

Light nonmethane hydrocarbons in seawater

C. Plass-Dülmer, R. Koppmann, M. Ratte, and J. Rudolph

Institut für Atmosphärische Chemie, Forschungszentrum Jülich, Jülich, Germany

Abstract. A database of dissolved C_2 - C_4 hydrocarbons in the surface water of the oceans is compiled based on more than 1000 measurements. Hydrocarbon emission rates are calculated using a diffusive microlayer approach and climatologic wind data. This database is used to calculate averages and ranges of variation, and an attempt is made to identify the environmental factors which have an impact on the hydrocarbons dissolved in seawater. The paper focuses on data obtained in situ since other techniques generally contain larger uncertainties. Mean concentrations are 134 pmol/L for ethene, 59 pmol/L for propene, and 37 pmol/L for 1-butene. Alkane concentrations are lower with an average value of 22 pmol/L for ethane and less than 14 pmol/L for the other alkanes and acetylene. Ninety percent of the concentrations of an individual compound generally ranges within an order of magnitude. Ethene concentrations are significantly anticorrelated with the transfer velocities of the sea-air exchange ($r = -0.49$; $r_{0.01} = 0.29$). Ethene concentrations are not correlated with the solar radiation, chlorophyll *a*, and the water temperature. Averaged emissions of C_2 - C_4 hydrocarbons extrapolated to the global ocean of 2.1×10^{12} g/yr are calculated, with ethene alone contributing about 40% to the total. Thus the oceanic source is on the low side of previous estimates and plays a minor role in global budgets compared to continental sources.

1. Introduction

Ocean emissions of light nonmethane hydrocarbons (NMHC) are important for both their impact on marine atmospheric chemistry and their contribution to global NMHC budgets. Owing to the large area of the oceans, even small fluxes of NMHC per unit area could result in large global oceanic emissions. Rudolph and Ehhalt [1981] concluded that the oceans are supersaturated with light NMHC and estimated that NMHC can have similar turnover rates as methane in the marine atmosphere. However, their estimates were based only on measurements in the atmosphere and the NMHC concentrations in seawater published by Swinnerton and Lamontagne [1974]. Thus they were not able to compare atmospheric observations with actual oceanic emissions. The first simultaneous measurements of NMHC in the atmosphere and in the ocean were published by Bonsang *et al.* [1988]. They measured NMHC concentrations in the surface water of the Indian Ocean which were considerably higher than the concentrations observed by Swinnerton and Lamontagne [1974]. Also, they observed unusually high atmospheric NMHC levels, but they did not give a budget comparing atmospheric removal with oceanic sources. The oceanic emission estimated by Bonsang *et al.* [1988] indicated that on a global scale the oceans might be a substantial source for atmospheric NMHC. Different results were found by other groups who made comparable studies in other ocean areas [Plass *et al.*, 1992; Plass-Dülmer *et al.*, 1993; Donahue and Prinn, 1993]. The most common approach for

calculating oceanic emissions utilizes the measured seawater concentrations of NMHC and transfer rates derived from ocean-atmosphere exchange models. Such estimates are lower than oceanic emissions by Bonsang *et al.* [1988]; however, they can differ by an order of magnitude [Plass-Dülmer *et al.*, 1993] mainly due to differences between the chosen data sets of dissolved hydrocarbons.

Light hydrocarbons dissolved in seawater have been measured during the past 25 years in more than 1000 samples. In the early measurements the major interest focused on oil exploration and oil pollution. Brooks and Sackett [1973], Brooks *et al.* [1973], and Frank *et al.* [1970] showed drastic increases of saturated hydrocarbons in the proximity of natural oil seeps and anthropogenic sources of oil pollution. In order to assess the extent of the oil pollution in the marine environment, Swinnerton and Lamontagne [1974] proposed baseline concentrations of C_1 - C_4 hydrocarbons estimated from all available open ocean data. These were used to set up a criterion in order to differentiate between open ocean clean water and water contaminated by hydrocarbons. Yet, the parameters which determine the concentrations of dissolved NMHC in the world's oceans are still not identified. Swinnerton and Lamontagne [1974] summed up the current understanding in some general observations: (1) The concentrations seem to be consistent from area to area. (2) The concentrations peak in the upper 0-150 m. (3) In this layer the olefins are generally more abundant than their saturated homologs. They attributed the peak concentrations to processes occurring faster than physical mixing, most probably correlated with the primary productivity. However, in anoxic waters they observed different vertical structures and concluded that the production processes in anoxic and oxygenated waters are different.

Copyright 1995 by the American Geophysical Union.

Paper number 94GB02416.
0886-6236/95/94GB-02416\$10.00

Table 1. Experimental Techniques Used in the Measurement of Oceanic C₂-C₄ Hydrocarbons

Technique described by				
Technique used by	Technique described by			
	<i>Swinerton and Linneboim</i> [1967a,b]	<i>Macdonald</i> [1976]	<i>Bonsang et al.</i> [1988]	<i>Donahue and Prinn</i> [1993]
	<i>Plass et al.</i> [1991]			
	<i>Plass et al.</i> [1992]			
	<i>Plass-Dümler et al.</i> [1993]			
	<i>Ratte et al.</i> [1993]			
	<i>Ratte</i> [1993]			
Routine sampling	continuous	stainless steel bucket	stainless steel cylinder or bucket	continuous ^a
Other samplers	Nansen, Niskin	Niskin, Blumer		continuous stainless steel bucket sampler
Sampling depth, routine, m	5		surface	11
Range, m	0 - 1300	0 - 400		0 - 100
Time of analysis	immediate ^b	immediate aboard	some months laboratory	immediate aboard
Location of analysis	aboard		6 L canisters	
Storage of sample	-	-		-
Stripping chamber	all glass, coarse frit	all glass, coarse frit	stripping chamber ^c	all glass, coarse frit
Volume, L	1.2	?	2	1.5
Water sample, volume, L	1	0.95	1.5	0.87, 1.07
Purge gas	He	He	He	He
Flow rate, mL/min	50	50	100	100
Purge gas volume, L	1	2.5	6	3
Traps in gas line	drying tube	?	K ₂ CO ₃	stainless steel tube (i.d. 2 mm) at 273 K
Cryofocusing	activated alumina	activated alumina	Tenax GC ^e	porous glass beads
Focusing temperature, K	196	196	153	77
Desorption temperature, K	363	363	473	343
GC column	activated alumina + 10% Nujol	durapak phenyl isocyanate	Al ₂ O ₃ /KCl ^f	Porapak QS

Length, m	1.2	5.5	50	7
Diameter, mm	4.8 o.d.	3.2 o.d.	0.25 i.d.	2 i.d.
Det. limit, pmol/L	2	?2	0.05	2
Stripping efficiency, %	"complete stripping"	?	(response time 8 - 50 min ^f)	> 90 (acetylene 80)
Accuracy, %	≤10	4 - 7 (butane 34)	30 - 50	10 - 40

^a Donahue and Prinn [1993] used a continuous equilibration technique developed by R. Weiss (SIO) and described by Butler et al. [1989].

^b Swinnerton and Lamontagne [1974] mention that most of the hydrocarbon measurements were made aboard ship.

^c Stripping chamber described by Kanakidou [1988]. Additionally, Bonsang et al. [1991] report the use of a headspace equilibration technique, without giving details.

^d Volume of headspace gas used for analysis [Donahue and Prinn, 1993].

^e GC method according to Bonsang et al. [1987]; by Bonsang et al. [1988] a packed column (n-octane on Porasil, 4 m, 1.6 mm o.d.) was used according to Bonsang and Lamberet [1985].

^f Relaxation time theoretically calculated for the equilibrator [Donahue and Prinn, 1993].

From the point of view of atmospheric chemistry, the knowledge of NMHC concentrations in ocean water is of limited value as long as no simultaneous measurements of the sea-air exchange rates are reported. However, emission estimates can be based on exchange rates derived from climatological data and the concentrations of NMHC. This paper presents our recent results and makes use of the large number of measurements now available to provide an overview of NMHC concentrations in the world's oceans. This database is then used to discuss possible causes for variations, and an attempt is made to identify factors which have an impact on the NMHC concentrations in seawater. Finally, the database will be used for a global estimate of oceanic NMHC emissions.

2. Experimental Methods

All measurements of NMHC in seawater are more or less based on the method developed by Swinnerton and Linnenbom [1967a]. They achieved detection limits of 10^{-12} mol/L of seawater using a purge and trap technique combined with gas chromatography using a flame ionization detector (GC-FID). A short overview of the sampling methods, the handling and storage of the samples, and the analytical techniques used by the different authors is given in Table 1.

Generally, stripping chambers similar to the one described by Swinnerton and Linnenbom [1967a] have been used. They consist of a glass cylinder with a coarse glass frit at the lower end. The water sample is transferred into the cylinder, and the dissolved gases are purged out of the water with helium. Donahue and Prinn [1993] used an equilibrator (see Table 1) and took samples from the headspace. They had no opportunity to test the equilibrator before the cruise and therefore estimate the accuracy of the overall method conservatively at 30-50%. Bonsang and coworkers first used a stripping chamber [Bonsang et al., 1988]; later they reported that the water samples were outgassed with helium by a headspace equilibration technique [Bonsang et al., 1991]. However, no details are given in the latter case.

The purge gas with the extracted hydrocarbons is dried by different types of traps mounted in the gas line (Table 1). Then the dried gas samples are cryogenically focused on columns (Table 1). Donahue and Prinn [1993] additionally applied a CO₂ and ozone trap since they used the same experimental setup as for the measurement of ambient air. No contamination due to the traps was reported, except for small amounts of 2-methylpropene observed by Donahue and Prinn [1993] in blank runs.

Details of the chromatographic columns are given in Table 1. Generally, the relevant C₂-C₄ hydrocarbons were sufficiently separated. In the early measurements by Swinnerton and Linnenbom [1967a,b], Brooks and Sackett [1973], and Brooks et al. [1973], ethene and ethane were not separated. Macdonald [1976] did not report ethane concentrations for his measurements in 1974 due to adsorption problems during the cryogenic focusing. The reported accuracies of the measured NMHC concentrations in seawater are between 10 and 50% (references stated in Table 1).

A completely different technique (not mentioned in Table 1) was developed by Brooks and Sackett [1973] and Brooks et al. [1973]. Using this method, they were able to measure relative

concentrations in contaminated areas over short time intervals. They used a booster pump with restricted inflow which strips about 50% of the dissolved gases from the water [Brooks and Sackett, 1973]. The stripped gases were directly injected onto the column without a focusing step. Additionally, in open ocean areas they report having used the technique of Swinnerton and Linnenbom [1967a], but for their results they do not clearly identify the technique used.

In all the investigations discussed here the sampling of the water was done either by continuous water intake lines or with water samplers. Some investigators compared different sampling methods in order to rule out contamination caused by either of the methods. Lamontagne *et al.* [1974] used Niskin samplers and a ship intake line. Macdonald [1976] sampled with stainless steel buckets and used Niskin and Blumer samplers. Plass-Dümler *et al.* [1993] used a stainless steel bucket for surface samples and an intake line in 11 m depth. None of these authors reported significant differences in the measured hydrocarbon concentrations which could be ascribed to sampling artifacts.

Most of the measurements were done immediately after sampling, hereafter referred to as *in situ* methods. In their first investigations, Swinnerton and Linnenbom [1967a,b] stored the water samples in 1-L glass bottles closed with tapered ground-glass stoppers; details about the conditions of storage were not given. These samples were reported to be stable for intervals between 2 hours and 1 month. However, they also observed differences between *in situ* samples and samples taken to the laboratory (R.A. Lamontagne, personal communication, 1992). Macdonald [1976] reported an increase in hydrocarbon concentrations in glass bottles when kept in the laboratory for some hours; again, the conditions were not described. Ratte *et al.* [1993] found increasing concentrations in quartz bottles exposed to sunlight, whereas samples kept in the dark showed no significant change during the observation period of 8 days (sample bottles were kept in an open container on deck of the research ship at ambient seawater temperature (between 280 and 290 K) [Ratte *et al.*, 1993]). Plass-Dümler [1992] observed constant C₂-C₄ hydrocarbon concentrations in water samples stored in stainless steel cylinders (electropolished) at about 300 K for 4 days; only ethane concentrations were significantly enhanced in two of the eight samples. Thus hydrocarbon concentrations in seawater samples have been reported to be stable in glass bottles in the dark or in stainless steel cylinders for several days up to a few weeks.

Swinnerton and Linnenbom [1967b], Swinnerton *et al.* [1977], and Frank *et al.* [1970] reported the addition of chemicals to the water sample in order to retard bacterial action. While no effect on NMHC concentrations is reported for the addition of sodium azide to the samples, the addition of mercuric chloride changed ethene to ethane and propene to propane [Swinnerton and Linnenbom, 1967b]. Plass *et al.* [1991] used filters (glass fiber, pore size 0.8 mm and 1.2 mm) to prevent phytoplankton and particles from entering the stripping chamber. They observed no influence of the filtering procedure on the NMHC concentrations.

