

EMISSIONS OF LIGHT NONMETHANE  
HYDROCARBONS FROM THE ATLANTIC  
INTO THE ATMOSPHERE

C. Plass-Dülmer, A. Khedim, R. Koppmann, F. J. Johnen,  
and J. Rudolph

Institut für Atmosphärische Chemie, Jülich, Germany

H. Kuosa

Tvärminne Zoological Station, Hanko, Finland

**Abstract.** During two Atlantic cruises of the German research vessel *Polarstern*, 1988 and 1989, the concentrations of light nonmethane hydrocarbons (NMHC) in seawater were measured. On the basis of a simple budget analysis, the oceanic mixed layer represents a NMHC reservoir with an internal production and a major loss by emission into the atmosphere. As a consequence, the concentrations of NMHC depend on the rates of ocean-atmosphere exchange: high exchange rates reduce the concentrations and vice versa. With the prevailing transfer velocities the emission rates were calculated according to ocean-atmosphere exchange models. The regional averages of the alkene emission rates vary by 1 order of magnitude. For ethene the maximum value was  $5 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ . The emissions of the various alkanes were generally below  $1 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ . The total  $\text{C}_2\text{-C}_4$  hydrocarbon emissions during both cruises average  $6 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , 70 % of which are alkene emissions, with ethene alone contributing 42 % to the total. No indications for enhanced emissions of NMHC at high phytoplankton concentrations or in the proximity to coastlines were observed. Thus we regard the emissions as representative for the mid-Atlantic and the season of the investigations, August to October. The calculated emission rates of the short-lived alkenes are validated by comparison with atmospheric measurements of NMHC. The emission rates are substantially lower than the majority of reported oceanic emission estimates by up to about 2 orders of magnitude.

## 1. INTRODUCTION

In recent years, oceanic emissions of light nonmethane hydrocarbons and their importance for the chemistry of the marine atmosphere received increasing interest [Rudolph and

Ehhalt, 1981; Bonsang et al., 1988; Donahue and Prinn, 1990; Koppmann et al., 1992; Plass et al., 1992]. The emission rates can be estimated from budget considerations based on atmospheric loss processes due to reactions with OH-radicals and ozone or by a direct calculation from oceanic NMHC concentrations using ocean-atmosphere exchange models. They differ between some  $10^8$  and some  $10^{11}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ . Owing to these large discrepancies, the impact of the oceanic NMHC emissions on the marine atmospheric chemistry is still controversial. Since for the higher emission estimates considerable effects on the atmospheric levels of ozone [Donahue and Prinn, 1990] and on the OH-radical concentration can be expected [Liu et al., 1989; Donahue and Prinn, 1990], the knowledge of the actual magnitude of oceanic emissions is very important.

In a previous paper we reported results of measurements of NMHC in seawater from a ship cruise in the region of the mid-Atlantic in September/October 1988 [Plass et al., 1992]. Oceanic emission rates of some  $10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  were calculated. These are clearly on the low side of the published estimates. However, at least for the short-lived alkenes, they are consistent with atmospheric removal rates [Koppmann et al., 1992].

Regarding the results of Plass et al. [1992] there is still the open question, whether the results from the cruise in 1988 are representative for the mid-Atlantic and what are the parameters which cause enhanced emissions. Thus in this paper we present a more sophisticated analysis of exchange rates between the ocean and the atmosphere. Another point which needs more consideration is the possible existence of concentration gradients in the upper few meters of the ocean. These could significantly affect the calculated emission rates which were based on the concentrations in 11 m depth [Plass et al., 1992]. Assuming homogeneous distributions of NMHC concentrations in the mixed layer only seems reasonable if the mixing is sufficiently fast relative to possible production and loss processes.

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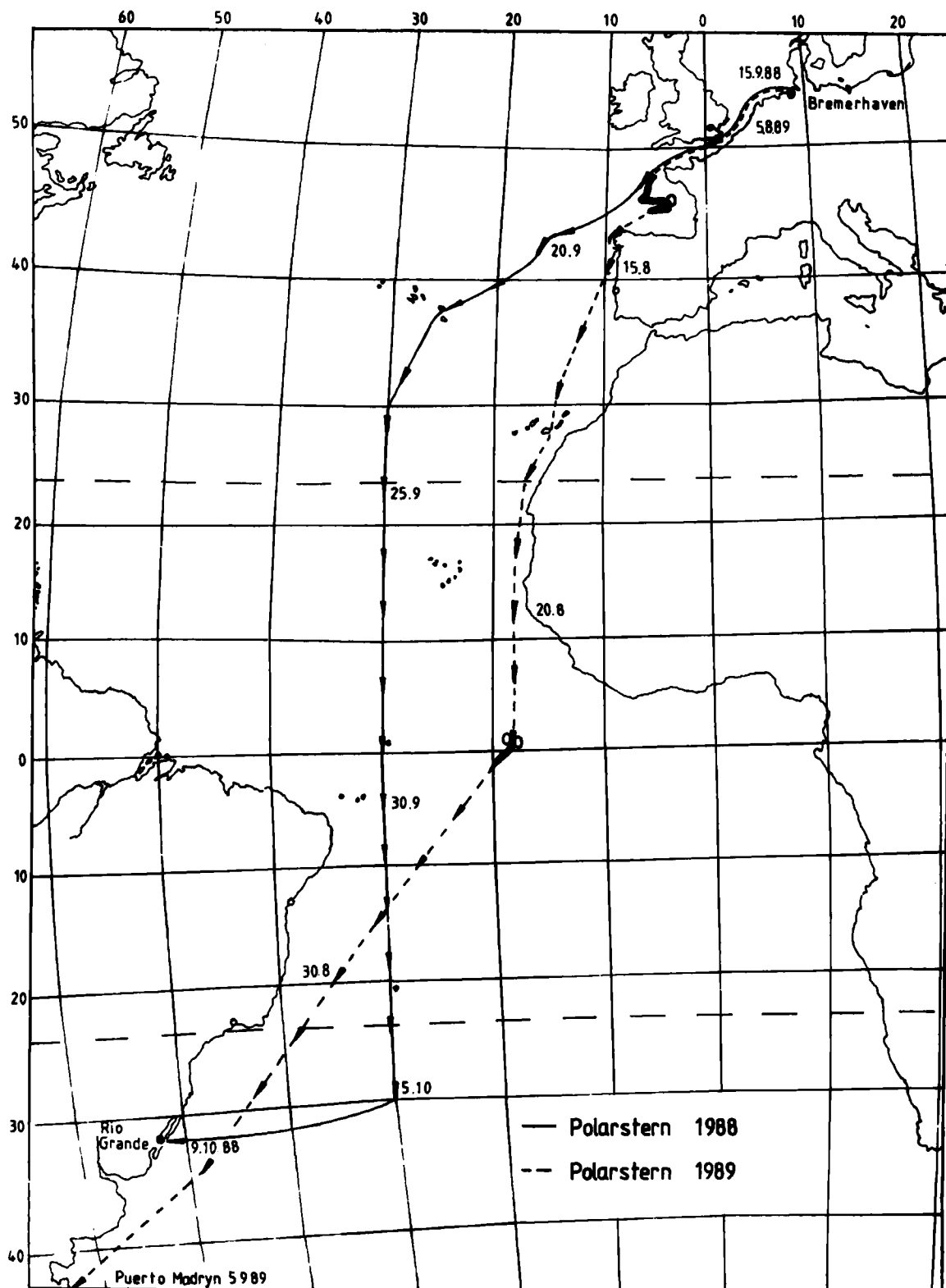


Fig. 1. Cruise tracks of R.V. *Polarstern*: ANT VIII/1 started September 15, 1988, at Bremerhaven, Germany, and ended October 9, 1988, in Rio Grande do Sul, Brazil; ANT VIII/1 started August 5, 1989, at Bremerhaven, Germany, and ended September 9, 1989, in Puerto Madryn, Argentina. The circles indicate the positions of the vertical profiles taken in 1989.

In this paper, measurements of NMHC in the surface water of the Atlantic and some vertical profiles obtained during a cruise in 1989 will be presented. This cruise included regions both of high and low biological primary productivity. This provides us with an extended data base of NMHC concentrations and emissions for the region of the mid-Atlantic. The simple budget of NMHC in the surface seawater presented by Plass et al. [1992] is improved, and our current knowledge of the NMHC production in the ocean and the main loss mechanism is discussed. The contribution of oceanic emissions to the atmospheric budgets of NMHC in the marine atmosphere will be estimated.

