	115	0.163	(0.0409)	135	-0.123	0.0772	134	0.124	0.0764
Butane	115	0.217	(0.0103)	135	-0.156	(0.0355)	134	0.094	0.1392
2-Methylpropene	115	0.194	(0.0192)	135	-0.286	(0.0005)	134	0.096	0.1341
cis-2-Butene	115	0.241	(0.0050)	134	-0.236	(0.0032)	133	0.079	0.1820
Cyclopentane	114	0.228	(0.0077)	134	-0.065	0.2267	133	0.076	0.1913
2-Methylbutene	115	0.237	(0.0057)	135	-0.161	(0.0312)	134	0.072	0.2032
Pentane	115	0.261	(0.0027)	135	-0.119	0.0842	134	0.019	0.4133
1,3-Butadiene	76	-0.559	(<0.0001)	90	0.000	0.5000	90	0.350	(0.0005)
P/PF									
Propane	23	0.538	(0.0058)	23	0.427	(0.0226)	23	0.156	0.2322
2-Methylpropane	23	0.477	(0.0126)	23	0.084	0.3468	23	0.025	0.4533
Butane	24	0.246	0.1190	24	0.035	0.4333	24	-0.006	0.4885
2-Methylpropene	21	0.256	0.1261	21	0.188	0.2002	21	0.105	0.3193
cis-2-Butene	22	0.394	(0.0355)	22	0.009	0.4836	22	0.028	0.4490
Cyclopentane	20	0.352	0.0625	20	0.030	0.4480	20	0.000	0.5000
2-Methylbutene	22	0.380	(0.0408)	22	0.009	0.4836	22	-0.006	0.4890
Pentane	23	0.355	(0.0479)	23	0.063	0.3838	23	-0.022	0.4589
1,3-Butadiene		too few data			too few data			too few data	

For each compound, n = number of data pairs available for calculation, ρ = value of Spearman's rank correlation statistic, and P = significance level for statistic (probability of erring by rejecting a null hypothesis of no correlation). Correlations significant at the $P < 0.05$ level are in parentheses.

shown in Table 7. DMS mole fractions estimated similarly are also consistent with the measured values of *De Bruyn et al.* [1998].

In order to put the quantitative impact of the measured NMHC species on the oxidative capacity of the MBL in perspective we calculated the ratio of the combined OH loss frequency due to all nine compounds to the OH loss frequency due to reaction with atmospheric CO measured during ACE 1 [*Kok et al.*, 1998]. The resulting OH loss due to the nine measured NMHC was highly variable but only occasionally exceeded 1% of the OH removal due to reaction with CO (see Figure 11, solid symbols). This is consistent with the results of *Donahue and Prinn* [1993] who estimated that the removal rate of OH due to C_2 through C_5 NMHC accounted for approximately 10% of OH removal in the equatorial Pacific MBL during SAGA 3. We also estimated the fractional OH loss frequency by reaction with DMS using DMS concentrations in air measured by *De Bruyn et al.* [1998] (see Figure 11, open symbols). This loss frequency is also highly variable, rarely exceeding 5% of that due to reaction with CO.

4. Summary

We have reported here the mole fractions of nine reactive NMHC measured in real time in air equilibrated with seawater aboard NOAA Ship *Discoverer* as a part of ACE 1 in November–December 1995. Concentrations of these NMHC in ocean

water were deduced from these measurements and generally lay within the ranges observed by other investigators in other parts of the world ocean and at other times. Concentrations generally decreased with increasing latitude. Comparison with a limited number (n=8) of DOC data obtained during transit from Hawaii

Table 7. Comparison Between Estimated (MIT) and Measured (UCI, [*Blake et al.*, 1998]) NMHC Mixing Ratios in Surface Air <100 m Above the Ocean Surface During the ACE 1 Intensive Period

	Propane		2-Methylpropane		Butane	
	MIT	UCI	MIT	UCI	MIT	UCI
N	275	209	297	209	290	209
Minimum	0.0046	3	0.0087	<3	0.0025	<3
25th Percentile	1.3		0.94		0.55	
Median	3		2.5		1.6	
75th Percentile	6		5.7		4.1	
Maximum	55	23	80	5	67	8
Mean	5		5.5		3.7	
Standard Deviation	7.1		18		3.7	
R.S.D., %	110	140	110	110	120	97

Units are pptv except for number of measurements (N) and relative standard deviation (R.S.D.) (%).