Bonsang *et al.* [1988, 1989, 1991] stripped the hydrocarbons from the water sample aboard the ship, but they stored the purge gas with the extracted hydrocarbons in 6-L stainless steel cylinders. The gas samples were analyzed subsequent to the cruise. Bonsang *et al.* [1988] reported having checked the

cylinders for storage stability. In atmospheric samples the alkane concentrations remained fairly constant, but the light alkene concentrations tended to increase. For most alkenes the increases were between 30 and 60% with a maximum of 250 parts per trillion (ppt) during periods of 9 and 40 days [Kanakidou, 1988].

3. Database

The global distribution of measurement sites for dissolved NMHC in surface seawater is shown in Figure 1. Only measurements from the upper 15 m are considered because in this case, vertical homogeneity can generally be assumed [Plass-Dümler *et al.*, 1993]. This upper layer controls the impact of the oceans on atmospheric chemistry since the emissions into the atmosphere are determined by the concentrations in this layer. About 1150 measurements have been published in this depth range.

For better clarity we arranged the available data into 44 data sets (Table 2). A data set consists of a minimum number of two measurements which were conducted in a single series by one investigator. Each data set is limited in time to a maximum of about 1 month and in space according to ocean regions or with a maximum extension of about 30° of latitude and longitude. Additionally, to data sets taken from the literature, we present recent data obtained in the Mediterranean Sea, North Sea, and Atlantic Ocean by Ratte [1993] (data sets 39-42 in Table 2).

The data sets are categorized according to different sample treatments (compare Table 2). We distinguish between data sets obtained by *in situ* measurements (*in situ*), chemicals added to the water sample (chemicals added), stripped hydrocarbons with purge gas stored in cylinders (cylinder), and data sets with no clear specification of the sample treatment (not specified). More than 70% of the data were obtained by *in situ* methods (compare Table 2). There are a few sample sets which cannot be unambiguously assigned to a category, as for the early measurements reported by Swinnerton and Lamontagne [1974] (data sets 1-17). It is only mentioned that most of the measurements were made aboard ship. For some of the data sets, additional information is available from further references. According to Lamontagne *et al.* [1974] data sets 12-16 were measured *in situ*. For data set 11, Swinnerton *et al.* [1977] mentioned the addition of sodium azide. Mercuric chloride has been added to samples collected by Brooks *et al.* [1973] which were analyzed by J.W. Swinnerton. These samples are probably those of data sets 9 and 10 for two reasons: First, Swinnerton and Lamontagne [1974] mention that these samples were taken in collaboration with J.E. Brooks, and second, the sampling times and locations agree.

In order to have a consistent database, results from GC-FLD systems which were not capable of separating alkenes and alkanes were rejected (data set 43 by Brooks and Sackett [1973]; data set 44 by Frank *et al.* [1970]; and the measurement numbers 11, 15, 16, 17, and 22 stated by Swinnerton and Lamontagne [1974]). Additionally, data obtained in rivers, lakes, near docksides, and on the ice shelf (results 18, 79, 133-143 stated by Swinnerton and Lamontagne [1974]) as well as a single measurement inside a lagoon [Bonsang *et al.*, 1989] are not included.

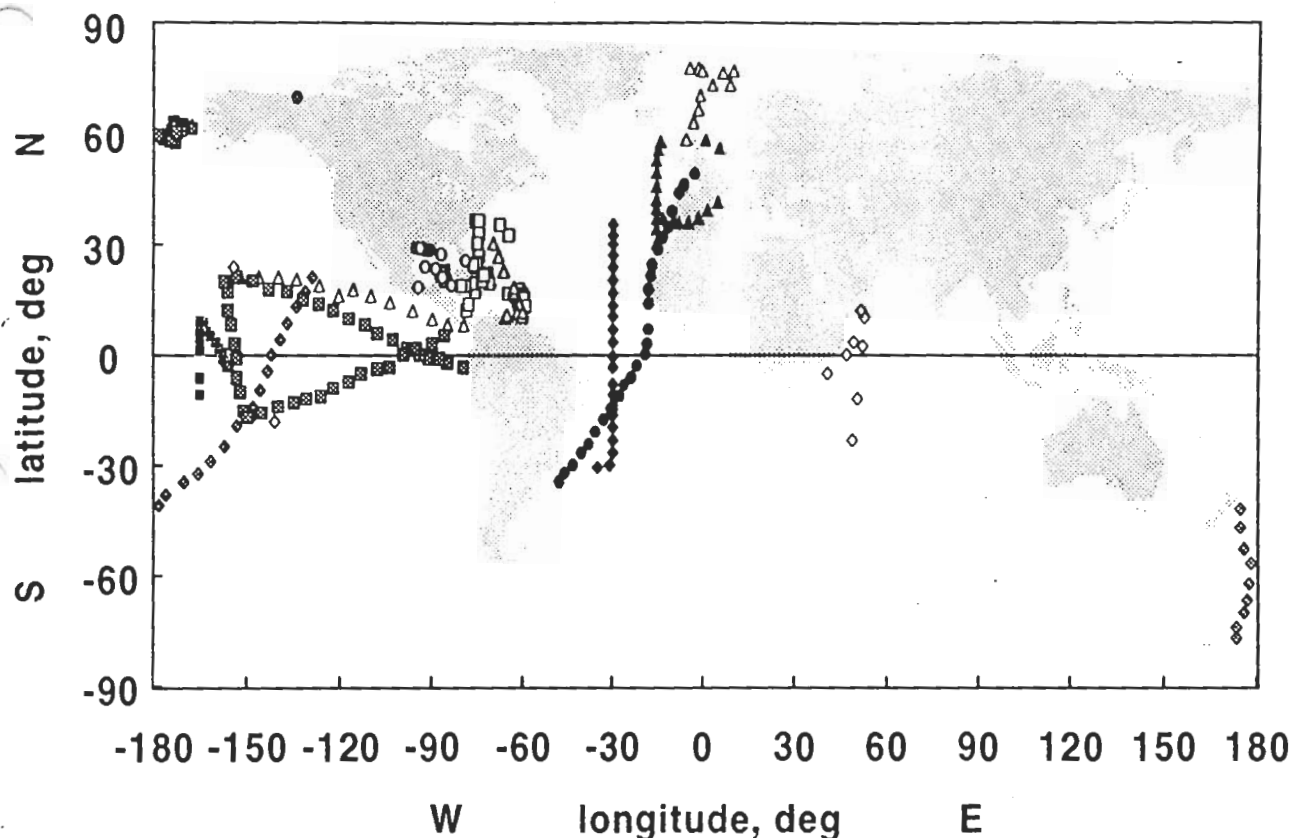


Figure 1. The global distribution of measurement sites of dissolved nonmethane hydrocarbons (NMHC). The symbols used, data sets, year of investigation, and reference(s) are as follows: in situ data: shaded diamonds, 12-16, 1972, and Swinnerton and Lamontagne [1974]; shaded squares, 18-24, 1974, 1977, and Lamontagne *et al.* [1975] and Lamontagne [1979]; shaded circles, 25-26, 1974-75, and Macdonald [1976]; solid diamonds, 31-33, 1988, and Plass *et al.* [1992]; solid circles, 34-37, 1989, and Plass-Dümler *et al.* [1993]; solid squares, 38, 1990, and Donahue and Prinn [1993] and N.M. Donahue (personal communication, 1991); solid triangles, 39-42, 1991, and Ratte [1993]. Other data: open squares, 1-4, 17, 1968-73, and Swinnerton and Lamontagne [1974]; open triangles, 5-8, 1971, and Swinnerton and Lamontagne [1974]; open circles, 9-11, 1971-72, and Swinnerton and Lamontagne [1974] and Swinnerton *et al.* [1977]; open diamonds, 27-30, 1985, 1987, and Bonsang *et al.* [1988, 1989].

4. Concentrations of C₂-C₄ Hydrocarbons in Surface Seawater²

In this section the data are presented with respect to the sample treatment as introduced in section 3. Seasonal and regional differences will be discussed in section 5.

4.1. Overview of Measured Concentrations

Table 3 summarizes the averages and the ranges of measured concentrations in the various data sets. In Table 4 the averages and ranges of in situ measurements are compared with non-in situ measurements. The in situ results are generally comparable to those of the not specified category, whereas concentrations from measurements of the other categories are larger by factors of 3-20. However, the number of measurements is substantially lower than in the in situ and not specified categories. The order of abundance for the various hydrocarbons is similar in all categories. For the in situ results, ethene concentrations are on

average the largest (134 pmol/L) followed by propene (59 pmol/L) and the sum of butenes (37 pmol/L). The alkane concentrations are of lower levels than the alkene concentrations with ethane (22 pmol/L) as the most abundant compound. Acetylene concentrations (14 pmol/L) make up about 5% of all C₂-C₄ hydrocarbons.

The latitudinal distributions of ethene and propene concentrations are shown in Figure 2. Ethene concentrations range over almost 3 orders of magnitude, 90% of the in situ data is between 42 pmol/L and 358 pmol/L (Table 3). No clear trend of concentrations with latitude exists. Propene concentrations depict a similar picture on a lower level. Figure 3 shows ethane and propane concentrations as function of latitude. The ranges of all observed concentrations again are about 3 orders of magnitude and 90% of the in situ data is found within the range of 1 order of magnitude (Table 4).

Figure 4 shows histograms of the ethene and ethane data on a logarithmic concentration scale. The in situ concentrations of

Table 2. Data Sets of Measured Hydrocarbon Concentrations in Surface Water

Data Set	Number of Samples	Date	Latitude	Longitude	Area ^a	Category ^b	Reference
1	7	June, 1968	22°-38°N	71°-77°W	C, n-A	?	<i>Swinnerton and Lamontagne [1974]</i>
2	18	April, 1969	10°-18°N	59°-65°W	C, n-A	?	<i>Swinnerton and Lamontagne [1974]</i>
3	3	Dec., 1969	32°-37°N	64°-75°W	C, n-A	?	<i>Swinnerton and Lamontagne [1974]</i>
4	5	May, 1970	12°-18°N	75°-79°W	C	?	<i>Swinnerton and Lamontagne [1974]</i>
5	53	May, 1971	10°-30°N	60°-70°W	C, n-A	?	<i>Swinnerton and Lamontagne [1974]</i>
6	30	May to June, 1971	8°-16°N	80°-110°W	e-P	?	<i>Swinnerton and Lamontagne [1974]</i>
7	36	June, 1971	16°-21°N	116°-152°W	n-P	?	<i>Swinnerton and Lamontagne [1974]</i>
8	95	Aug., 1971	58°-78°N	6°W-10°E	n-A	?	<i>Swinnerton and Lamontagne [1974]^{c,d}</i>
9	7	June, 1971	28°-29°N	92°-95°W	G	a	<i>Swinnerton and Lamontagne [1974]^e</i>
10	13	Oct., 1971	19°-29°N	84°-94°W	G	a	<i>Swinnerton and Lamontagne [1974]^e</i>
11	9	June, 1972	25°N	79°W	off Miami	a	<i>Swinnerton and Lamontagne [1974]^f</i>
12	10	Nov., 1972	13°-21°N	129°-134°W	n-P	i	<i>Swinnerton and Lamontagne [1974]^e</i>
13	26	Nov., 1972	9°S-9°N	137°-146°W	e-P	i	<i>Swinnerton and Lamontagne [1974]^e</i>
14	29	Nov. to Dec., 1972	14°S-35°S	148°-170°W	s-P	i	<i>Swinnerton and Lamontagne [1974]^e</i>
15	31	Dec., 1972	37°-57°S	175°-185°W	s-P	i	<i>Swinnerton and Lamontagne [1974]^e</i>
16	14	Dec., 1972	57°-77°S	183°-187°W	s-P	i	<i>Swinnerton and Lamontagne [1974]^e</i>
17	21	June to July, 1973	18°-25°N	70°-86°W	G, C, n-A	?	<i>Swinnerton and Lamontagne [1974]</i>
18	55	Feb. to March, 1974	3°S-10°N	80°-117°W	e-P	i	<i>Lamontagne et al. [1975]^e</i>
19	47	March, 1974	12°-21°N	122°-157°W	n-P	i	<i>Lamontagne et al. [1975]^e</i>
20	33	March, 1974	8°N-10°S	155°-152°W	e-P	i	<i>Lamontagne et al. [1975]^e</i>
21	43	March to April, 1974	11°-17°S	151°-126°W	s-P	i	<i>Lamontagne et al. [1975]^e</i>
22	64	April, 1974	9°S-5°N	122°-86°W	e-P	i	<i>Lamontagne et al. [1975]^e</i>
23	56	July to Aug., 1977	57°-63°N	173°-178°W	n-P	i	<i>Lamontagne [1979]</i>
24	40	July to Aug., 1977	60°-63°N	168°-173°W	n-P	i	<i>Lamontagne [1979]</i>
25	20	Aug., 1974	69°-71°N	130°-139°W	s-BS	i	<i>Macdonald [1976]</i>
26	32	Aug., 1975	69°-71°N	130°-139°W	s-BS	i	<i>Macdonald [1976]</i>
27	4	April, 1985	23°-0°S	40°-50°E	s and e-IO	c	<i>Bonsang et al. [1988]</i>
28	4	April, 1985	2°-12°N	49°-53°E	n and e-IO	c	<i>Bonsang et al. [1988]</i>
29	2	May, 1987	24°N	154°W	off Hawai	c	<i>Bonsang et al. [1989]</i>
30	3	June, 1987	18°S	141°W	off Hao	c	<i>Bonsang et al. [1989]</i>
31	22	Sept., 1988	8°-35°N	30°W	n-A	i	<i>Plass et al. [1992]^g</i>
32	14	Sept., 1988	3°S-8°N	30°W	e-A	i	<i>Plass et al. [1992]^g</i>
33	29	Sept. to Oct., 1988	4°S-30°S	30°-35°W	s-A	i	<i>Plass et al. [1992]^g</i>
34	21	Aug., 1989	44°-49°N	3°-8°W	BoB	i	<i>Plass-Dülmer et al. [1993]^g</i>
35	15	Aug., 1989	23°-38°N	10°-17°W	n-A	i	<i>Plass-Dülmer et al. [1993]^g</i>
36	30	Aug., 1989	0°-23°N	17°-19°W	n and e-A	i	<i>Plass-Dülmer et al. [1993]^g</i>
37	46	Aug. to Sept., 1989	0°-35°S	20°-48°W	s-A	i	<i>Plass-Dülmer et al. [1993]^g</i>
38	20	March, 1990	10°S-10°N	155°-167°W	e-P	i	<i>Donahue and Prinn [1993]^h</i>