## 2. EXPERIMENTAL

In Figure 1 the cruise tracks of *ANT VII/1* in September/October 1988 and *ANT VIII/1* in August/September 1989 are shown. Plass et al. [1991, 1992] have already described the experimental setup for measurements of NMHC in seawater and the results from the cruise in 1988. Here only a brief overview will be given: NMHC concentrations in the ocean were measured by in situ gas chromatography. In 1989 the measurements covered the latitude range between 50°N and 35°S. Samples of seawater were taken in 11 m depth. In order to avoid contamination by the ship, the intake line extended 0.5 m beyond the hull of the ship. The intake line was permanently flushed with seawater at a flow rate of about  $1 \text{ m}^3 \text{ h}^{-1}$ , and the samples were split off from that flow.

Surface samples of seawater from the upper 0.5 m of the ocean were collected with a stainless steel bucket. Immediately after sampling the water was filtered and the analysis was started within less than 15 min. The bucket was reconditioned by mechanical cleaning and heating at 370 K for more than 1 hour. The method was checked for reproducibility by repeated measurements of surface water at the same position. The relative variations of consecutive measurements were below 20 %. However, two surface measurements from August 8 and 9 have experimental uncertainties of up to 50 %. Here the ship drifted at low wind velocities, and contamination from the ship cannot be ruled out completely.

A specially designed sampler was used to collect water from depth down to 100 m. It was optimized for minimal contamination and minimal loss of the highly volatile hydrocarbons during sampling. In Figure 2 the sampler is shown schematically. During sampling, seawater passes the intake line (1 m, ID 2 mm) and an algae filter (glass fiber, Whatman GF/F, pore size  $0.8 \mu\text{m}$ ) into a sample and a flushing container, 2 dm<sup>3</sup> each. The only material in contact with the sample is stainless steel, except for the teflon seals in the ball valves (Whitey) and the glass fiber filter. For sampling the evacuated containers were installed in the pressure tank (Figure 2) with the pressurized valve closed and the other valves opened. The sampler was lowered to the required water depth, and the valve was opened automatically. The containers were filled within 5-10 min, depending on the water pressure. Subsequently, the pressurized valve was closed again. After the sampler was brought back on deck, the valves at the sample containers were closed, the filled containers were removed and replaced by evacuated ones. Thus five samples from depth between the surface and 100 m could be collected within 90 min. The samples were analyzed

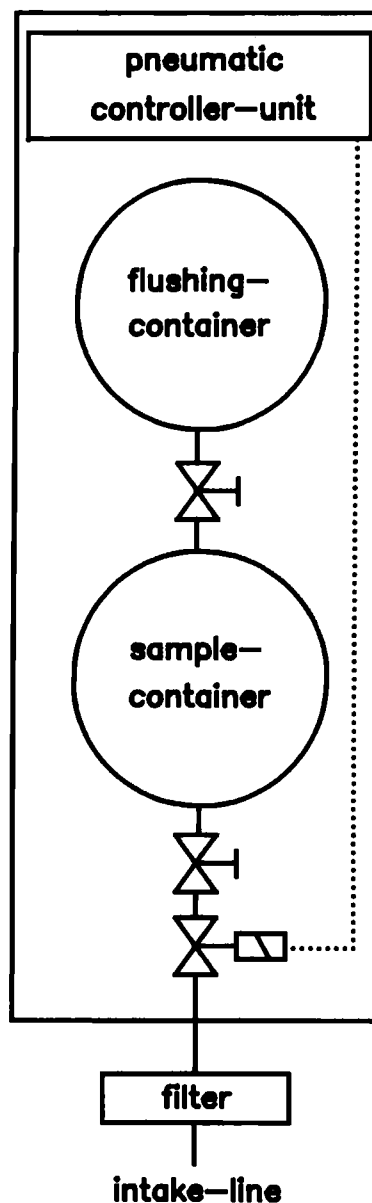


Fig. 2. Schematic drawing of the sampler; hand valves are installed at both sides of the sample container, a pressurized valve between filter and sample container.

for NMHC within 15 hours. The system was checked for possible contaminations, the stability of the samples in the containers and gas loss during sampling. The resulting errors of the alkene and alkane concentrations were less than 20 % and about 35 % for acetylene. After use, the containers were flushed three times with helium and evacuated. During the final evacuation step the containers were heated at about 370 K.

The dissolved hydrocarbons were stripped from the seawater sample with Helium (for details, cf. Plass et al. [1991]). This allowed use of identical gas chromatographic techniques for

the measurement of hydrocarbons in seawater and in the atmosphere. Details of the gas chromatographic techniques have been published elsewhere [Rudolph et al., 1986, 1990; Koppmann et al., 1992]. The hydrocarbons were cryogenically preconcentrated and the  $C_2$ - $C_4$  hydrocarbons were separated on a packed column (6 m, 2 mm ID, Porapak QS, 100/120 mesh). The hydrocarbons were measured by a flame ionization detector (FID). The gas chromatographic system was calibrated by comparison with a reference air of known composition. The reproducibilities of the measurements were better than 30 % for the  $C_2$ - $C_4$  hydrocarbons, the lower limits of detection were some pMol/L ( $10^{-12}$  Mol per L seawater).

During the cruise in 1989 about 110 samples from 11 m depth, three vertical profiles, and five samples of surface water from the upper 0.5 m were measured. The positions of the depth profiles are indicated by the circles in Figure 1: one in the Bay of Biscay (depth of mixed layer  $z_M = 25$  m) and two at the equator ( $z_M = 70$  m). The depth of the thermocline was adopted as the depth of the mixed layer.

### 3. RESULTS

#### 3.1. Characterization of the Investigated Ocean Areas

In the mid-Atlantic regional differences in the physical, chemical, and biological parameters of the seawater exist mainly due to current systems and associated upwelling regions. In the area of investigation, the mid-Atlantic, two major upwelling regions are encountered. Off the northwest coast of Africa there is a strong continental upwelling between 15°N and 23°N and equatorial upwelling occurs approximately between 5°S and 10°N [Sverdrup et al., 1942]. The cruises in 1988 and 1989 followed different tracks (Figure 1), and some difficulties are implied in comparing the obtained results. We will distinguish between ocean areas with upwelling and areas without direct influence of upwelling. The exact locations of the upwelling regions were determined from the minima of the seawater surface temperature. This resulted in the subjects 35°N-8°N, 8°N-3°S, and 3°S-30°S for the 1988 cruise [Plass et al., 1992] and 38°N-23°N, 23°N-2°S, and 2°S-35°S for the 1989 cruise. The equatorial region was broader in 1989 than in 1988, since we included the continental upwelling region off northwest Africa.

Estimates of the phytoplankton biomass were based on the counting of cell numbers in samples of surface water. In the 1989 cruise, considerable differences in the phytoplankton biomasses of up to a factor of 20 were found with maxima of 15  $\mu\text{gC/L}$  in the upwelling regions and a minimum of less than 0.8  $\mu\text{gC/L}$  in the south Atlantic.

#### 3.2. NMHC Concentrations in Seawater

In Figure 3a the latitudinal distributions of ethene in seawater are shown, in Figure 3b the distributions of ethane (data of the cruise in 1988 are from Plass et al. [1992]). Table 1 summarizes the mean concentrations from the different watermasses (according to section 3.1). South of the equator the concentrations were similar in 1988 and 1989. However, the high concentrations of about 600 pMol/L for ethene and ethane observed at 30°N in 1988 were not found in 1989.

Plass et al. [1992] reported proportionality between different

alkenes and between different alkanes with correlation coefficients better than 0.95 for all latitude ranges of 1988. The 1989 data generally showed poorer correlations. Again, the highest correlation coefficients (0.76-0.93) were found for correlations between different alkenes, whereas no significant correlations were found between different alkanes and between alkenes and alkanes.

The latitudinal pattern of ethene (Figure 3a) is similar to those of the other alkenes (not shown), but the ethene concentration are higher (Table 1). Generally, the alkanes show comparable latitudinal patterns as ethane but lower concentrations.