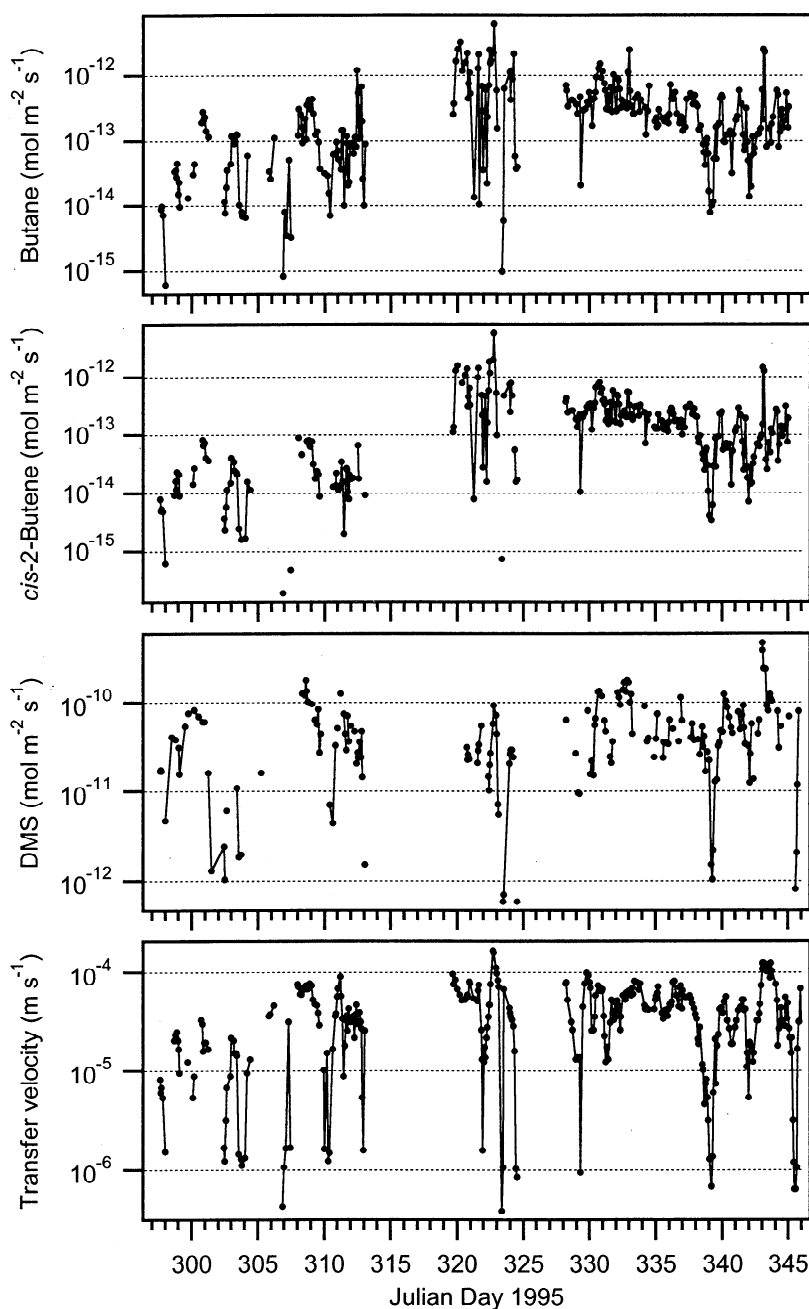


Figure 10. Sea-to-air fluxes calculated from the measured equilibrator headspace concentrations and wind speeds during the cruise for a representative alkane (butane), a representative alkene (*cis*-2-butene), and DMS. Also shown is the transfer velocity W computed from measured wind speeds (see text).

to Tasmania suggested that higher NMHC concentrations were associated with higher DOC levels. During the ACE 1 intensive study period west and south of Tasmania the differences in NMHC concentrations among water masses, while frequently significant, were not related in a simple direct or inverse way to any of the six ancillary physical and chemical variables. The only correlations that showed some consistency during the entire leg were with T and nitrate, an essential nutrient for phytoplankton growth.