ethene do not follow normal distribution (significance level <0.0001) but follow a lognormal distribution (median 109 pmol/L and a standard deviation of a factor of 1.9; significance level 0.043; n=838). Also, for the other categories of data, ethene concentrations follow lognormal distribution but the center of the distribution is shifted to 190 (not specified, standard deviation of factor 1.7), 372 (chemicals added, standard

deviation of factor 2.3), and 616 (cylinders, standard deviation of factor 2.3)(all concentrations in picomoles per liter). Ethane distributions are asymmetric and tailing toward higher concentrations. This is observed for all the data categories. The distribution of neither the in situ data nor not specified data fits a lognormal or a normal distribution, e.g., significance level <0.0001 for the in situ measurements (n=814). Both the ethene

Table 2. (continued)

Data Set	Number of Samples	Date	Latitude	Longitude	Area ^a	Category ^b	Reference
39	23	April, 1991	36°-42°N	5°E-6°W	MS	i	<i>Ratte</i> [1993]
40	59	April to May, 1991	30°-50°N	6°-16°W	n-A	i	<i>Ratte</i> [1993]
41	48	May, 1991	52°-58°N	14°-16°W	n-A	i	<i>Ratte</i> [1993]
42	14	May, 1991	55°-59°N	0°-5°E	NS	i	<i>Ratte</i> [1993]
43	>100	Oct., 1971	19°-30°N	87°-95°W	G	i	<i>Brooks and Sackett</i> [1973]
44	1	Sept., 1968	23°-29°N	89°-95°W	G	a	<i>Franck et al.</i> [1970]

^a Area codes: n, north; e, equatorial; s, south; A, Atlantic; BoB, Bay of Biscay; BS, Beaufort Sea; C, Caribbean; G, Gulf of Mexico; IO, Indian Ocean; MS, Mediterranean Sea; NS, North Sea; P, Pacific.

^b i, in situ; ?, not specified; a, chemicals added to sample; c, stripped NMHC stored with purge gas in cylinders.

^c Only daily averages of up to eight measurements are given.

^d Samples were collected in collaboration with W.D. Smith.

^e Samples were collected in collaboration with *Brooks et al.* [1973].

^f Samples were collected in collaboration with J. Bunt.

^g Data tables from *Plass* [1992].

^h Data extracted from the figures by *Donahue and Prinn* [1993] and N.M. Donahue (personal communication, 1991).

and ethane concentrations generally exceed 4 pmol/L which is well above the detection limit of about 1 pmol/L. Thus the steep cutoff observed for ethane toward low concentrations is not caused by analytical limitations.

4.2. Relations Between Different Hydrocarbons

Linear relations between different hydrocarbons have been reported by several authors [*Lamontagne et al.*, 1974; *Bonsang et al.*, 1988; *Plass et al.*, 1992]. Figure 5 presents concentration ratios for the various data sets and data categories. While generally fairly constant ratios are observed, some of the ratios differ substantially with respect to mean ratio and standard deviation. This may be due to real variability, sampling artifacts, large uncertainties at extremely low concentrations, and calibration errors.

Ratios between different alkenes or between different alkanes from in situ data sets (listed in Table 5) are generally identical to the average within a factor of 2 (Figure 5). Ethene-propene ratios are significantly enhanced in data sets with chemicals added. Data sets of the not specified category generally show a larger scatter of the data than the in situ data sets, and ethene-propene ratios are on average higher than in in situ data sets. The data sets of the cylinder category result in alkane ratios similar to the in situ data, alkene ratios show larger scatter, and especially data set 30 differs from the in situ average. Ethene-ethane ratios are not constant in any of the data categories. Mean ratios between ethene and ethane of different data sets can differ by more than an order of magnitude.

Thus in situ data generally differ in two aspects from other categories of data: absolute concentrations are lower (see section 4.1) and ratios among some of the hydrocarbons, especially the alkenes, are more constant. Although some of the non-in situ data sets are comparable to the in situ data sets with respect to these features, in general, the deviations and the scatter in the ratios are higher for non-in situ data. There is no way to decide

if these differences are "real" or due to the storage process. However, since data of the non-in situ categories have a principally larger uncertainty due to the additional storage process and the data appear to differ from in situ results, we think it is not appropriate to compile the data of different categories into one database. Thus we will focus on the in situ measurements.

5. Dissolved NMHC in the Oceans: Geographical Distributions and Parameters Influencing Concentrations

The following discussions of the distribution of hydrocarbons in seawater are focused on ethene. In some cases, ethane is also considered. Both are the most abundant compounds of the C₂-C₄ alkenes and alkanes, respectively, and as discussed in section 4 the concentrations of C₃ and C₄ hydrocarbons are well related to the C₂ hydrocarbons. In the case of acetylene, butanes, and butenes the number of available data is much lower (compare Table 3) and less appropriate to derive representative distributions.

In order to identify those factors which have an impact on NMHC concentrations, possible relations between concentrations and physical or biological parameters will be tested in a correlation analysis. For this purpose a database is set up.

5.1. Data for a Global and Seasonal Grid

From Figure 1 it is apparent that there are regions with fairly dense data coverage (e.g., Gulf of Mexico and the Caribbean area) and regions where measurements are scarce or absent (e.g., the eastern Pacific and the southern oceans). A discussion of the distributions of the NMHC concentrations using all original measurements would give too much weight to those regions and

Table 3. Hydrocarbon Concentrations in the Various Data Sets

Data Set	Ethane	Propane	Sum of Butanes	Ethene	Propene	1-Butene	Acetylene
All data	30 (77), 1-1769 5-76	17 (52), 0.9-1295 2-59	20 (173), 0.4-4375 1-59	178 (192), 7-2609 46-450	68 (141), 2-3326 20-148	47 (94), 5-1253 12-111	16 (25), 0.5-416 4-29
90% range							
1	49 (8), 45-67	6 (7), 2-22	trace	198 (74), 134-321	47 (35), 18-129	-	-
2	trace	2 (0.2), 2-3	trace	89 (25), 31-152	15 (14), 2-36	-	-
3	16 (20), 2-45	3 (1), 2-5	trace	265 (160), 147-491	18 (6), 13-27	-	-
4	5 (6), 2-18	11 (17), 2-45	trace	343 (18), 330-375	92 (84), 49-259	-	-
5	9 (4), 2-18	5 (2), 2-9	trace	224 (73), 98-304	59 (20), 22-89	-	-
6	9 (3), 5-14	11 (8), 5-27	trace	401 (65), 299-491	96 (35), 63-161	-	-
7	8 (2), 5-13	5 (-), -	trace	241 (48), 179-317	36 (8), 27-49	-	-
8	63 (11), 45-85	41 (15), 18-63	trace	135 (40), 76-223	51 (20), 27-85	-	-
9	134 (83), 45-272	227 (436), 31-1295	33 (30), 2-89	502 (139), 232-670	27 (22), 5-76	-	-
10	154 (162), 1-424	79 (62), 31-237	511 (1291), 18-4375	160 (69), 76-268	24 (51), 5-170	-	-
11	63 (-), -	54 (-), -	196 (-), -	1161 (-), -	214 (-), -	-	-
12	12 (2), 7-13	12 (2), 5-13	8 (2), 6-13	107 (11), 98-121	63 (11), 29-67	-	-
13	12 (1), 11-14	16 (2), 14-19	16 (18), 5-58	216 (27), 174-255	132 (18), 98-152	-	-
14	8 (2), 6-10	10 (4), 5-17	4 (4), 2-13	131 (15), 112-156	83 (16), 63-112	-	-
15	14 (4), 9-21	12 (3), 7-16	trace	166 (29), 116-205	64 (23), 40-107	-	-
16	24 (18), 14-89	23 (11), 13-58	4 (5), 2-22	153 (82), 89-424	61 (25), 40-147	-	-
17	10 (4), 5-18	5 (2), 2-11	4 (5), 2-27	346 (92), 201-536	87 (18), 54-112	-	-
18	19 (4), 13-24	15 (7), 8-28	-	325 (128), 150-498	99 (36), 44-153	-	-
19	9 (2), 6-11	3 (1), 2-6	-	104 (51), 74-307	35 (7), 23-50	-	-
20	10 (1), 8-12	3 (1), 2-4	-	135 (25), 105-173	57 (10), 43-71	-	-
21	7 (1), 5-9	3 (1), 2-4	-	141 (23), 120-188	61 (6), 50-67	-	-
22	15 (4), 9-21	7 (3), 3-12	-	266 (98), 92-432	90 (22), 60-141	-	-
23	11 (5), 4-27	9 (3), 4-27	-	82 (16), 45-143	40 (39), 4-308	-	-
24	10 (4), 4-31	9 (4), 4-22	-	81 (20), 49-134	37 (13), 9-103	-	-
25	-	8 (8), 1-41	2 (2), 0.4-11	40 (16), 7-72	34 (16), 4-71	-	-
26	37 (16), 19-80	16 (8), 5-40	4 (2), 1-9	62 (30), 32-185	61 (27), 30-159	-	-
27	342 (110), 223-517	188 (54), 115-261	144 (39), 85-189	1042 (493), 488-1610	520 (138), 348-656	147 (55), 95-233	-
28	41 (7), 34-50	32 (7), 24-38	24 (5), 16-30	311 (41), 254-367	132 (15), 113-155	35 (8), 22-43	-
29	97 (17), 80-114	99 (6), 93-105	83 (3), 80-86	607 (24), 583-631	285 (5), 280-289	69 (3), 67-72	52 (5), 46-57
30	937 (695), 67-1769	489 (312), 62-801	359 (225), 42-542	1715 (1129), 122-2609	2241 (1402), 262-3326	774 (503), 80-1253	179 (170), 23-416

Data Set	Ethane	Propane	Sum of Butanes	Ethene	Propene	1-Butene	Acetylene
31	222 (148), 52-639	65 (46), 15-192	37 (30), 7-132	246 (121), 88-546	125 (60), 38-286	71 (30), 29-145	7 (3), 1-16
32	69 (49), 30-235	22 (15), 10-65	14 (9), 6-36	165 (47), 97-247	78 (34), 38-176	44 (16), 23-85	5 (1), 3-6
33	13 (6), 5-27	6 (2), 2-10	4 (2), 2-9	63 (14), 38-84	31 (9), 14-46	18 (7), 5-27	4 (1), 1-6
34	14 (6), 7-28	6 (3), 2-15	9 (3), 5-17	161 (66), 98-372	61 (13), 38-89	43 (10), 23-63	13 (6), 6-29
35	9 (2), 5-13	8 (3), 4-15	3 (2), 2-8	108 (31), 66-167	44 (16), 21-79	32 (8), 18-45	8 (3), 5-15
36	17 (6), 7-26	10 (4), 4-23	5 (3), 2-13	129 (17), 92-157	44 (9), 25-59	34 (7), 22-51	10 (4), 4-17
37	14 (4), 9-25	5 (1), 2-8	3 (1), 2-8	66 (26), 31-136	30 (11), 9-53	22 (8), 9-40	10 (3), 6-17
38	8 (1), 6-10	4 (1), 3-6	1 (0.3), 0.8-1.5	83 (20), 40-117	38 (9), 20-57	10 (3), 15-49 ^a	<4
39	34 (35), 17-172	24 (24), 7-120	35 (41), 2-192 ^b	168 (58), 62-249	94 (41), 31-181	86 (56), 14-200	22 (23), 5-107
40	18 (5), 12-46	10 (3), 4-18	9 (9), 2-60 ^b	69 (18), 30-99	41 (16), 11-92	38 (29), 8-189	19 (4), 11-31
41	20 (5), 12-33	8 (2), 5-12	5 (2), 1-10 ^b	56 (10), 40-86	27 (4), 19-40	22 (6), 9-35	26 (3), 21-31
42	60 (45), 25-188	23 (26), 11-116	15 (14), 8-65 ^b	111 (18), 74-156	61 (10), 42-81	42 (12), 14-54	23 (6), 15-35

Values in picomoles per liter. For each column, values are mean concentration (standard deviation), minimum-maximum. Dashes, no measurements reported; trace, close to or below the detection limit.