#### 3.3. Vertical Profiles of NMHC

In Figure 4, some of the profiles of NMHC concentrations in the upper 100 m of the ocean are shown. The highest NMHC concentrations are always found within the mixed layer. The vertical profile from the Bay of Biscay differs from the others by pronounced gradients between the upper 20 m and below as a result of a mixed layer of only 25 m depth compared with 70 m at the equator. Table 2 gives a list of the  $C_2$  and  $C_3$  hydrocarbon concentrations in surface water. For comparison, concentrations obtained in 11 m depth are included. These refer to mean values of the two measurements performed closest to the sampling time of the surface water. Table 3 summarizes the ratios between concentrations in surface water and 11 m depth for the  $C_2$ - $C_4$  hydrocarbons by means of averages weighted with their reciprocal squared errors. The weighted averages were preferred to arithmetic averages, since some of the measurements have large experimental uncertainties.

The vertical profiles and surface samples provide information about NMHC gradients in the upper 20-30 m of the Atlantic. Vertical variations in the alkene and acetylene concentrations are less than 30 %. Consequently, the alkene and acetylene concentrations measured in 11 m depth can be regarded as representative for at least the upper 20 m of the mixed layer including the uppermost 0.5 m. For the alkanes, vertical gradients in the upper 30 m occasionally exist with increasing concentrations toward the surface, for example, up to a factor of 5 higher concentrations at the surface than in 11 m depth. In that case the concentrations obtained at 11 m depth may underestimate the concentrations at the surface substantially.

### 4. DISCUSSION

Oceanic emission rates were calculated with an ocean-atmosphere exchange model [Liss and Merlivat, 1986; Watson et al., 1991] based on our measurements of the NMHC concentrations in seawater and the atmosphere (R. Koppmann, unpublished data, 1991). The emission fluxes are given by

$$F = k_w (c_w - c_a/H) \quad (1)$$

where  $k_w$  is the transfer velocity for individual NMHC calculated as follows:  $k_w$  for  $\text{CO}_2$  according to Liss and Merlivat [1986] with the temperature dependence of the Schmidt number for  $\text{CO}_2$  [Jähne et al., 1987],  $k_w$  for  $\text{CO}_2$  was then transformed for individual NMHC according to

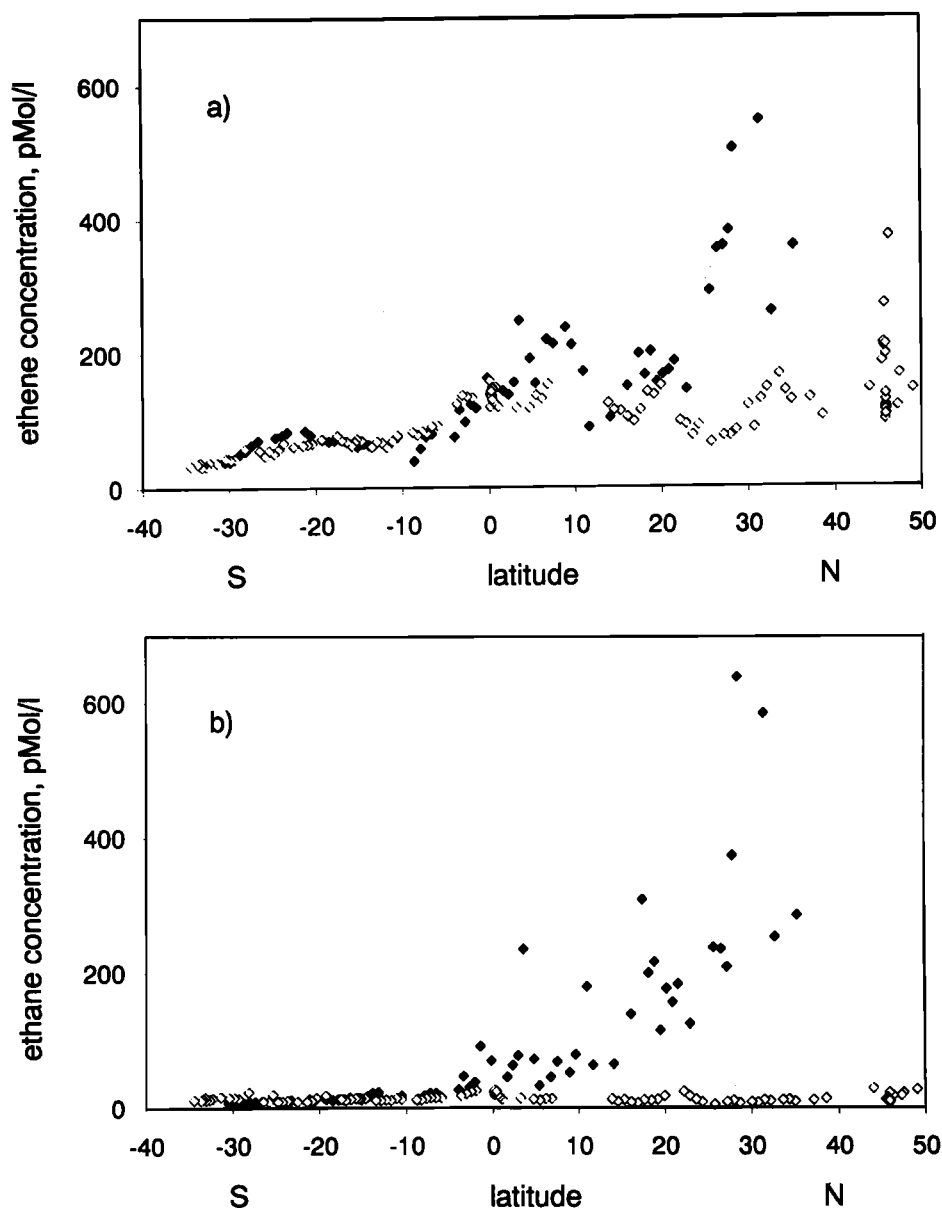


Fig. 3. Latitudinal distribution of the (a) ethene concentration and (b) ethane concentration in seawater. The open symbols are data from 1989; the filled symbols are data from 1988 [Plass et al., 1992].

Kanakidou [1988] with slight modifications: diffusion constants were calculated according to Wilke and Chang [1955] with the molar volumes at boiling point from Himmelblau [1964] or derived from the critical volumes [Reid and Sherwood, 1966] according to Perry and Chilton [1973];  $c_w$  is the NMHC concentration in the seawater,  $c_a$  is the NMHC concentration in the atmosphere, and  $H$  is the dimensionless Henry's law constant. Values were taken from McAuliffe [1966] and Wilhelm et al. [1977].

The oceanic mixed layer is highly supersaturated by more than an order of magnitude for most light NMHC relative to the atmosphere except for acetylene with supersaturations

between 4 and 8. Similar results have been reported previously [Bonsang et al., 1988; Plass et al., 1992]. For the highly supersaturated hydrocarbons, equation (1) may be simplified

$$F = k_w (c_w) \quad (2)$$

#### 4.1. Impact of Vertical Gradients on Oceanic NMHC Emissions

The emission rates are proportional to the concentration gradient across the surface film with a typical thickness of several  $10 \mu\text{m}$  [Liss and Merlivat, 1986; Broecker and Peng,

TABLE 1. NMHC Concentrations in Seawater

compound	1988 <sup>a</sup>				1989			
	35°N-30°S	35°N-8°N	8°N-3°S	3°S-30°S	50°N-35°S	38°N-23°N	23°N-2°S	2°S-35°S
ethene	147 (110)	246 (123)	165 (49)	63 (14)	107 (52)	108 (32)	129 (17)	69 (31)
propene	73 (57)	125 (61)	78 (35)	31 (9)	41 (16)	43 (16)	44 (9)	30 (12)
1-butene	42 (30)	71 (30)	44 (16)	18 (7)	30 (11)	31 (7.7)	34 (6.6)	22 (8.0)
ethane	96 (129)	221 (151)	69 (51)	13 (6)	14 (5.5)	9.1 (2.0)	17 (6.0)	14 (4.3)
propane	29 (38)	65 (46)	21 (16)	5.8(1.8)	6.4 (3.6)	7.5 (2.2)	9.0 (4.6)	4.5 (1.4)
i-butane	2.7(3.1)	4.9(4.0)	2.9(1.4)	1.2(0.9)	1.4 (1.1)	1.1 (0.8)	0.9 (0.5)	1.1 (0.8)
n-butane	15 (21)	32 (28)	10.4(8.3)	2.8(1.4)	3.5 (2.4)	2.2 (1.5)	4.2 (2.6)	2.7 (1.1)
acetylene	5.1(2.9)	6.6(2.9)	4.7(1.0)	4.1(1.3)	10.3 (3.9)	7.1 (1.5)	10 (3.6)	10 (2.6)

<sup>a</sup> Data are from Plass et al. [1992].