Combining our seawater measurements with wind speed measurements to calculate transfer velocities, we also deduced sea-to-air fluxes for these NMHC. These results, indicating modest open-ocean emissions of nine C_3 - C_5 NMHC in this part of the

global ocean, imply that these hydrocarbons play a negligible role in MBL atmospheric chemistry compared to CO and a small role compared to DMS and the C_2 - C_3 hydrocarbons that we were not able to measure during this cruise (i.e., ethane, ethene, and propene). The need remains to determine fluxes of other C_2 - C_3 hydrocarbons and some C_4 and C_5 alkenes, notably isoprene, through measurements in this and other regions of the world ocean [Donahue and Prinn, 1990; Thompson *et al.*, 1993]. Accurate simultaneous atmospheric measurements are needed to check on the consistency of these fluxes with calculated atmospheric destruction rates. There is also a need to understand better the processes that produce observed NMHC distributions in the water column and their geographic variability.

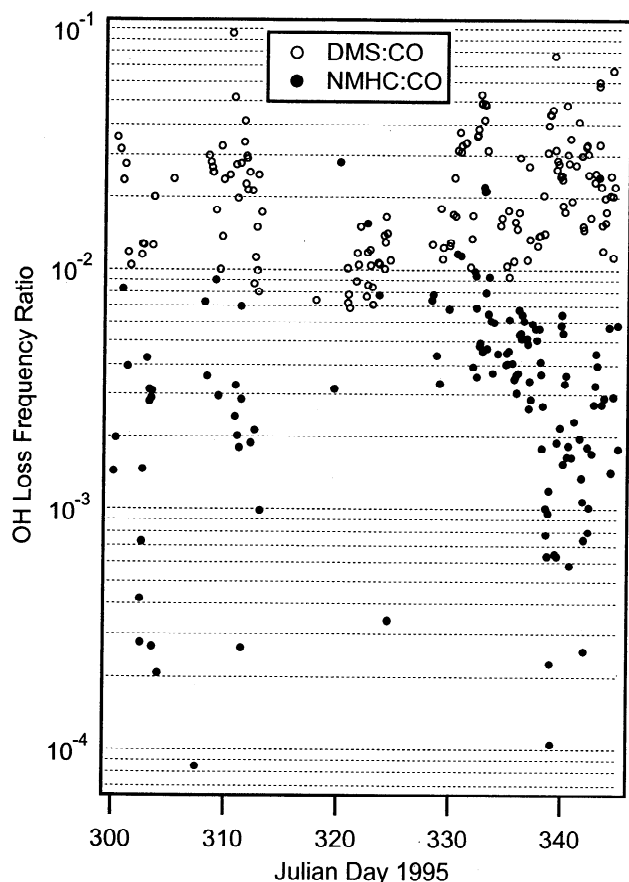


Figure 11. OH loss frequency due to the nine measured NMHC combined (solid symbols) and DMS (open symbols) relative to OH loss frequency by reaction with CO in surface air during ACE 1.

Acknowledgments. We thank A. Deshpande (MIT) for assisting with data reduction; P. Quinn, J. Johnson, V. Kapustin, D. Hamilton, and the staff of NOAA/PMEL, who offered indispensable help during the ACE 1 cruise; Captain S. Manzo and the crew of the NOAA Ship *Discoverer* for a safe and enjoyable voyage; D. Riemer of the University of Miami for providing and allowing use of his alkene data prior to publication; N. Donahue of Harvard University and N. Blake of the University of California at Irvine for helpful discussions; several reviewers for very constructive criticism; and L. Kubrick for assistance with manuscript preparation. This research is a contribution to the International Global Atmospheric Chemistry (IGAC) Core Project of the International Geosphere-Biosphere Programme (IGBP) and is part of the IGAC Aerosol Characterization Experiments (ACE). Our research was funded by NSF through grants ATM 92-16340 and ATM 96-10145 to MIT.