^a Sum of butenes

^b Only n-butane measured, i-butane not available.

seasons where intensive campaigns with a large number of measurements have been carried out. On the other hand, a too extreme averaging, e.g., using only the averages of the 42 data sets, may smooth out systematic variations. As a compromise, we decided to average the data geographically for a grid of 10° longitude \times 10° latitude and for a time period of 1 month ($10^\circ \times 10^\circ \times 1$ month). This results in a coverage of about 2% or 75 of the total of more than 5000 cells with in situ data. If all data categories are considered, 122 cells are covered with data. Besides the scarce data coverage in the southern oceans, the majority of data from northern and southern latitudes higher than 20° were obtained in summer and only a few in winter (Table 6).

In addition to limitations due to data coverage, concentration averages for particular cells may not be representative. This is obvious for grid cells with scarce data coverage; occasionally, only one measurement exists. The range of naturally occurring variations in the concentrations can be estimated from intensive measurements within a cell, which easily accounts for a factor of 2 and more [e.g., Plass *et al.*, 1992; Swinnerton *et al.*, 1977; Macdonald, 1976].

Such variations are not unexpected since the NMHC concentrations are established by a complex balance of production and loss processes in the surface layer of the ocean which generally is not in a steady state [Plass-Dümler *et al.*, 1993]. In order to identify the parameters which impact on the production and loss processes a database of parameters was set up according to the grid for concentrations ($10^\circ \times 10^\circ \times 1$ month). Based on our present state of knowledge, the production of NMHC in seawater is strongly influenced by the concentration of dissolved organic carbon (DOC) and the solar insolation [Wilson *et al.*, 1970; Ratte *et al.*, 1993]. As a measure of the solar insolation, we used the global solar radiation at noontime according to an analytical expression at clear sky conditions reported by Paltridge and Platt [1976] which summarizes their results obtained at Aspendale, Australia. Information about DOC concentrations is still very limited and strongly dependent on the analytical method [Suzuki *et al.*, 1992; Wangersky, 1993]. Global and seasonal distributions of DOC obtained by a single method are, to our knowledge, not yet available. Thus we presently can only refer to potential sources of DOC such as phytoplankton and coastal inputs. Additionally, it has been discussed that phytoplankton activity has an impact on the alkene concentration in seawater [Swinnerton and Lamontagne, 1974; Wilson *et al.*, 1970]. As a measure of phytoplankton activity, we used the chlorophyll *a* concentrations from monthly or seasonally averaged composites of the Coastal Zone Colour Scanner on board of the Nimbus 7 satellite [Feldman *et al.*, 1989]. Coastal influences were considered by accounting for the distance from the coast. Furthermore, the seawater temperature is an important factor in biological and chemical processes and thus was also considered. The temperature of surface seawater was taken from climatological averages [Brown *et al.*, 1989].

The only loss process identified so far is the emission into the atmosphere. It is proportional to the concentration gradient and the transfer velocity. For light alkenes and alkanes the atmospheric concentrations can generally be neglected [Plass *et al.*, 1992], and thus the emissions are proportional to the seawater concentrations. The transfer velocity is calculated according to Liss and Merlivat [1986]. We based the calculation

Table 4. Concentrations of Light Hydrocarbons in In Situ Measurements Compared to Other Data

Compound	In Situ (12-16, 18-26, 31-42) ^a	Not Specified (1-8, 17)	Chemicals Added (9-11) ^a	Cylinders (27-30)
Ethane	22 (44) 6.3 - 52 (814)	29 (27) 2 - 75 (268)	84 (95) 9 - 401 (44)	349 (484) 35 - 974 (13)
Propane	11 (14) 2.3 - 24 (826)	18 (19) 2.0 - 62 (268)	78 (186) 18 - 273 (45)	196 (230) 27 - 605 (13)
Sum of butanes	7.4 (12) 1.1 - 29 (348)	2.2 (1.6) 2.0 - 2.0 ^b (268)	184 (629) 9 - 357 (46)	147 (167) 25 - 494 (13)
Ethene	134 (95) 42 - 358 (838)	217 (112) 76 - 446 (268)	562 (432) 99 - 1161 (44)	906 (806) 254 - 2414 (13)
Propene	59 (36) 21 - 135 (834)	56 (32) 22 - 102 (268)	113 (109) 4.5 - 352 (45)	762 (1067) 130 - 3134 (13)
Sum of butenes	37 (29) 10 - 95 (308)	-	-	536 (970) 36 - 2563 (13)
Acetylene	14 (10) 4.3 - 29 (313)	-	-	128 (146) 23 - 416 (5)

For each column, values are mean concentration (standard deviation)(pmol/L) 90% range (pmol/L)(number of measurements)

^a In addition to the data sets of Table 2 some miscellaneous samples were considered (from references of Table 2).

^b More than 90% of the values at the detection limit of about 2 pmol/L.

on frequency distributions of wind velocities from monthly composites of climate atlases [Marine General Staff, 1953; U.S. Navy, 1957] and seawater temperatures. The transfer velocities were determined from the frequency distribution of the wind velocities by first calculating the transfer velocity for each wind speed at the given temperature and subsequently averaging according to the distribution. This method is more reliable than a calculation of transfer velocities from mean wind velocities due to the nonlinear relationship between wind and transfer velocities [Liss and Merlivat, 1986].

Values of all the above parameters were determined for all cells for which NMHC measurements exist. However, they generally refer to estimates or climatologic values. These can deviate substantially from real values for individual cells. Variations of a factor of 2 and more for the transfer velocity and the chlorophyll *a* concentration can be expected.

5.2. Relations Between NMHC Concentrations and Environmental Parameters

All the various uncertainties in the potential controlling parameters and NMHC concentrations discussed in the section 5.1 set a considerable limitation to what may be expected from linear correlations. For the in situ data (75 grid points) no significant linear correlations for ethane with any of the parameters exist. Also for ethene no significant positive correlation is observed. But ethene concentrations are significantly anticorrelated with the transfer velocities ($r=-0.49$; $|r|>0.29$ is significant on the 1% level)(Figure 6, solid symbols). Taking all 121 data points (all categories), some correlations which are statistically significant are observed. However, they are dominated by the high concentrations measured in the data category cylinder. As an example, Figure 6 shows the ethene concentrations as a function of the transfer velocities. The anticorrelation observed in the in situ data ($r=-0.46$) is damped

($r=-0.25$) due to some data of category cylinder and chemicals added which are substantially different from the other data.

Of all parameters considered, the transfer velocities have the largest impact on ethene concentrations. This allows us to generalize previous results for investigations in the Atlantic [Plass et al., 1992; Plass-Dülmer et al., 1993]. Emissions into the atmosphere were found to be the major loss process for alkenes and, in some cases, also for alkanes. However, a correlation coefficient of $r=-0.49$, though significant, can only explain 24% of the variance. Thus apart from the substantial limitations discussed above, it appears that further parameters are of importance for the balance of light NMHC in seawater, especially for the production process. In a first and rough approximation, the atmospheric emission rates of alkenes can be assumed to be the only loss process and thus should be balanced by production. In this context, the concentrations are a less appropriate measure for the production rates than the emission rates. Consequently, high alkene concentrations can be due to both high alkene production rates and/or low transfer velocities.

Figure 7 gives an example showing such a situation. The concentrations of ethene measured in situ in the equatorial Pacific (30°S-30°N) during various investigations clearly decrease toward higher western longitude (Figure 7a). This feature could, at first sight, be interpreted as being due to decreasing ethene production with increasing distance from the upwelling regions off the American coast. In consequence, this would suggest a relation between hydrocarbon concentrations and biological productivity. However, for the ethene emission rates no such trend with longitude exists (Figure 7b). On average, the transfer rates exhibit a reverse trend with longitude compared to the concentrations: They increase due to higher wind velocities where the concentrations decrease. The product of both (the emission rates) is unchanged. Thus the decrease in the ethene concentrations toward higher western longitudes (Figure 7a) is explained in the most simple manner by fairly

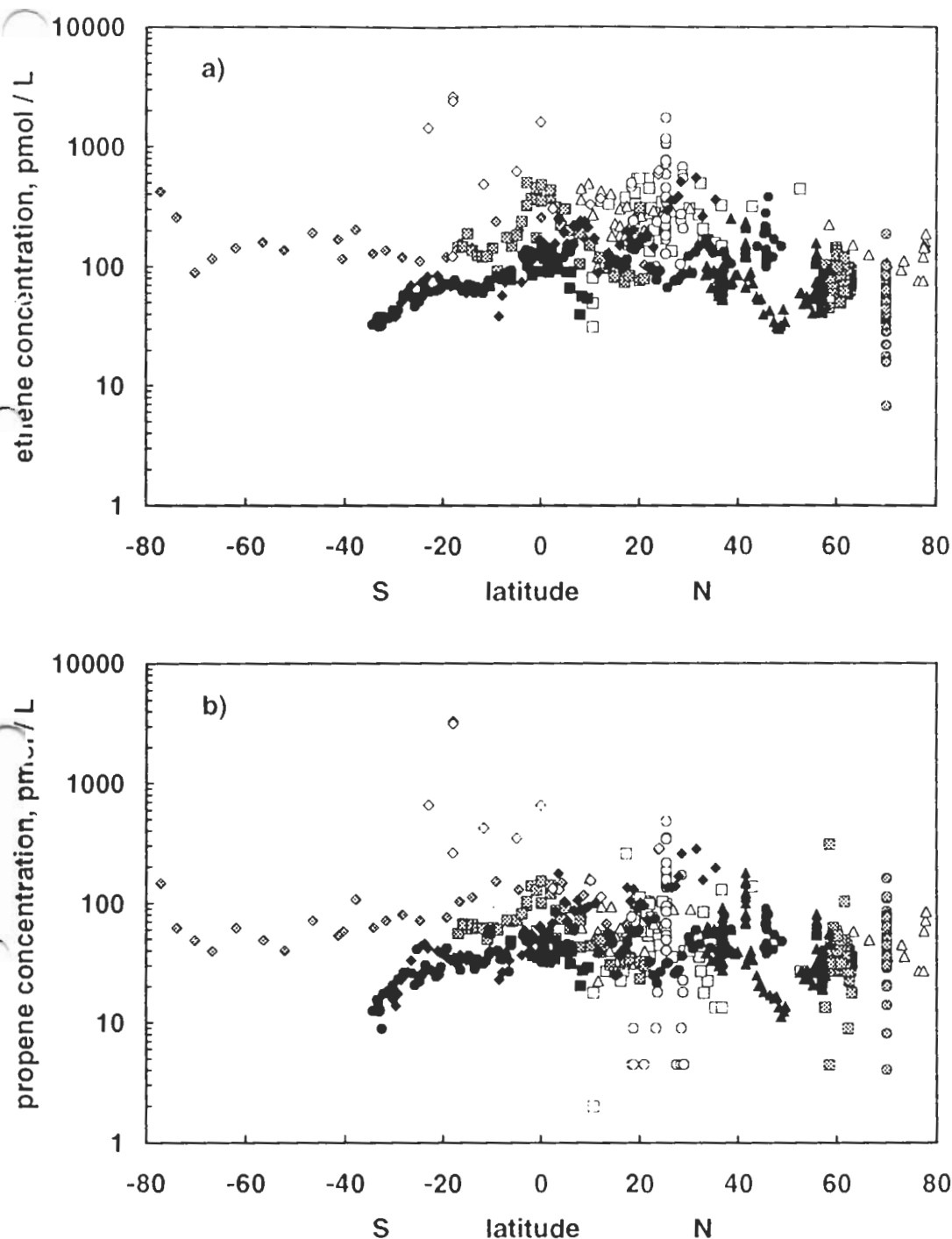


Figure 2. The latitudinal distribution of (a) ethene and (b) propene concentrations in surface seawater; symbols as in Figure 1 (solid and shaded symbols are used for in situ measurements; open symbols are used for other data categories). Each point represents a single measurement or a daily average. Concentrations reported as "trace" were given the value of the detection limit in the reference.

constant production and increasing transfer rates. In this context, indications for links with biology remain.