Concentrations are in pMol/L. Regional averages, standard deviations are in paranthesis.

1982]. Beyond this film a constant concentration in the bulk seawater is assumed. However, as we have shown above in the case of alkanes, concentration gradients in the upper 20 m are observed. Also, some of the vertical profiles of light alkanes and alkenes reported in the literature show concentration maxima at the surface or in depth between 20 and 80 m with up to fourfold enhanced concentrations [Swinerton and Linnenbom, 1967; Linnenbom and Swinerton, 1970; Swinerton and Lamontagne, 1974; Brooks and Sackett, 1973; Macdonald, 1976; Bonsang and Lambert, 1990].

Concentration maxima can be expected when the mixing processes are slower than production or loss processes in the mixed layer. A quantitative description of the intensity of vertical mixing is not yet available; however, it is related to the wind stress applied on the surface [Osborn, 1986]. In Figure 5 the ratios of the concentrations from the surface and 11 m depth are plotted as a function of the wind velocity for ethene and ethane (concentrations taken from Table 2). For ethene the surface concentrations are close to the concentrations in 11 m depth independent of the wind velocity. In contrast, the ratios between ethane concentrations at the surface and in 11 m depth tend to increase with decreasing wind velocity up to a ratio of 5 at a wind velocity of 2 m/s. Above about 7 m/s, no significant gradient in ethane concentrations can be observed. However, the low number of data and the large spread only allow to state a potential gradient of ethane at low wind velocities. These features for ethene and ethane are also observed for the other C<sub>2</sub>-C<sub>4</sub> alkenes and alkanes, respectively (Tables 2 and 3). From our data we cannot exclude the possibility of a concentration gradient within the uppermost 0.5 m. However, it seems unlikely since the intensity of vertical mixing is highest in that layer.

The oceanic alkene and acetylene emissions can be reliably calculated from concentrations in 11 m depth according to equations (2) and (1), respectively. However, for the calculation of the alkane emissions, vertical concentration gradients at low wind velocities have to be considered. At these conditions the local emissions may be underestimated by up to a factor of 5 (cf. Figure 5). However, recalculation using the alkane gradients shown in Figure 5 would enhance the

regionally averaged alkane emissions by less than 15 % compared to calculations based on the concentrations at 11 m depth. This effect is small since only 30 % of the data were measured at wind velocities below 7 m/s and the corresponding transfer rates are low. The latter is due to the nonlinear relationship between wind and transfer velocities [Liss and Merlivat, 1986]. Therefore the contribution of emissions at low wind velocities to the regional averages is small. Thus for the calculation of regionally averaged emissions it is justified to neglect alkane gradients in the upper part of the mixed layer.

In the following we will calculate emission rates from the measurements of NMHC at 11 m depth. This is appropriate for most conditions except for the alkanes at wind velocities below 7 m/s.

#### 4.2. Time Scales of Representative Oceanic Emissions

The emission rates calculated according to equations (1) or (2) using transfer velocities derived from the actual local wind velocities measured aboard the ship may be regarded as "actual emissions", which are representative on time scales of the persistence of the actual wind velocities, for example, hours to days. Such "actual emissions" are important for the determination of the actual contributions of oceanic sources to the budgets of NMHC in the marine atmosphere (cf. sections 4.4 and 4.5).

The actual emissions are quite variable in time and may deviate substantially from the local averages for longer time periods. These averages can be used to estimate source and loss processes in the seawater. The calculation of "mean local emissions" requires the knowledge of the variations in time of both the transfer velocities and the concentrations of NMHC in seawater. However, data from measurements at a fixed location over a longer time period are not available. Thus we can only consider the variations of hydrocarbon concentrations as may be expected from a budget of hydrocarbons in the mixed layer of the ocean.

Plass et al. [1992] proposed a simple balance equation of NMHC in the oceanic mixed layer in order to estimate the production and loss processes, the latter consisting of

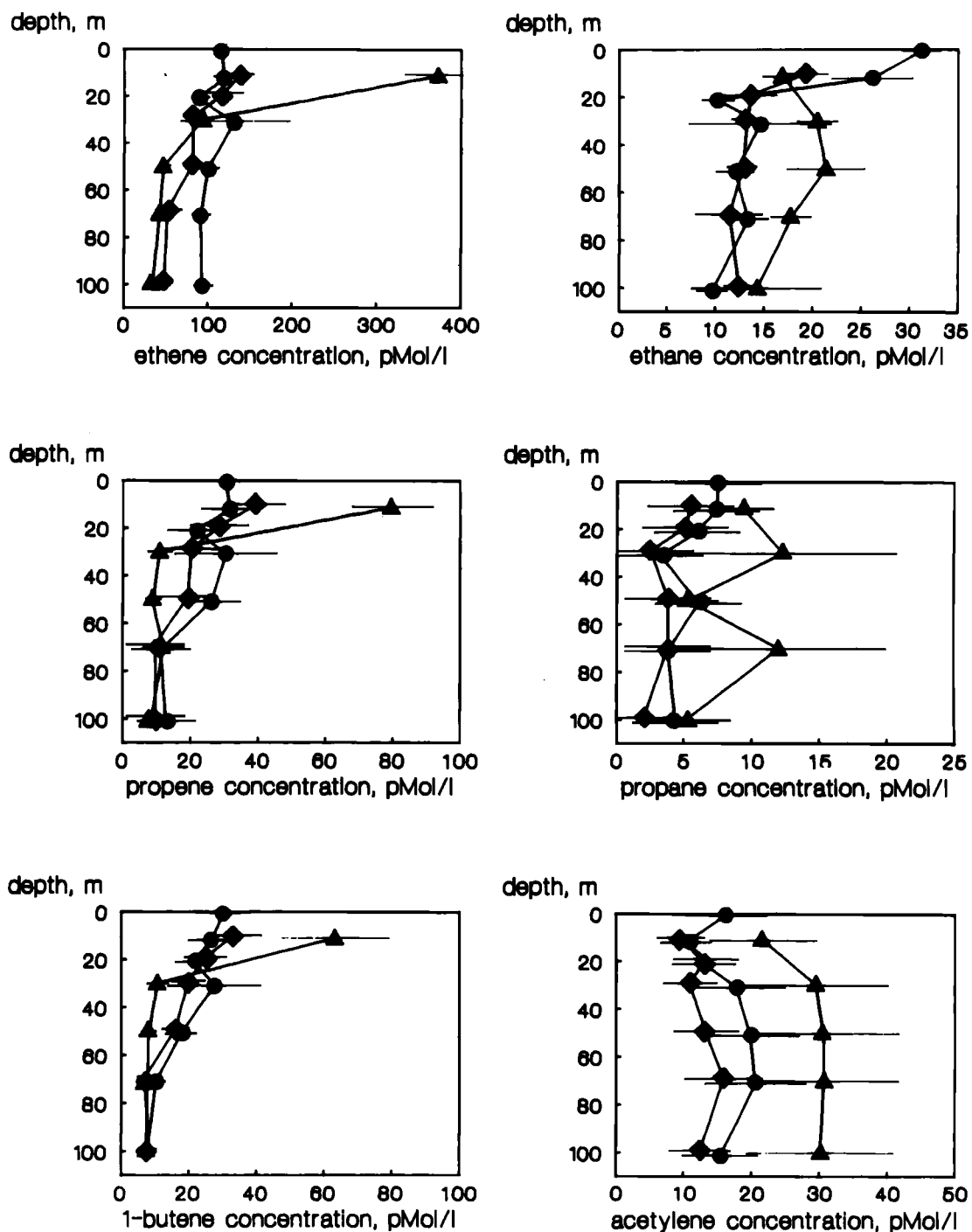


Fig. 4. Vertical profiles of some NMHC. Bay of Biscay-profile (triangles): August 10, 6:00 p.m.; 46°N, 4°W; depth of water  $z_D$ , 166 m; depth of mixed layer  $z_M$ , 25 m; equator-profile 1 (diamonds): August 22, 6:00 a.m.; 0°N, 18°W;  $z_D$ , 7000 m;  $z_M$ , 70 m; equator-profile 2 (circles): August 24, 11:00 a.m.; 0°N, 18°W;  $z_D$ , 7000 m;  $z_M$ , 70 m.