References

- Apel, E., J. Calvert, and F. Fehsenfeld, The Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Tasks 1 and 2, *J. Geophys. Res.*, **99**, 16,651–16,664, 1994.
- Atkinson, R., Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds, *J. Phys. Chem. Ref. Data Monogr.*, **1**, 268 pp., 1989.
- Atkinson, R., and W. Carter, Kinetics and mechanisms of the gas phase reactions of ozone with organic compounds under atmospheric conditions, *Chem. Rev.*, **83**, 437–470, 1984.
- Atlas, E., W. Pollock, J. Greenberg, and L. Heidt, Alkyl nitrates, nonmethane hydrocarbons, and halocarbon gases over the equatorial Pacific Ocean during SAGA 3, *J. Geophys. Res.*, **98**, 16,933–16,947, 1993.
- Bates, T.S., et al., Processes controlling the distribution of aerosol particles in the lower marine boundary layer during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, **103**, 16,369–16,383, 1998a.
- Bates, T.S., B.J. Huebert, J.L. Gras, F.B. Griffiths, and P.A. Durkee, International Global Atmospheric Chemistry [IGAC] Project's First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, **103**, 16,297–16,318, 1998b.
- Blake, N., O. Wingenter, D. Blake, and S. Rowland, Aircraft measurements of the latitudinal and seasonal variations of NMHC during ACE 1, *Eos Trans. AGU*, **77**(46), Fall Meet. Suppl., F75, 1996.
- Bonsang, B., and G. Lambert, Nonmethane hydrocarbons in an oceanic atmosphere, *J. Atmos. Chem.*, **2**, 257–271, 1985.
- Bonsang, B., M. Kanakidou, G. Lambert, and P. Monfray, The marine source of C₂–C₆ aliphatic hydrocarbons, *J. Atmos. Chem.*, **6**, 3–20, 1988.
- Bonsang, B., M. Kanakidou, and G. Lambert, Sur la faible variabilité de composition relative des hydrocarbures légers non méthaniques dissous dans l'eau de mer superficielle, *C. R. Acad. Sci. Paris, Série II*, **308**, 495–500, 1989.
- Bonsang, B., C. Polle, and G. Lambert, Evidence for marine production of isoprene, *Geophys. Res. Lett.*, **19**, 1129–1132, 1992.
- Brooks, J.M., and W.M. Sackett, Sources, sinks, and concentrations of light hydrocarbons in the Gulf of Mexico, *J. Geophys. Res.*, **78**, 5248–5258, 1973.
- Brooks, J.M., A.D. Fredericks, and W.M. Sackett, Baseline concentrations of light hydrocarbons in Gulf of Mexico, *Environ. Sci. Technol.*, **7**, 639–642, 1973.
- Butler, J.H., J.W. Elkins, and A.M. Thompson, Tropospheric and dissolved N₂O of the West Pacific and East Indian Oceans during the El Niño Southern Oscillation Event of 1987, *J. Geophys. Res.*, **94**, 14865–14877, 1989.
- Dacey, J.W.H., S.G. Wakeham, and B.L. Howes, Henry's law constants for dimethylsulfide in freshwater and seawater, *Geophys. Res. Lett.*, **11**, 991–994, 1984.