Another feature often discussed in the literature is the observation of enhanced concentrations in the region of the equatorial current compared to higher latitudes, which is generally assumed to be a consequence of high primary

productivity in the equatorial upwelling region [Lamontagne *et al.*, 1974, 1975; Ehhalt and Rudolph, 1984]. Figure 8 compares ethene concentrations and emissions obtained in six different transects of the equator. The line represents the results by Lamontagne *et al.* [1974] which show a broad concentration maximum with about a factor of 2 higher concentrations between

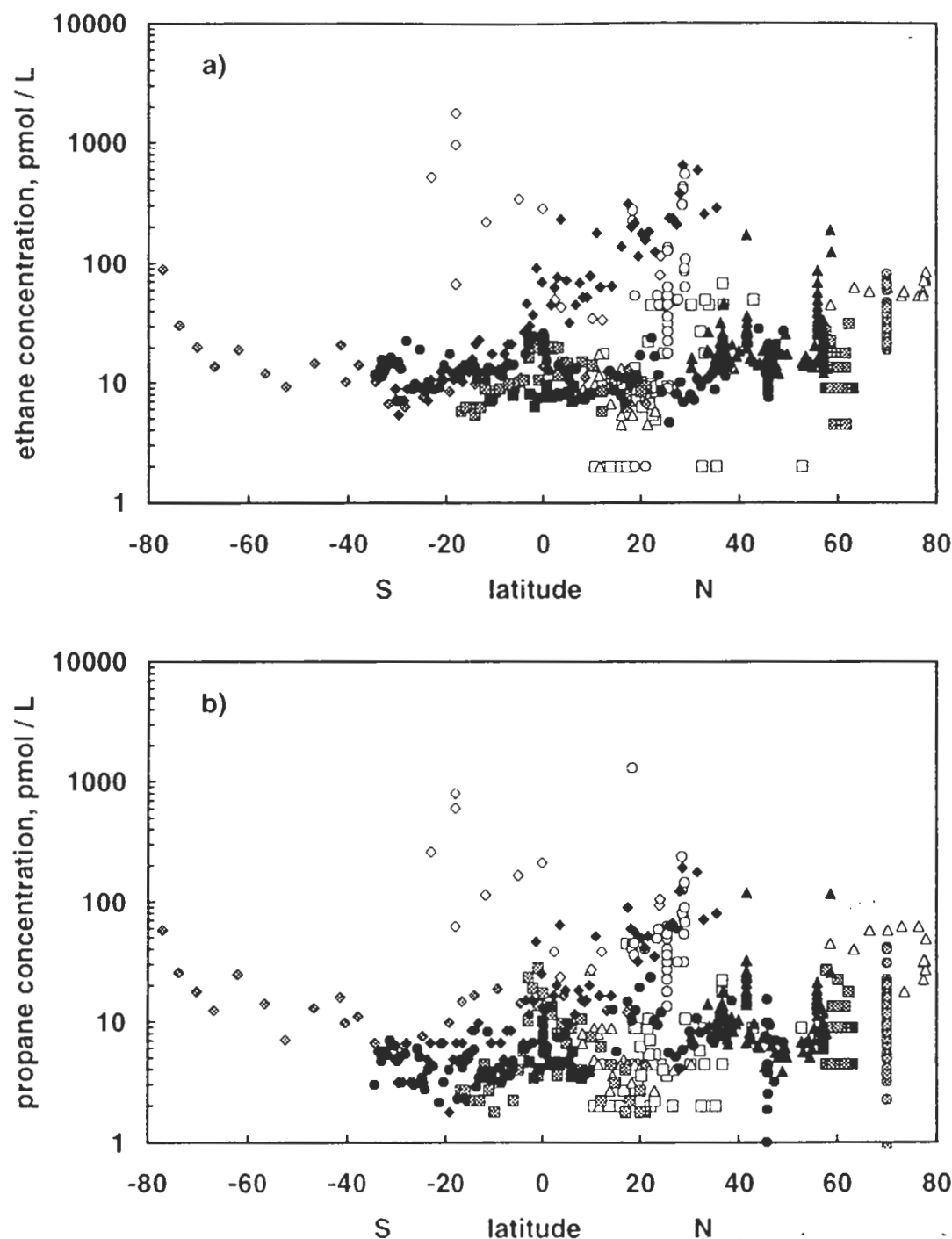


Figure 3. The latitudinal distribution of (a) ethane and (b) propane concentrations in surface seawater; symbols as in Figure 1.

10°N and 10°S. Some of the other transects show similar but less pronounced maxima; others do not. Again, there is no indication for systematically enhanced emissions near the equator. Low transfer velocities in the center of the Intertropical Convergence Zone (ITCZ) are the most probable reason for enhanced concentrations in this region.

Seasonal changes can be discussed for same or nearby grids in different months. Since in tropical regions the climatic changes with season are less pronounced we will focus on extratropical areas. The database only contains two such areas. Figure 9 shows the ethene concentrations and the calculated emission rates for the months of measurements. However, the

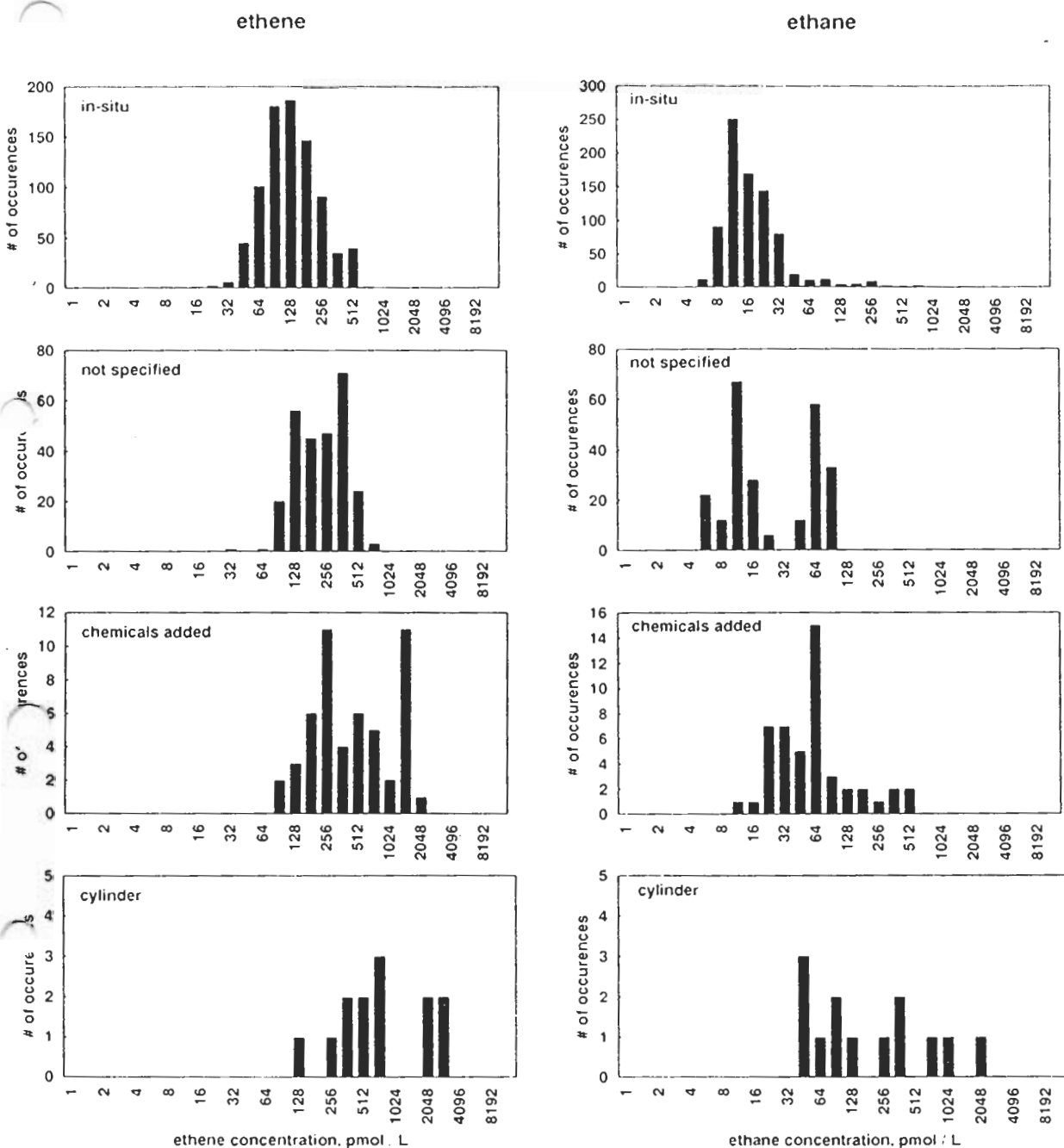


Figure 4. Histograms of the concentrations of ethene and ethane.

situation is complicated since only for one area (Figure 9b) can in situ data be compared. Data with chemicals added (Figure 9a) were considered here since they compose the most extensive study of this kind by Swinnerton *et al.* [1977] for the period February to June in the Gulf Stream off Miami (Figure 9a). Furthermore, the samples with sodium azide added were analyzed within a period of 2 hours [Swinnerton *et al.*, 1977] and are possibly reliable. Samples taken in the coastal environment [Swinnerton *et al.*, 1977] were not considered here because apart

from climatological influences, local contaminations or interactions between water and bottom might interfere. The concentrations are constant for February to March and increase by more than a factor of 2 in May and June. The transfer velocities show an opposite trend so that the emission rates are unchanged for the whole period. However, owing to the use of climatologic data for the calculation of the transfer velocities, the emission rates are substantially uncertain. For a region in the Atlantic (Figure 9b), enhanced ethene concentrations and

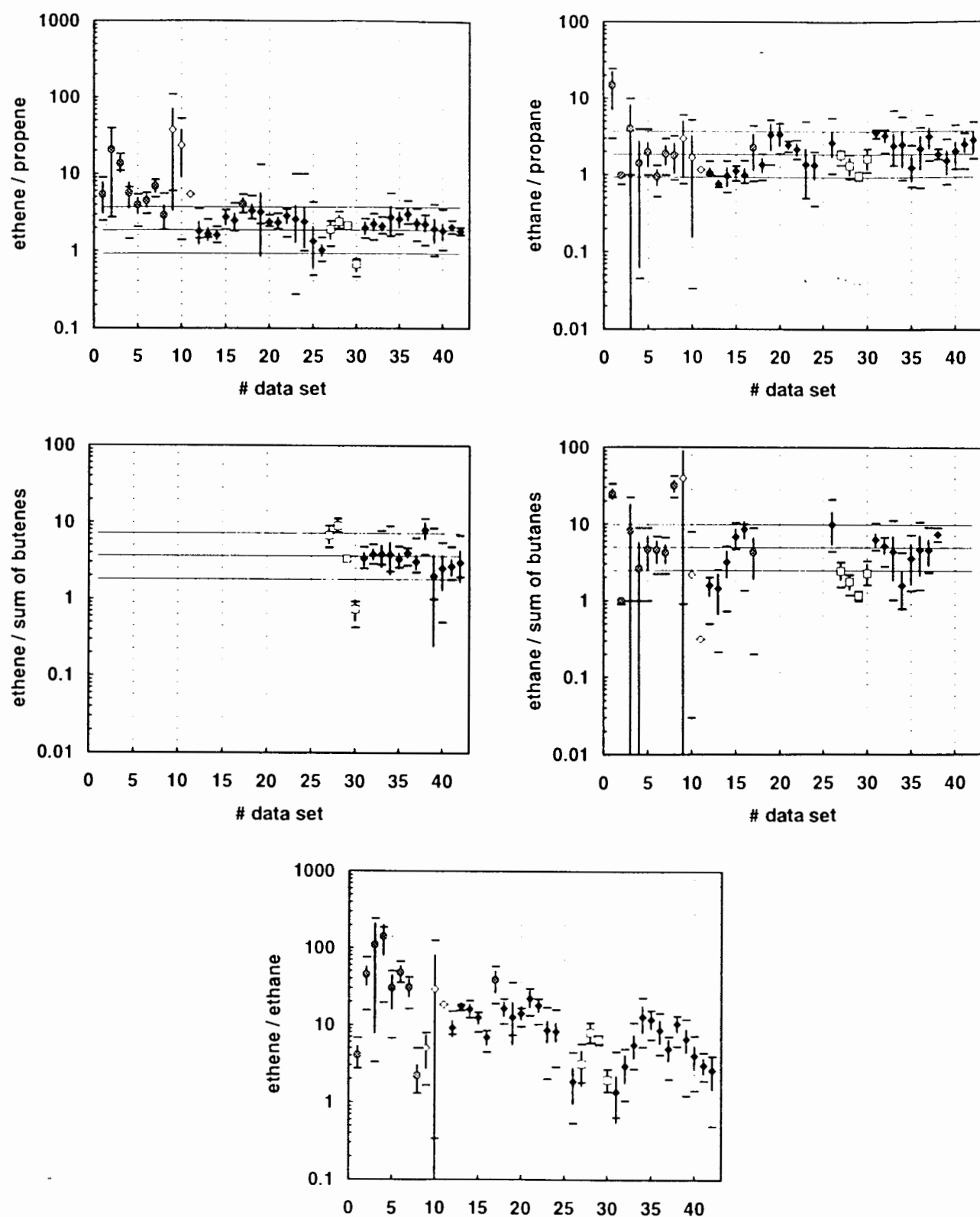


Figure 5. Concentration ratios of different hydrocarbons in the various data sets: averages (solid diamonds, in situ; shaded circles, not specified; open diamonds, chemicals added; open squares, stripped hydrocarbons stored in cylinders), standard deviations (bars), and upper and lower limits (dashes) are indicated. Mean concentration ratios of in situ data (thick line, see text) and a range of a factor of 2 above and below the mean are indicated by the thin lines.