TABLE 2. Ethene and Ethane Concentrations Measured in the Surface Water Compared to 11 m Depth

Latitude, Time	Ethene		Propene		Ethane		Propane		Acetylene	
	Surface	11 m	Surface	11 m	Surface	11 m	Surface	11 m	Surface	11 m
46°N, Aug. 8, 1500	125 (25)	116 (9)	68 (8)	64 (7)	38 (10)	8 (5)	11 (3)	4 (1)	8 (4)	11 (1)
46°N, Aug. 9, 1500	88 (44)	118 (9)	41 (21)	65 (7)	18 (9)	8 (5)	10 (5)	4 (1)	10 (4)	9 (1)
46°N, Aug. 10, 1200	173 (19)	164 (22)	69 (10)	69 (8)	23 (2)	16 (1.5)	7 (4)	8 (1)	19 (2)	18 (2)
7°N, Aug. 20, 1700	93 (19)	140 (20)	39 (9)	50 (7)	14 (3)	13 (2)	6 (3)	4 (3)	8 (3)	8 (3)
1°N, Aug. 24, 1000	116 (17)	129 (11)	31 (9)	39 (6)	31 (3)	25 (3)	8 (3)	7 (2)	16 (2)	12 (1)

Concentrations are in pMol/L. Errors are in parenthesis.

TABLE 3. Ratios Between Concentrations Measured at the Surface and in 11 m Depth: Weighted Averages of Five Measurements and Their Errors

Compound	Ratio
ethene	$0.89 \pm 0.08$
propene	$0.91 \pm 0.09$
1-butene	$0.95 \pm 0.18$
ethane	$1.29 \pm 0.11$
propane	$1.36 \pm 0.38$
n-butane	$1.66 \pm 0.42$
i-butane	$0.92 \pm 0.47$
acetylene	$1.11 \pm 0.10$

destruction in the seawater and emission to the atmosphere:

$$d/dt (c_w z_M) = P - (D_o + k_w) c_w \quad (3)$$

where  $z_M$  is the depth of the mixed layer;  $P$  is the production rate per surface area; and  $D_o$  is the destruction rate constant per surface area (assuming first-order destruction).

In this simple box model, homogenous hydrocarbon concentrations are assumed. It cannot be used for substances that show vertical gradients and is therefore not appropriate for the alkanes at low wind velocities (section 4.3). The hydrocarbon concentrations are controlled by the parameters  $z_M$ ,  $P$ ,  $D_o$ , and  $k_w$ . Thus the analysis of the variations of NMHC concentrations in time must consider the time scales of the variability of these parameters.

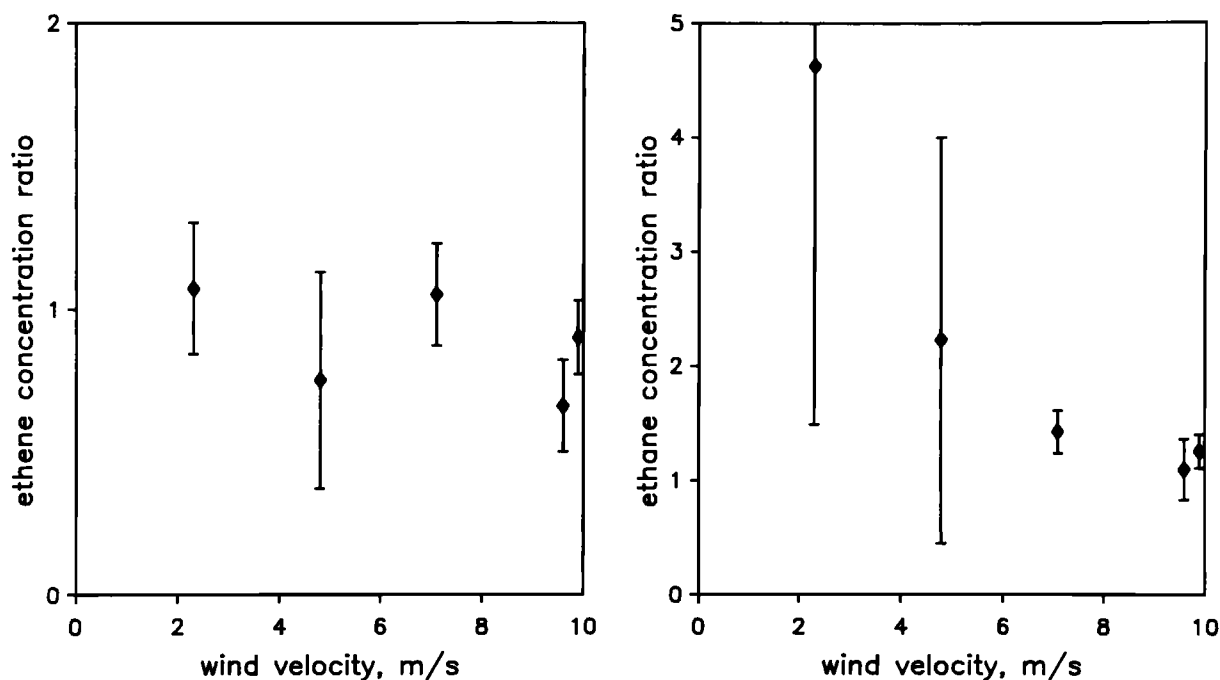


Fig. 5. Ratios of the concentrations measured at the surface and in 11 m depth for ethene and ethane.



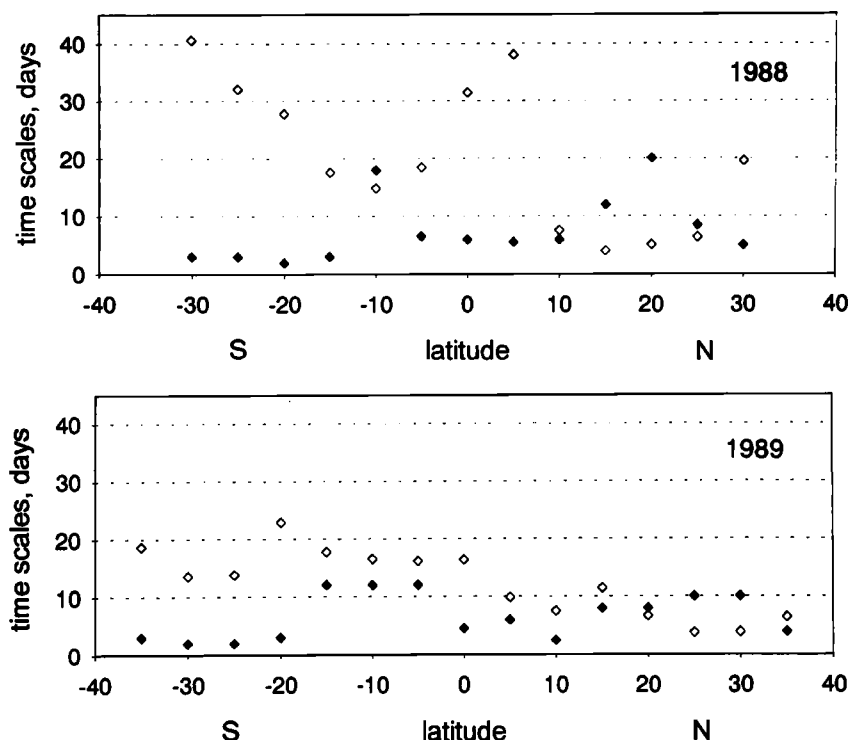


Fig. 6. Characteristic time scales: the fluctuation periods of the wind velocities (filled symbols) and the emission times ( $\tau_E$ , open symbols).