- De Bruyn, W.J., T.S. Bates, J.M. Caine, and E.S. Saltzman, Shipboard measurements of dimethyl sulfide and SO₂ southwest of Tasmania during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, **103**, 16,703–16,712, 1998.
- Donahue, N.M., Nonmethane hydrocarbon chemistry in the remote marine atmosphere, Ph.D. thesis, 128 pp., MIT Cent. for Global Change Sci., Cambridge, Mass., 1991.
- Donahue, N.M., and R.G. Prinn, Nonmethane hydrocarbon chemistry in the remote marine boundary layer, *J. Geophys. Res.*, **95**, 18,387–18,411, 1990.
- Donahue, N.M., and R.G. Prinn, In situ nonmethane hydrocarbon measurements on SAGA 3, *J. Geophys. Res.*, **98**, 16,915–16,932, 1993.
- Finlayson-Pitts, B.J., and J.N. Pitts Jr., *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, John Wiley, New York, 1986.
- Greenberg, J.P., and P.R. Zimmerman, Nonmethane hydrocarbons in remote tropical, continental and marine atmospheres, *J. Geophys. Res.*, **89**, 4767–4778, 1984.
- Griffiths, F.B., T.S. Bates, P.K. Quinn, L.A. Clementson, and J.S. Parslow, Oceanographic context of the First Aerosol Characterization Experiment (ACE 1): A physical, chemical, and biological overview, *J. Geophys. Res.*, this issue.
- Hainsworth, A.H.W., A.L. Dick, and J.L. Gras, Climatological context of the First Aerosol Characterization Experiment (ACE 1): A meteorological and chemical overview, *J. Geophys. Res.*, **103**, 16,319–16,340, 1998.
- Jones, G.B., M.A.J. Curran, H.B. Swan, R.M. Greene, F.B. Griffiths, and L.A. Clementson, Influence of different water masses and biological activity on dimethylsulphide and dimethylsulphoniopropionate in the subantarctic zone of the Southern Ocean during ACE 1, *J. Geophys. Res.*, **103**, 16,691–16,702, 1998.
- Kok, G.L., A.S.H. Prévôt, R.D. Schillawski, and J.E. Johnson, Carbon monoxide measurements from 76°N to 59°S and over the South Tasman Sea, *J. Geophys. Res.*, **103**, 16,731–16,736, 1998.
- Lamontagne, R.A., J.W. Swinnerton, and V.J. Linnebon, C₁–C₄ hydrocarbons in the North and South Pacific, *Tellus*, **26**, 71–77, 1974.
- Lamontagne, R.A., W.D. Smith, and J.W. Swinnerton, C₁–C₃ hydrocarbons and chlorophyll *a* concentrations in the equatorial Pacific Ocean, in *Analytical Methods in Oceanography*, *Adv. Chem. Ser.*, vol. 147, edited by T.R.P. Gibb Jr., pp. 163–171, Am. Chem. Soc., Washington, D. C., 1975.
- Lee, R.F., and J. Baker, Ethylene and ethane production in an estuarine river: Formation from the decomposition of polyunsaturated fatty acids, *Mar. Chem.*, **38**, 25–36, 1992.