Table 5. Ratios Between the Concentrations of Light Alkenes and Alkanes

Ratio of compounds	In Situ Data	Percent of Ratios ^a Within a Factor of 2 of Average (Number of Ratios)	
	Average (Standard Deviation)	In Situ Data	All Data
Ethene/propene	2.3 (0.5)	94 (834)	85 (1166)
Ethene/1-butene	3.6 (1.4)	84 (303)	82 (316)
Ethane/propane	2.1 (0.9)	76 (779)	74 (1075)
Ethane/sum of butanes	4.7 (1.6)	57 (213)	49 (276)

^a Ratios from measurements above the detection limit are used.

emissions in the summer compared to spring are observed. However, these measurements were generally not made in the same $10^\circ \times 10^\circ$ grid cell, a factor which adds substantial uncertainty to the trend. Thus the available data from same or nearby areas do not allow identification of seasonal trends in the ethene emission rates. The ethene emission rates from all in situ data (Figure 10) separated according to seasons show no indications for systematic trends with season at given latitude bands.

According to the balance of NMHC in the mixed layer, correlations between the parameters suspected to play a role in the NMHC production and the emission rates seem more promising than correlations between these parameters and concentrations. However, single and multiple parameter linear correlations of ethene and ethane emission rates (all data categories) were generally poor. For the in situ data the following correlations exceeding the 1% significance level ($|r| > 0.29$) were found. The ethene emissions are anticorrelated with increasing northern and southern latitude ($r = -0.45$). The ethane emissions are correlated with the longitude ($r = 0.30$, western longitudes negative). On average, the ethane emissions (in situ) from the Atlantic ($0.60 \pm 0.77 \times 10^8$ molecules $\text{cm}^{-2} \text{s}^{-1}$) exceed those of the Pacific ($0.15 \pm 0.12 \times 10^8$ molecules $\text{cm}^{-2} \text{s}^{-1}$) by a factor of 4, a difference which was not found for alkenes. In the early studies by Brooks and Sackett [1973] and Swinnerton and Lannontagne [1974] a clear correlation between oil pollution and abundance of alkanes was reported. Thus higher alkane emissions from the Atlantic are compatible with a larger degree of oil pollution in the Atlantic than in the Pacific. However, an attempt to associate enhanced alkane concentrations with major oil spills (data for 1984 to 1988 by courtesy of the International Maritime Organization, London) was not successful.

6. Global NMHC Emissions From the Oceans

Based on the ethene and ethane emission rates of the $10^\circ \times 10^\circ \times 1$ month grid, average emissions can be calculated. Ethene and ethane emissions are extrapolated to the global ocean. This is done in Table 7 based on the in situ data, all data, and an upper limit for 90% of all data. Additionally, the standard deviations of the emissions based on the in situ data are given. The emissions of C_3 and C_4 hydrocarbon are scaled to the C_2 emissions using the ratios defined in section 4.2. This method is preferred to a direct calculation from the data since the data coverage and accuracy are not as good for the C_3 and C_4 hydrocarbons as for ethene and ethane. The correction of the transfer rates for the various NMHC basically considers the different molar volumes in the calculation of the diffusion constants and is described elsewhere [Plass-Dümler et al., 1993].

The oceanic emissions of light NMHC from in situ data sum to 2.1×10^{12} g/yr with 1.8×10^{12} g/yr or 85% due to alkene emissions (Table 7). Ethene alone contributes about 40% to the total emission. Compared to these numbers, oceanic emissions based on all data are higher by a factor of about 2 and the 90% upper limits is higher by factors between 2.5 and 3.5 (Table 7). In total, the 90% upper limit gives a value of 5.5×10^{12} g/yr. This level may be interpreted as an estimate of the upper limit of oceanic emissions based on the available data. The calculated oceanic emissions are on the low side of previous estimates (e.g., 50×10^{12} g/yr by Bonsang et al. [1988], 21×10^{12} g/yr by Ehrlert and Rudolph [1984], and 2.9×10^{12} g/yr for ethene alone by Sawada and Totsuka [1986]; for more details, compare Plass-Dümler et al. [1993]). The emission estimates presented here are still substantially uncertain because the temporal and spatial

Table 6. Regional and Seasonal Coverage of the $10^\circ \times 10^\circ \times 1$ Month Grid With In Situ NMHC Measurements

Latitude Range	Number of Grid Cells			
	Nov.-Jan.	Feb.-April	May-July	Aug.-Oct.
< 20°S	10	0	0	5
20°S-20°N	5	24	0	10
> 20°N	1	6	4	10

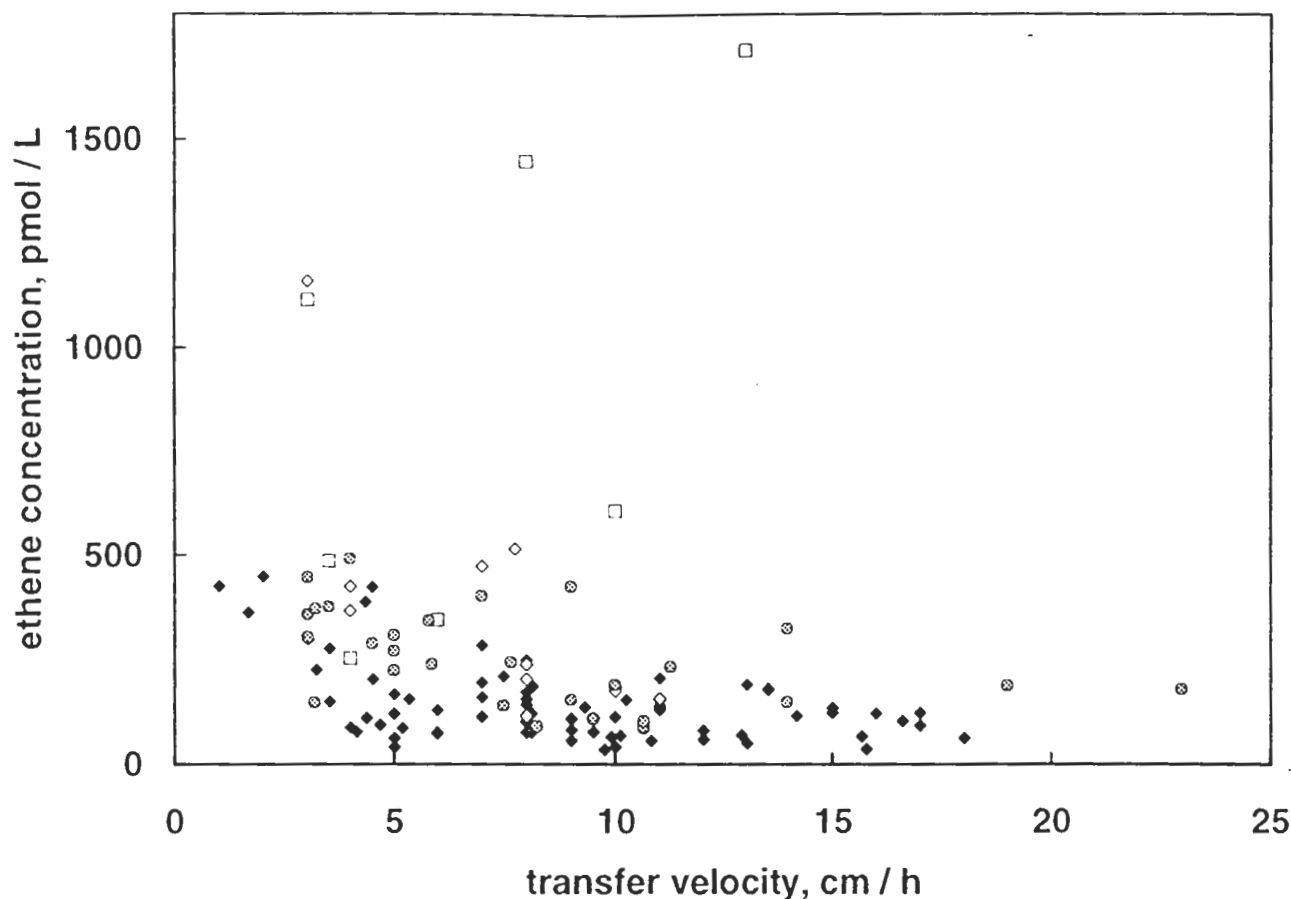


Figure 6. Ethene concentration ($10^{\circ} \times 10^{\circ} \times 1$ month database) as a function of the transfer velocity (solid diamonds, in situ; shaded circles, not specified; open diamonds, chemicals added; open squares, stripped hydrocarbons stored in cylinders).

variations of the concentration fields are poorly defined by the existing data and the transfer rates are only climatologic averages. However, the database is substantially larger than in previous estimates and thus, the numbers given in Table 7 are probably the most reliable global oceanic emission estimate so far.

Acetylene emissions can not be calculated from the concentrations in the seawater alone since for acetylene ocean and atmosphere are close to equilibrium [Plass *et al.*, 1992]. The calculation of oceanic emission or uptake rates thus would require the knowledge of the atmospheric acetylene concentrations which do not exist for most of the hydrocarbon measurements in seawater. However, an upper limit of acetylene emissions can be given by the ethane emission rate. The concentrations in seawater (section 4.1) are lower for acetylene, and ethane is larger supersaturated in seawater compared to atmosphere than acetylene [Plass *et al.*, 1992; Plass-Dülmer *et al.*, 1993; Kanakidou *et al.*, 1988]. The upper limit of oceanic acetylene emissions of $0.16-0.54 \times 10^{12}$ g/yr is on the low side of a previous estimate of $0.2-1.4 \times 10^{12}$ g/yr by Kanakidou *et al.* [1988].

7. Conclusions

An extensive database for NMHC concentrations in seawater has been compiled using all measurements (>1000) which have been reported to our knowledge. In most investigations the water samples were measured in situ on board the ship. However, in some investigations, chemicals were added to the water samples; in others the extracted gases were stored with the purge gas in cylinders until analysis in the laboratory on land. The results of these investigations deviate from the in situ measurements in either or both of the following aspects: The concentration ratios between different NMHC and their absolute levels which are generally higher for non-in situ measurements. However, since no intercomparisons among the methods have been performed, we cannot definitely ascribe the cause of the deviation to the methods used. Nevertheless, we think that all results not obtained by in situ measurements must be treated with great caution. We therefore focused on the in situ data.

Ethene is the most abundant of the C_2-C_4 hydrocarbons with average concentrations for the in situ data of 134 pmol/L, a range of variation between 7 and 550 pmol/L, and 90% of the

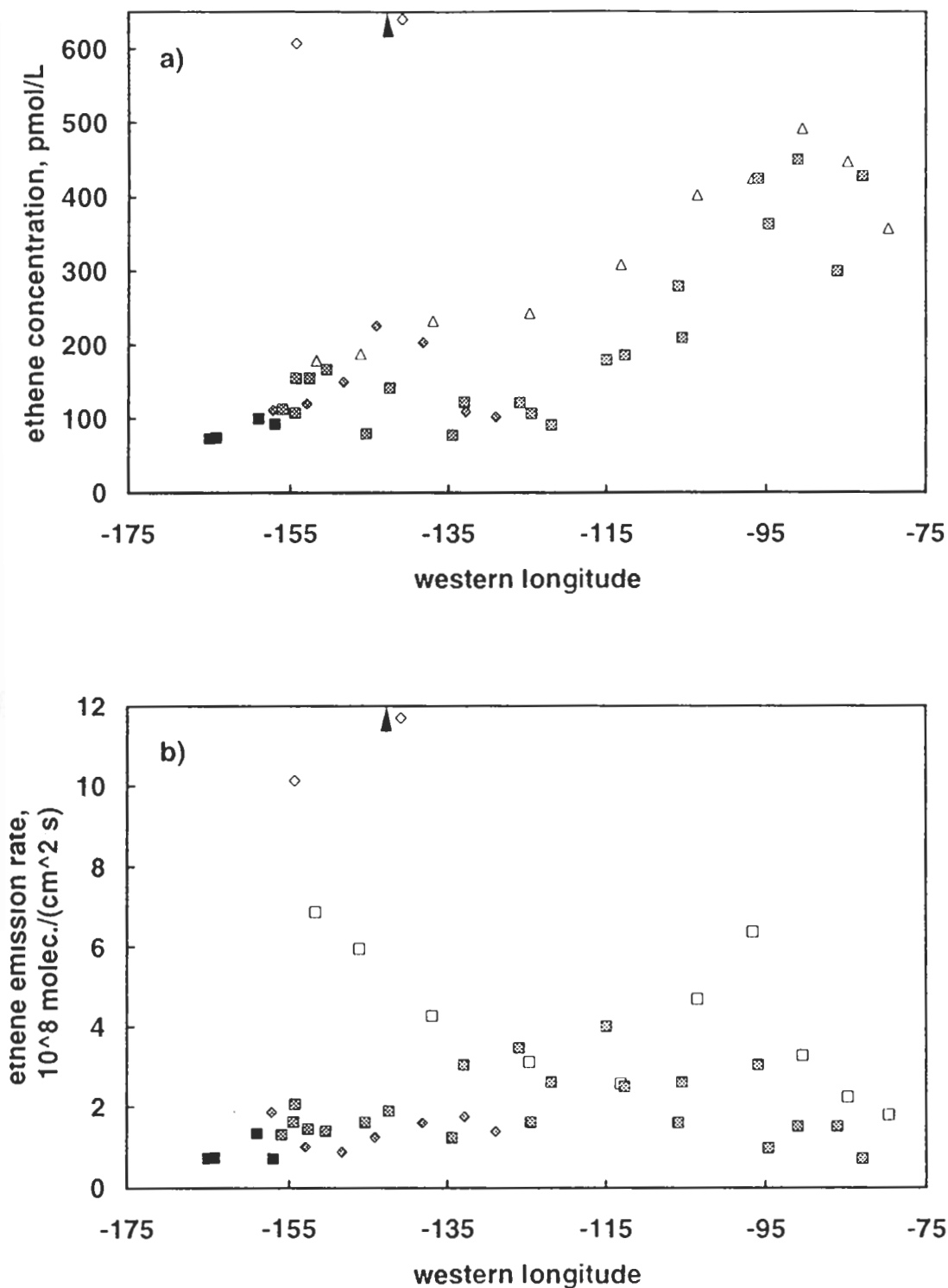


Figure 7. (a) Ethene concentrations and (b) emission rates versus the western longitude for a region of the equatorial Pacific (30°S - 30°N); symbols as in Figure 1: shaded diamonds, 12-16, 1972, and Swinnerton and Lamontagne [1974]; shaded squares, 18-22, 1974, and Lamontagne et al. [1975]; solid squares, 38, 1990, and Donahue and Prinn [1993]; open triangles, 6-7, 1971, and Swinnerton and Lamontagne [1974]; open diamonds, 29-30, 1987, and Bonsang et al. [1989] (data point corresponding to set 30 at 141°W is out of range of Figure 7: 1715 pmol/L , $37 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$).