M. Ratte et al. (Production mechanism of  $C_2$ - $C_4$  hydrocarbons in seawater: Field measurements and experiments, submitted to *Global Biogeochemical Cycles*, 1992) (hereinafter referred to as Ratte et al., submitted manuscript, 1992) have not found any indications for significant destruction of alkenes in the seawater. Thus we assume that temporal changes in  $D_o$ , which must be small anyway, can be neglected. On the other hand, the production rates of alkenes seem to depend on the presence of light and of dissolved organic carbon (DOC) [Wilson et al., 1970; Ratte et al., submitted manuscript, 1992]. For the investigated region of the mid-Atlantic in September the diurnal averages of the solar insolation is, as a first approximation, assumed to be constant. DOC concentrations are reported to be fairly constant in space and change on time scales of several months within less than a factor of 3 [Williams, 1975; Ittekkot, 1982; Martin and Fitzwater, 1992]. In addition to a photochemical production from DOC a direct production from algae seems possible [Wilson et al., 1970]. Thus the time scales for stable phytoplankton densities in the open ocean have to be considered, which are generally some 10 days [Tait, 1968]. The main change of the depth of the oceanic mixed layer ( $z_M$ ) occurs with season. We therefore assume a constant value of  $z_M$  for the time scales under consideration. The above parameters may be assumed to be stable for some 10 days. It will be shown below that possible diurnal cycles of the production rate do not affect this budget.

The parameter with the largest variability is the transfer velocity  $k_w$ . Values of  $k_w$  were calculated from wind velocity

charts of the "European Center for Medium-Range Weather Forecast" (Reading, U.K.). Since the wind velocity charts are limited in their spatial resolution we will use averages for 5 deg of latitude. Typical times for changes of the wind velocities between local high and low values, denoted here as fluctuation periods of the wind velocities, are in the range of some days to about 20 days (Figure 6). With transfer velocities averaged over about 2 weeks, a characteristic relaxation time  $\tau$  of the concentrations in the mixed layer can be derived from equation (3):

$$\tau = z_M / (D_o + k_w) \quad (4)$$

An upper limit of  $\tau$  is the emission time  $\tau_E = z_M/k_w$ , which gives the relaxation time for conditions of negligible oceanic destruction. This is the time constant of the hydrocarbon loss from the mixed layer due to the emission into the atmosphere. The depth of the mixed layer was taken as the depth of the thermocline which was measured daily. The resulting time scales  $\tau_E$  range between 3 and 40 days (Figure 6).

Thus the mixed layer acts as a reservoir which is stable against short time perturbations like diurnal variations of the production rates or short-term variations of the transfer velocities. Consequently, for budget estimates we have considered the transfer velocities that are representative on the time scale of the emission times. If the fluctuation times of wind velocities are shorter than the emission times, we use transfer velocities integrated over a period of at least 2 weeks which were derived from the wind velocity charts. If this is

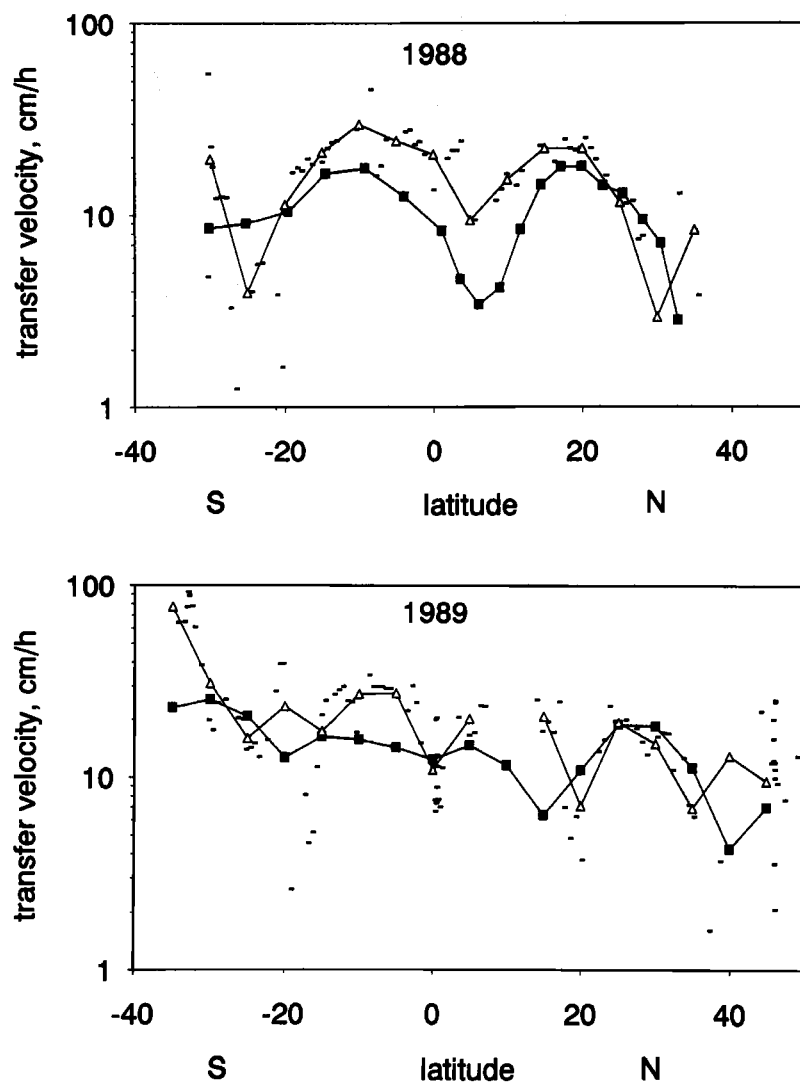


Fig. 7. Transfer velocities calculated from different wind data sets: from wind velocities measured aboard the ship (dots), from the 5° latitudinal averages of thus calculated transfer velocities (open triangles), and from wind velocity charts (Reading, U.K.) for a period of 2 weeks by first calculate transfer velocities and average thereafter (filled squares).

not the case, we use transfer velocities calculated from the actually measured wind velocities aboard the ship on account of their better accuracy. The use of different sets of wind velocity data on the resulting transfer velocities has a significant effect, as illustrated in Figure 7 for the data from both cruises. Transfer velocities calculated from the actually measured wind data can deviate by factors of 3 and more from the integrated values. These deviations are due to fluctuations of the wind velocities on short time scales, for example, days or hours. The averages of the actual transfer velocities for 5° latitude can differ from the 2-week averages by factors of 2.

By use of the appropriate transfer velocities, budget estimates and mean local emissions can be calculated which represent the prevailing conditions on the time scales of the stability of the parameters.

#### 4.3. Production and Destruction Rates in the Mixed Layer

Plass et al. [1992] assumed steady state conditions in their simple box balance of the mixed layer and reduced equation (3) to

$$c_w = P / (D_o + k_w) \quad (5)$$

This simple box model of the mixed layer needs some revisions. First, as discussed above, the appropriate transfer velocities on time scales of the emission times have to be considered. Second, alkane budgets bear more uncertainties than alkene budgets due to the vertical gradients observed in the alkane concentrations at low transfer velocities. For acetylene a budget cannot be set up. Other than the alkenes