- Levy, H., II, Normal atmosphere: Large radicals and formaldehyde concentrations predicted, *Science*, 173, 141-143, 1971.
- Liss, P.S., and L. Merlivat, Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, pp. 113-127, D. Reidel, Norwell, Mass., 1986.
- Liss, P.S., and P.G. Slater, Flux of gases across the air-sea interface, *Nature*, 247, 181-184, 1974.
- Liu, S.C., S. McKeen, and M. Trainer, Impacts of biogenic nonmethane hydrocarbons on the troposphere, in *Our Changing Atmosphere*, Proceedings of 28th Liege International Astrophysical Colloquium, Liege, Belgium, June 26-30, edited by P. Crutzen, K.C. Gerard, and R. Vander, pp. 419-431, Eur. Geophys. Union, Université de Liège, 1989.
- Macdonald, R.W., Distribution of low-molecular-weight hydrocarbons in southern Beaufort Sea, *Environ. Sci. Technol.*, 10, 1241-1246, 1976.
- MacKay, D., and W.Y. Shiu, Critical review of Henry's law constants for chemicals of environmental interest, *J. Phys. Chem. Ref. Data*, 10, 1175-1199, 1981.
- Mauldin, R.L., III, G.J. Frost, G. Chen, D.J. Tanner, A.S.H. Prévôt, D.D. Davis, and F.L. Eisele, OH measurements during the First Aerosol Characterization Experiment (ACE 1): Observations and model comparisons, *J. Geophys. Res.*, 103, 16,713-16,730, 1998.
- McKay, W.A., M.F. Turner, B.M.R. Jones, and C.M. Halliwell, Emissions of hydrocarbons from marine phytoplankton—Some results from controlled laboratory experiments, *Atmos. Environ.*, 30, 2583-2593, 1996.
- Milne, P.J., D.D. Riemer, R.G. Zika, and L.E. Brand, Measurement of vertical distribution of isoprene in surface seawater, its chemical fate, and its emission from several phytoplankton monocultures, *Mar. Chem.*, 48, 237-244, 1995.
- Parsons, T.R., Y. Maita, and C.M. Lalli, *A Manual of Chemical and Biological Methods for Seawater Analysis*, Pergamon, Tarrytown, N. Y., 1984.
- Plass, C., R. Koppmann, and J. Rudolph, Light hydrocarbons in the surface water of the mid-Atlantic, *J. Atmos. Chem.*, 15, 235-251, 1992.
- Plass-Dülmer, C., A. Khedim, R. Koppmann, F.J. Johnen, and J. Rudolph, Emissions of light nonmethane hydrocarbons from the Atlantic into the atmosphere, *Global Biogeochem. Cycles*, 7, 211-228, 1993.
- Plass-Dülmer, C., R. Koppmann, M. Ratte, and J. Rudolph, Light nonmethane hydrocarbons in seawater, *Global Biogeochem. Cycles*, 9, 79-100, 1995.
- Ratte, M., C. Plass-Dülmer, R. Koppmann, and J. Rudolph, Horizontal and vertical profiles of light hydrocarbons in sea water related to biological, chemical, and physical parameters, *Tellus, Ser. B*, 47, 607-623, 1995.
- Riemer, D., W. Pos, and R. Zika, Photochemical production of NMHC in seawater: A process involving DOM, *Eos Trans. AGU*, 77(46), Fall Meet. Suppl., F256, 1996.
- Roether, W., Field measurements of gas exchange, in *Dynamic Processes in the Chemistry of the Upper Ocean*, edited by J.D. Burton, P.G. Brewer, and R. Chesselet, pp. 117-128, Plenum, New York, 1986.
- Rudolph, J., and D.H. Ehhalt, Measurements of C₂-C₃ hydrocarbons over the North Atlantic, *J. Geophys. Res.*, 86, 11,959-11,964, 1981.
- Singh, H.B., and L.J. Salas, Measurement of selected light hydrocarbons over the Pacific Ocean: Latitudinal and seasonal variations, *Geophys. Res. Lett.*, 9, 842-845, 1982.
- Singh, H.B., and P.R. Zimmerman, Atmospheric distribution and sources of nonmethane hydrocarbons, in *Gaseous Pollutants: Characterization and Cycling*, edited by J.O. Nriagu, pp. 177-235, John Wiley, New York, 1992.
- Stickel, R.E., J.M. Nicovich, S. Wang, Z. Zhao, and P.H. Wine, Kinetic and mechanistic study of the reaction of atomic chlorine with dimethyl sulfide, *J. Phys. Chem.*, 96, 9875-9883, 1992.
- Swinnerton, J.W., and R.A. Lamontagne, The oceanic distribution of low molecular weight hydrocarbons, *Environ. Sci. Technol.*, 8, 657-663, 1974.
- Thompson, A.M., et al., Ozone observations and a model of marine boundary layer photochemistry during SAGA 3, *J. Geophys. Res.*, 98, 16,955-16,968, 1993.
- Wilson, D.F., J.W. Swinnerton, and R.A. Lamontagne, Production of carbon monoxide and gaseous hydrocarbons in seawater: Relation to dissolved organic carbon, *Science*, 168, 1577-1579, 1970.
- Wingenter, O.W., D.R. Blake, N.J. Blake, B.C. Sive, and F.S. Rowland, Tropospheric hydroxyl and atomic chlorine concentrations, and mixing timescales determined from hydrocarbon and halocarbon measurements made over the Southern Ocean, *J. Geophys. Res.*, this issue.
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(Received September 29, 1998; revised February 11, 1999; accepted February 15, 1999.)