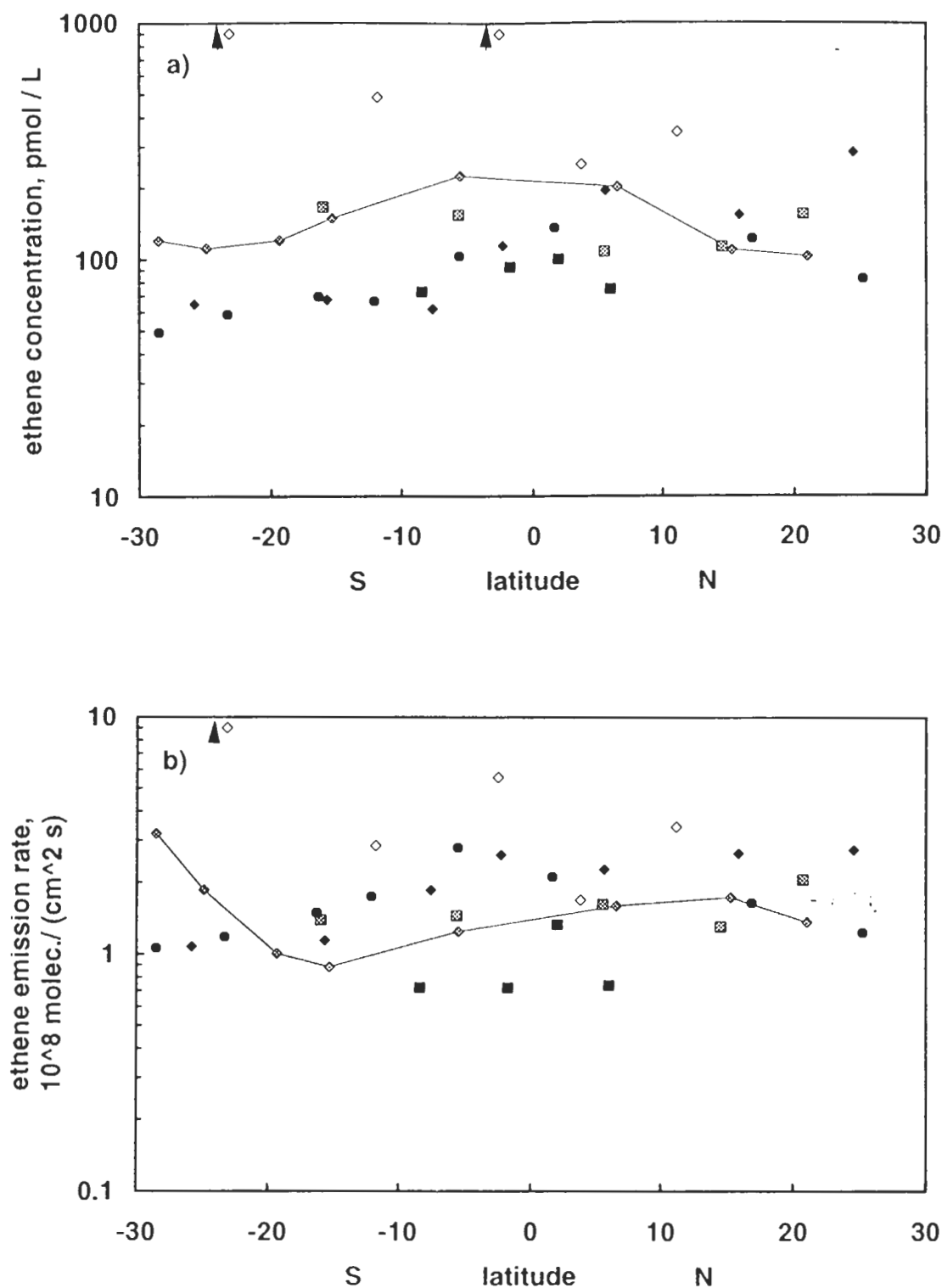


Figure 8. (a) Ethene concentrations and (b) emission rates versus the latitude for six equator transections; symbols as in Figure 1: Shaded diamonds and line, 12-14, 1972, and Swinnerton and Lamontagne [1974]; shaded squares, 19-21, 1974, and Lamontagne *et al.* [1975]; solid diamonds, 31-33, 1988, and Plass *et al.* [1992]; solid circles, 35-37, 1989, and Plass-Dülmer *et al.* [1993]; solid squares, 38, 1990, and Donahue and Prinn [1993]; open diamonds, 27-28, 1985, and Bonsang *et al.* [1988] (values out of range at 23°S, 1449 pmol/L and $19 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$; at 2°S, 1116 pmol/L).

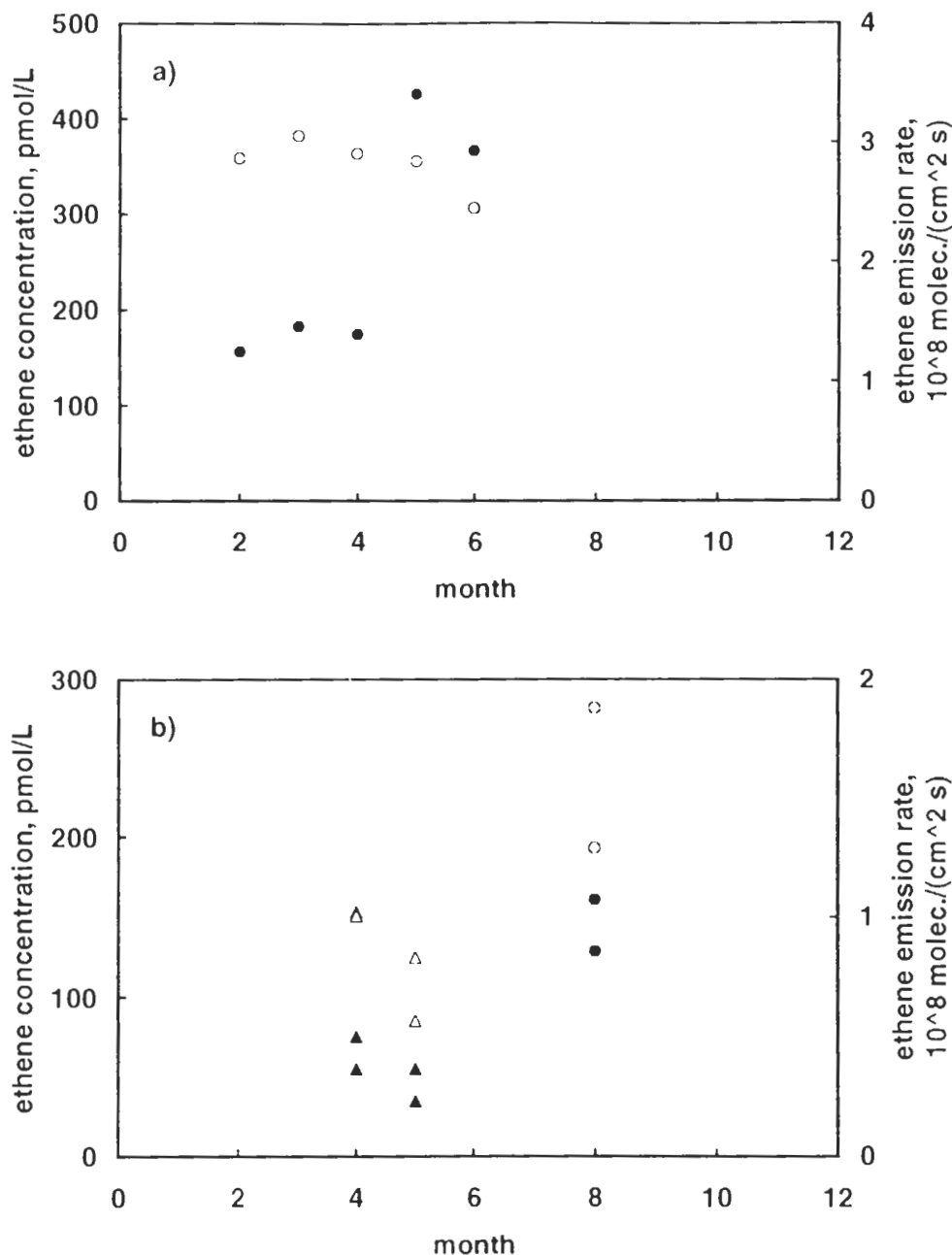


Figure 9. Seasonal changes of ethene concentrations (solid symbols) and emission rates (open symbols) at three locations: (a) Gulf Stream off Miami (25°N, 79°W), Swinnerton *et al.* [1977]; (b) Atlantic area off west Africa and west Europe (33°-53°N, 5°-18°W), circles, Plass-Dühlmer *et al.* [1993], and triangles, Ratte [1993].

data falls between about 40 and 350 pmol/L. The ethene, propene, and butene concentrations follow lognormal distributions; alkane concentrations neither fit a normal nor a lognormal distribution. As already reported for small data sets, some of the NMHC concentrations are found in nearly constant ratios: Propene and butenes follow the concentrations of ethene at lower levels. The same is observed for ethane and the C₃-C₄ alkanes. Thus ethene and ethane can be taken as "lead substances" for the light alkenes and alkanes, respectively.

Ethene especially plays a predominant role, since it contributes more than 40% to the total concentrations of dissolved C₂-C₄ hydrocarbons.

Linear correlations were tested in order to better understand the production and loss mechanisms of NMHC in seawater. Alkene concentrations were found to be significantly anticorrelated with the transfer velocities for sea-air exchange. No significant correlations of alkene concentrations were observed with irradiation, water temperature, latitude,