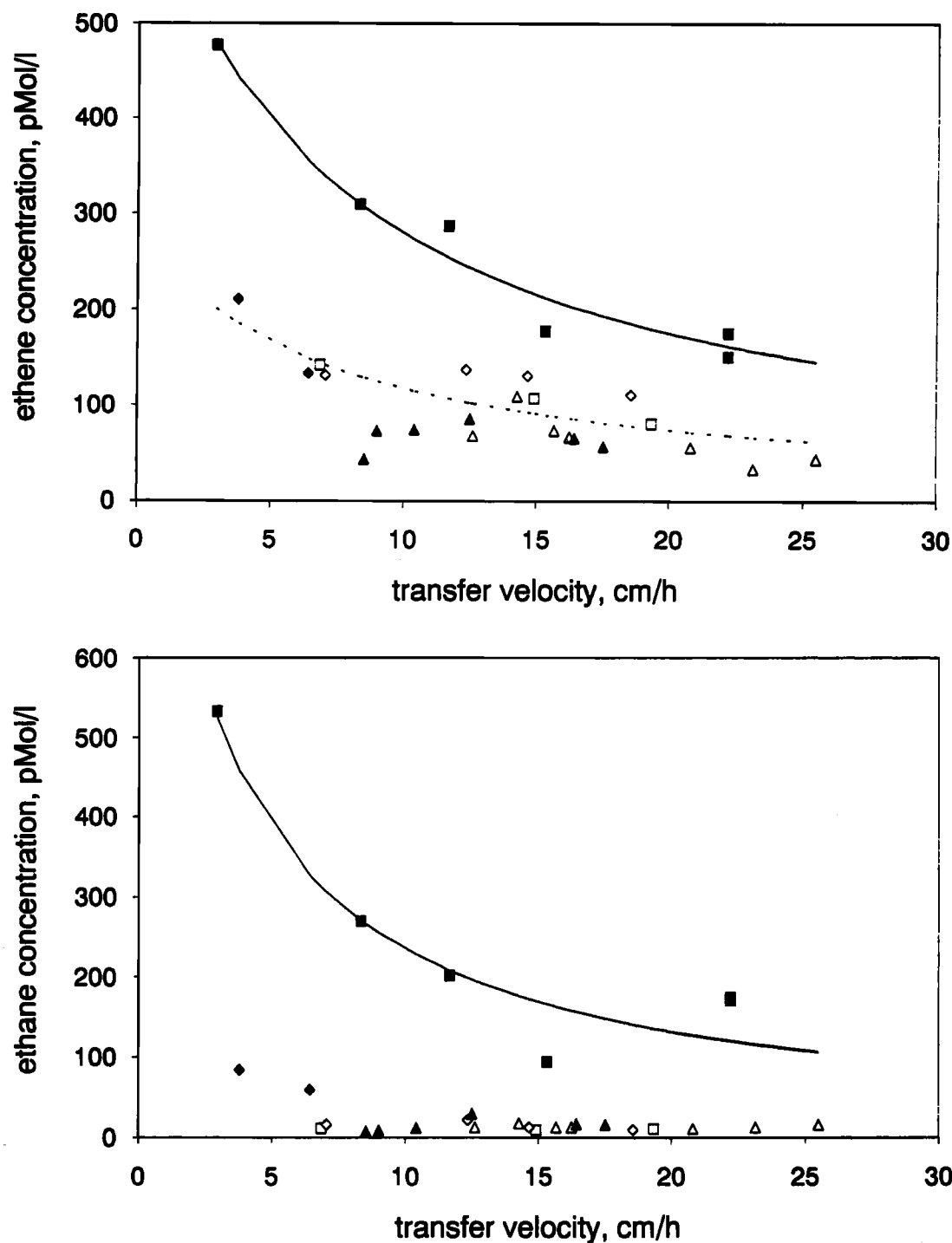


Fig. 8. Concentrations of ethene and ethane as function of the transfer velocity (averages for  $5^\circ$  latitude). The open symbols are data from 1989:  $38^\circ\text{N}$ - $23^\circ\text{N}$  (squares),  $23^\circ\text{N}$ - $2^\circ\text{S}$  (diamonds),  $2^\circ\text{S}$ - $35^\circ\text{S}$  (triangles); the filled symbols are data from 1988:  $35^\circ\text{N}$ - $8^\circ\text{N}$  (squares),  $8^\circ\text{N}$ - $3^\circ\text{S}$  (diamonds),  $3^\circ\text{S}$ - $30^\circ\text{S}$  (triangles). The lines are the results of the least squares fits according to equation (5): solid for  $35^\circ\text{N}$ - $8^\circ\text{N}$  in 1988 and dashed for the 1989 data.

and alkanes, the calculation of acetylene emissions has to consider the atmospheric concentrations according to equation (1). These are not available for the integration period of the budget,  $\tau_E$ . Finally, there is a principal difficulty in applying the budget, since we did not measure the variations of hydrocarbons in time at a single location but along the tracks of ship cruises. Thus reasonable fit parameters from equation (5) can only be expected in regions of low spatial variability of  $P$  and  $D_0$ . Also, the spatial variability of the transfer velocities should be high, and the emissions into the atmosphere should amount to a substantial loss in the total budget. However, spatially homogeneous values of  $P$  and  $D_0$  are least probable in the regions with the largest time constants  $\tau_E$ , for example, the regions south of the equator.

In Figure 8 the results for ethene and ethane are shown for different ocean regions of the cruises in 1988 and 1989, Table 4 lists the values of the fit parameters  $P$  and  $D_0$  for the regions, where spatially fairly constant production and destruction rates were obtained. The best results with standard deviations of the production rates of about 20 % or less and regression coefficients of 0.99 were found for the data from 1988 between 35°N and 8°N. Here the short emission time of generally less than 10 days and the uniform conditions of the remote ocean (30°W) may have contributed to an adequate description of the seawater budget by our simple model. The alkene data of the 1989 cruise showed no significant differences in the fit parameters between the three latitude ranges considered. A fit of all alkene data from 1989 yields standard deviations for production rates of better than 30 %. In most regions the conditions for the alkane budget were not met and alkanes will not be considered in the following discussion.

The alkene destruction rate constants in Table 4 range between 6 and 7.5 cm/hour and have errors between 20 % and 75 %. However, these errors are underestimated, since they do not consider errors which are due to the limitations of the budget. The destruction rate constants critically depend on the

concentrations measured at low transfer velocities for which the time constants  $\tau_E$  of the system are largest. For these conditions the steady state assumption in the budget bears the largest uncertainties, which in turn increases the error of the destruction rate constant.

The transfer velocities in Table 4 are by a factor of about 2 higher than the destruction rate constants  $D_0$  of the alkenes. Additionally, Ratte et al. (submitted manuscript, 1992) do not find any indications for a destruction of alkenes in glass bottles filled with seawater. Thus destruction in seawater does not appear to be an important loss process for the alkenes and equation (5) can be approximated by

$$c_w = P / k_w \quad (6)$$

In this formulation the production rate represents the mean local emission. The latitudinal distribution of the production rates of ethene calculated according to equation (6) range from below  $10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  to  $6 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  (Figure 9a). Generally, the highest ethene production rates are found north of 8°N during the 1988 cruise, the lowest south of 8°N during the same cruise. In contrast, the ethene production rates for the 1989 cruise showed a much smoother profile. These differences in the profiles should provide information on the production mechanism. From results of laboratory experiments, Wilson et al. [1970] suggested a production mechanism of NMHC by photodegradation of dissolved organic carbon (DOC) possibly released by phytoplankton. Ratte et al. (submitted manuscript, 1992) conclude from field measurements that photochemistry is involved in the production process and that at least a part of the precursors of the alkenes are biologically produced. Unfortunately, DOC concentrations are not available for both cruises. Absolute estimates of the phytoplankton biomass for the 1989 cruise are shown in Figure 9b, for the 1988 cruise only relative estimates are available with fairly constant biomass and slightly enhanced values in the equatorial upwelling zone. Compared

TABLE 4. Production Rate  $P$  and Destruction Rate Constant  $D_0$  From a Least Squares Fit According to Equation (5)

Compound	Cruise	Latitude Range	$P$ , $10^8$ molecules $\text{cm}^{-2} \text{s}^{-1}$	$D_0$ , $\text{cm hour}^{-1}$	$r$	$k_w$ , <sup>a</sup> $\text{cm hour}^{-1}$	$F$ , <sup>b</sup> $10^8$ molecules $\text{cm}^{-2} \text{s}^{-1}$
ethene	1988	35°N- 8°N	7.4 (0.8)	6.5 (1.3)	0.99	13	4.6
	1989	38°N-35°S	3.2 (0.9)	6.7 (4.9)	0.97	15	2.1
propene	1988	35°N- 8°N	3.5 (0.6)	6.3 (2.0)	0.99	12	2.1
	1989	38°N-35°S	1.1 (0.2)	6.1 (3.3)	0.98	13	0.74
1-butene	1988	35°N- 8°N	2.1 (0.4)	7.5 (2.6)	0.99	11	1.1
	1989	38°N-35°S	0.83 (0.22)	6.7 (4.0)	0.98	12	0.52
ethane	1988	35°N- 8°N	4.5 (1.0)	2.5 (1.4)	0.99	12	3.8
propane	1988	35°N- 8°N	1.1 (0.2)	1.7 (1.1)	0.99	11	1.0
n-butane	1988	35°N- 8°N	0.47 (0.09)	0.90 (0.71)	0.99	10	0.45
i-butane	1988	35°N- 8°N	0.07 (0.02)	0.98 (0.83)	0.99	10	0.07

<sup>a</sup> Mean transfer velocities calculated from 5° latitudinal averaged transfer velocities which were derived from wind velocities either actually measured or taken from charts of the European Center for Medium Range Weather Forecast (Reading, U.K.).