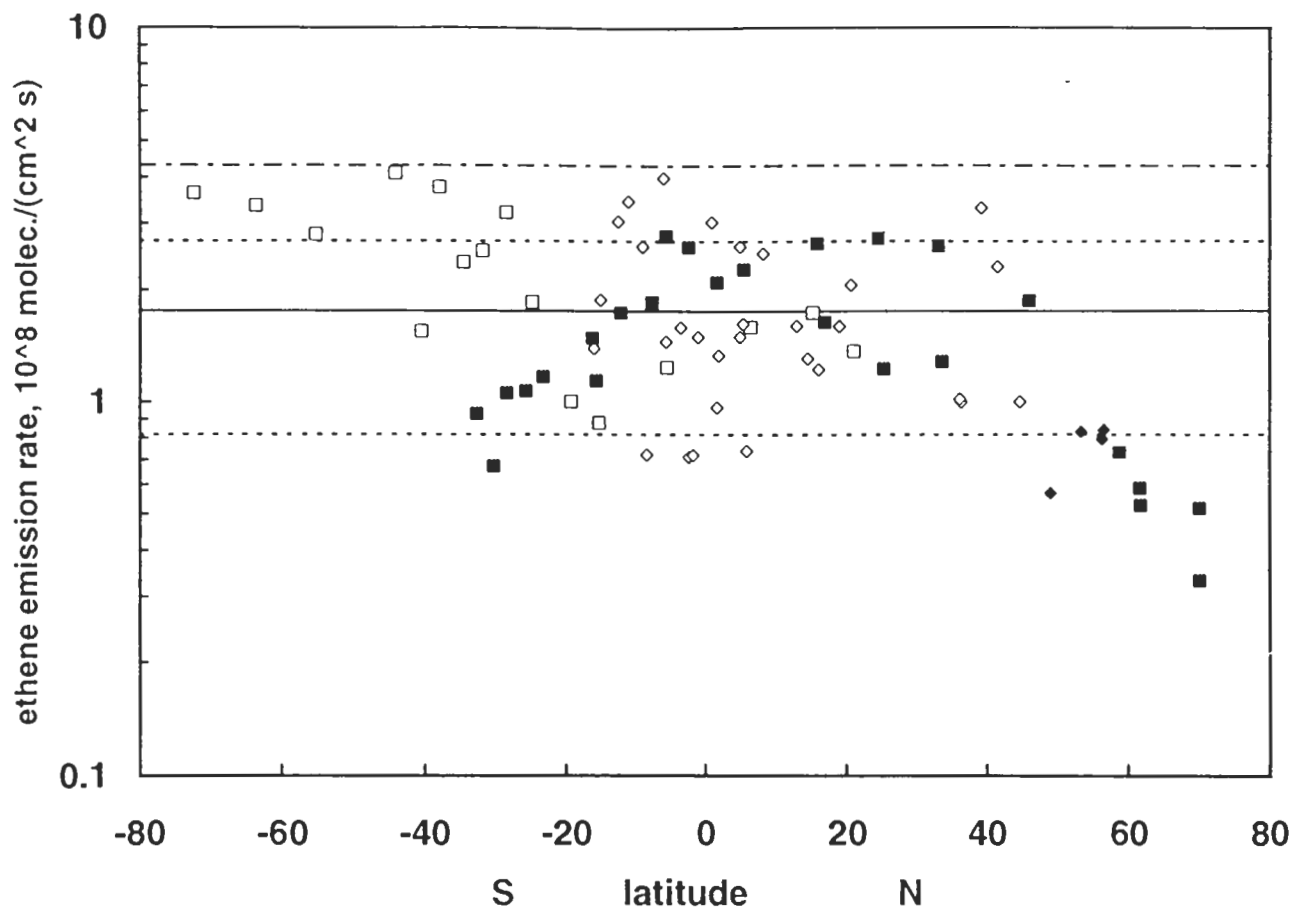


Figure 10. Ethene emission rates as a function of latitude (based on in situ data of the $10^\circ \times 10^\circ \times 1$ month grid), different seasons are indicated by the symbols: open squares, November-January; open diamonds, February-April; closed diamonds, May-July; closed squares, August-October; the solid line gives the mean emission of 1.8×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$, the dotted lines give the range of the standard deviation of 0.9×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$, and the dash-dotted line gives the 90% upper limit of all data of 4.3×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$.

Table 7. Global NMHC Emissions From the Oceans

Compound	In Situ	σ^a	All Data	90% Upper Limit ^b
Ethene	0.89	0.47	1.40	2.17
Propene	0.52	0.30	0.82	1.27
Sum of butenes	0.40	0.21	0.63	0.97
$\Sigma \text{C}_2\text{-C}_4$ alkenes	1.80		2.85	4.41
Ethane	0.16	0.26	0.32	0.54
Propane	0.10	0.11	0.20	0.35
Sum of butanes	0.06	0.09	0.11	0.19
$\Sigma \text{C}_2\text{-C}_4$ alkanes	0.32		0.63	1.07
$\Sigma \text{C}_2\text{-C}_4$ hydrocarbons	2.13		3.48	5.48

Values in 10^{12} g/yr.

^a Standard deviations of in-situ data.

^b Upper limit of 90% of all data.

chlorophyll *a* concentration, and the proximity to coastlines. However, results of this correlation analysis are restricted due to the limited data coverage and the use of climatological values for the parameters and not those prevailing during the measurements. Finally, DOC concentrations which are believed to determine the alkene production [Wilson *et al.*, 1970; Ratte *et al.*, 1993] are not available. So far, the only parameter identified to have an impact on the alkene concentrations is the transfer rate. This implies that high alkene concentrations do not necessarily indicate high emission rates, as has been widely assumed in the past. For example, enhanced concentrations at the equator or close to coastlines have been ascribed to large alkene production rates as a follow of the high primary productivity in these regions. However, transfer velocities are reduced in these areas and can consistently explain the enhanced concentrations without the need of higher alkene production rates. Thus no indications for a direct link between alkene production and primary productivity exist. Also, seasonal changes of alkene emission rates cannot be identified from the data.

A different situation exists for alkane concentrations. Here, no significant correlations with any of the parameters are observed. It is surprising that no anticorrelation with the transfer velocity is observed since emissions are a loss mechanism for all hydrocarbons. This may be due to either a very inhomogeneous distribution of the alkane production or high internal turnover rates in the mixed layer of the ocean with dominant loss mechanisms other than emissions to the atmosphere.

The calculation of global oceanic emission rates remains the subject of substantial uncertainty even though the number of available data is large. This is mainly due to the scarce spatial and temporal data coverage of about 2%. However, an estimate utilizing the database compiled here is probably more reliable than some of the previous estimates. For the C₂-C₄ hydrocarbons, emissions based on in situ data sum up to 2.1×10^{12} g/yr, with ethene alone contributing 40% to the total. An upper limit of 5.5×10^{12} g/yr is estimated which is larger than 90% of all calculated emission rates based on all data categories. This upper limit does not consider uncertainties of the diffusive microlayer approach according to Liss and Merlivat [1986]. The global oceanic emissions are on the low side of previous estimates, and the role of oceanic emissions in global NMHC budgets appears to be of minor importance. Nevertheless, in the remote marine atmosphere the ocean is the dominant source of alkenes [Plass-Dümler *et al.*, 1993] which have a local impact on the photochemistry [Donahue and Prinn, 1990].

The conclusions remain limited in some aspects, since the data coverage is not uniform. Also, there are still a number of open questions, and some points should be considered in future investigations. Clearly, there is a lack of data from the southern oceans and a lack of complete seasonal cycles at one location. Future measurements of dissolved NMHC should be combined with the measurements of those parameters which are known to have an impact on NMHC concentrations: the wind speed, the insolation, the total DOC concentration, and the photochemical reactive fraction of DOC [Ratte, 1993].

References

- Bonsang, B., and G. Lambert, Nonmethane hydrocarbons in an oceanic atmosphere, *J. Atmos. Chem.*, 2, 257-271, 1985.
- Bonsang, B., M. Kanakidou, and G. Lambert, Non methane hydrocarbon chemistry in the atmosphere of an equatorial forest: A case of indirect photochemical production of OH radicals, *Geophys. Res. Lett.*, 14, 1250-1253, 1987.
- 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, On the low relative composition variability of light nonmethane hydrocarbons dissolved in seawater, *C. R. Acad. Sci., Ser. 2*, 308, 495-500, 1989.
- Bonsang, B., D. Martin, G. Lambert, M. Kanakidou, J.C. Le Rouley, and G. Sennequier, Vertical distribution of nonmethane hydrocarbons in the remote marine boundary layer, *J. Geophys. Res.*, 96, 7313-7324, 1991.
- Brooks, J.E., 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.E., A.D. Fredericks, W.M. Sackett, and J.W. Swinnerton, Baseline concentrations of light hydrocarbons in Gulf of Mexico, *Environ. Sci. Technol.*, 7, 639-642, 1973.
- Brown, J., A. Colling, D. Park, J. Phillips, D. Rothery, and J. Wright, *Ocean Circulation*, edited by G. Bearman, 238 pp., Pergamon, New York, 1989.
- Butler, J.H., J.W. Elkins, and T.M. Thompson, Tropospheric and dissolved N₂O of the west Pacific and east Indian Oceans during the El Nino southern oscillation event of 1987, *J. Geophys. Res.*, 94, 14,865-14,877, 1989.
- Donahue, N.M., and R.G. Prinn, Nonmethane hydrocarbon chemistry in the remote marine atmosphere, *J. Geophys. Res.*, 95, 18387-18411, 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.
- Ehhalt, D.H., and J. Rudolph, On the importance of light hydrocarbons in multiphase atmospheric systems, *Ber. der Kernforschungsanlage Jülich, Jül-1942*, 43 pp., 1984.
- Feldman, G.C., A.Y. Yoder, M.R. Lewis, and P.A. Blanchard, Ocean color from space, report U.S. Global Ocean Flux Study Off., Woods Hole Oceanogr. Instit., Woods Hole, Mass., 1989.
- Frank, D.J., W. Sackett, R. Hall, and A. Fredericks, Methane, ethane and propane concentrations in Gulf of Mexico, *Am. Assoc. Petr. Geol. Bull.*, 54, 1933-1938, 1970.
- Kanakidou, M., Contribution à l'étude des sources des hydrocarbures légers non méthaniques dans l'atmosphère, dissertation, Univ. de Paris VII, Paris, 1988.
- Kanakidou, M., B. Bonsang, J.C. Le Rouley, G. Lambert, D. Martin, and G. Sennequier, Marine source of atmospheric acetylene, *Nature*, 333, 51-52, 1988.
- Lamontagne, R.A., Distribution of carbon monoxide and C₁-C₄ hydrocarbons in the northeastern portion of the Bering Sea during the summer of 1977, *Rep. 8356*, Nav. Res. Lab., Washington, D.C., 1979.
- Lamontagne, R.A., J.W. Swinnerton, and W.J. Linnenbom, 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*, edited by T.R.P. Gibb Jr., *Adv. Chem. Ser.*, 147, 163-171, 1975.
- Linnenbom, V.J., and J.W. Swinnerton, Low molecular weight hydrocarbons and carbon monoxide in seawater, in *Organic Matter in Natural Waters*, edited by D.W. Hood, pp. 455-467, University of Alaska Press, Fairbanks, 1970.
- 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-Menard, pp. 113-127, D. Reidel, Norwell, Mass., 1986.

- Macdonald, R.W., Distribution of low molecular weight hydrocarbons in southern Beaufort Sea, *Environ. Sci. Technol.*, **10**, 1241-46, 1976.
- Marine General Staff, *Morskoi Atlas*, vol. 2, *Fiziko-geograficheskij*, edited by the Moskva, Russia, 1953.
- Paltridge, G.W., and C.M.R. Platt, *Radiative Processes in Meteorology and Climatology*, 318 pp., Elsevier, New York, 1976.
- Plass, C., R. Koppmann, and J. Rudolph, Measurements of dissolved nonmethane hydrocarbons in seawater, *Fresenius Z. Anal. Chem.*, **339**, 746-749, 1991.
- 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., Die Bedeutung der Ozeane als Quelle für leichte Kohlenwasserstoffe in der Atmosphäre, dissertation, Univ. zu Köln, Cologne, Germany, 1992.
- Plass-Dülmer, C., A. Khedim, R. Koppmann, F.J. Johnen, J. Rudolph, and H. Kuosa, Hydrocarbon emissions from the Atlantic, *Global Biogeochem. Cycles*, **7**, 211-228, 1993.
- Ratte, M., C. Plass-Dülmer, R. Koppmann, J. Rudolph, and J. Denga, Production mechanism of C₂-C₄ hydrocarbons in seawater: Field measurements and experiments, *Global Biogeochem. Cycles*, **7**, 369-378, 1993.
- Ratte, M., Untersuchungen zum Produktionsmechanismus leichter Nichtmethan-Kohlenwasserstoffe im Meerwasser, dissertation, Rheinisch-Westfälische Technische Hochschule Aachen, Aachen, Germany, 1993.
- Rudolph, J., and D.H. Ehhalt, Measurements of C₂-C₅ hydrocarbons over the North Atlantic, *J. Geophys. Res.*, **86**, 11,959-11,964, 1981.
- Sawada, S., and T. Totsuka, Natural and anthropogenic sources and fate of atmospheric ethylene, *Atmos. Environ.*, **20**, 821-832, 1986.
- Suzuki, Y., E. Tanoue, and H. Ito, A high-temperature catalytic oxidation method for the determination of dissolved organic carbon in seawater: Analysis and improvement, *Deep-Sea Res., Part A*, **39**, 185-198, 1992.
- Swinerton, J.W., and R.A. Lamontagne, The oceanic distribution of low-molecular-weight hydrocarbons, *Environ. Sci. Technol.*, **8**, 657-663, 1974.
- Swinerton, J.W., and V.J. Linnenbom, Determination of C₁ to C₄ hydrocarbons in seawater by gas chromatography, *J. Gas Chromatogr.*, **5**, 570-573, 1967a.
- Swinerton, J.W., and V.J. Linnenbom, Gaseous hydrocarbons in seawater: Determination, *Science*, **156**, 1119-1120, 1967b.
- Swinerton, J.W., R. A. Lamontagne, and J.S. Bunt, Field study of carbon monoxide and light hydrocarbon production related to natural biological processes, *Rep. 8099*, Nav. Res. Lab., Washington, D.C., 1977.
- U.S. Navy, *Marine Climatic Atlas of the World*, vol. 3, *Indian Ocean*, *Navair 50-1C-529*, Washington D.C., 1957.
- Wangersky, P.J., Dissolved organic carbon methods: A critical review, *Mar. Chem.*, **41**, 61-74, 1993.
- Wilson, D.F., J.W. Swinerton, and R.A. Lamontagne, Production of carbon monoxide and gaseous hydrocarbons in seawater: Relation to dissolved organic carbon, *Science*, **168**, 1577-1579, 1970.

R. Koppmann, C. Plass-Dülmer, M. Ratte, and J. Rudolph, Institut fuer Atmosphärische Chemie, Forschungszentrum Juelich, 52425 Juelich, Germany. (e-mail: r.koppmann@kfa-juelich.de; chr.plass-duelmer@kfa-juelich.de; m.ratte@kfa-juelich.de)

(Received September 10, 1993; revised September 7, 1994; accepted September 15, 1994.)