<sup>b</sup> Mean emission rates calculated from 5° latitudinal averages of seawater concentrations and transfer velocities.

Here  $r$  is the correlation coefficient,  $k_w$  is the transfer velocity, and  $F$  is the emission rate.

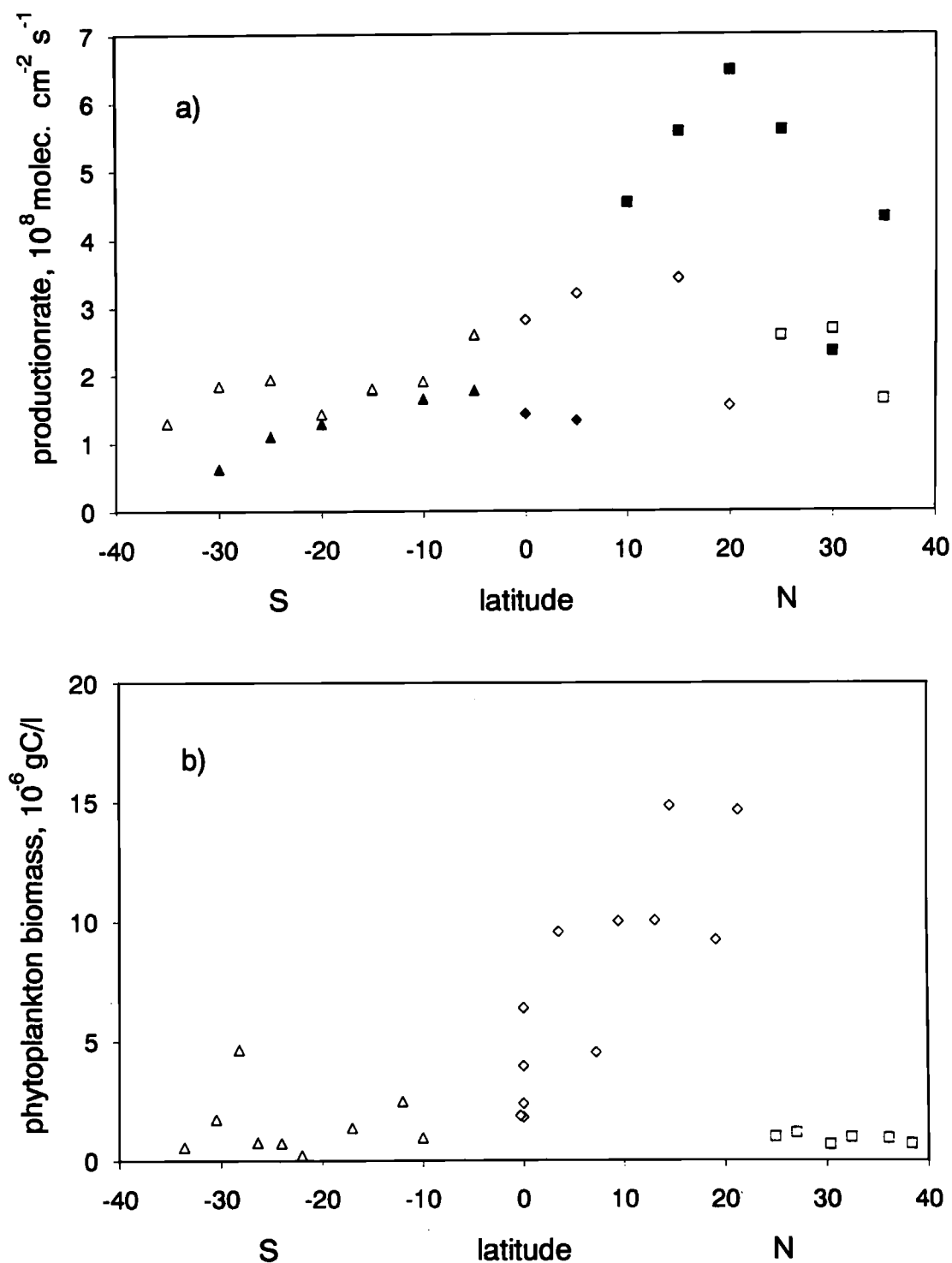


Fig. 9. Latitudinal distribution of (a) the production rate of ethene approximated according to equation (6); and (b) the phytoplankton biomass from the cruise in 1989. The filled symbols are data from 1988: 35°N–8°N (squares), 8°N–3°S (diamonds), 3°S–30°S (triangles); the open symbols are data from 1989: 38°N–23°N (squares), 23°N–0° (diamonds), 0°–35°S (triangles).

TABLE 5. Actual Emission Rates of C<sub>2</sub>-C<sub>4</sub> Hydrocarbons

Compound	1988 <sup>a</sup>				1989			
	35°N-30°S	35°N-8°N	8°N-3°S	3°S-30°S	38°N-35°S	38°N-23°N	23°N-2°S	2°S-35°S
ethene	31 (22)	47 (19)	39 (22)	16 (10)	27 (16)	22 (8)	27 (12)	28 (14)
propene	14 (12)	21 (12)	17 (14)	7.0 (4.4)	9.0 (5.3)	7.5 (3.0)	8.2 (4.6)	11 (4.9)
1-butene	7.5 (5.7)	12 (5)	8.7 (6.1)	3.8 (2.5)	6.0 (3.7)	5.3 (2.0)	5.0 (2.2)	7.1 (3.5)
ethane	19 (24)	39 (25)	18 (20)	3.6 (3.0)	4.1 (3.6)	1.9 (0.9)	3.3 (1.7)	6.1 (4.4)
propane	5.0 (6.0)	9.6 (6.9)	5.3 (5.4)	1.4 (1.1)	1.6 (1.3)	1.5 (0.9)	1.5 (0.8)	1.9 (1.6)
i-butane	0.5 (0.4)	0.7 (0.4)	0.6 (0.4)	0.3 (0.2)	0.3 (0.4)	0.2 (0.2)	0.1 (0.1)	0.4 (0.5)
n-butane	2.4 (2.8)	4.6 (3.0)	2.4 (2.6)	0.6 (0.9)	0.7 (0.6)	0.4 (0.3)	0.6 (0.4)	0.8 (0.6)
acetylene	0.2 (0.6)	0.3 (0.5)	0.2 (0.7)	0.1 (0.7)	2.3 (1.6)	1.1 (0.4)	1.6 (0.8)	3.0 (1.7) <sup>b</sup>
ethene <sup>c</sup> k <sub>w</sub> , cm/hour	16 (10)	14 (8)	16 (8)	17 (11)	15 (9)	12 (6)	13 (7)	28 (20)

<sup>a</sup> Data are from Plass et al. [1992].

<sup>b</sup> Measurements of acetylene in 1989 were carried out only north of 31°S; thus this emission value only represents the range 2°S-31°S.

<sup>c</sup> The transfer velocity for ethene is also valid for acetylene and ethane within an error of 5%, but it is higher than the transfer velocities for the C<sub>3</sub> and C<sub>4</sub> hydrocarbons by about 15 % and 25 %, respectively.

Rates are in 10<sup>7</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>. Regional averages, standard deviations are in paranthesis.

to the production rates (Figure 9a) an opposite pattern of the plankton biomass was found: a constant level during the 1988 cruise and high variability in 1989. There are no significant correlations between the biomass and the alkene production rates. Also, the averaged insolation is not significantly different between both cruises since they took place in the same season. Thus no simple correlation with either the biomass or the insolation or a combination of both can explain the latitudinal patterns and the differences observed in the production rates for both cruises. Additionally, proximity to the coastline of southwest Europe and northwest Africa is not associated with enhanced production rates.

#### 4.4. Oceanic Emissions From the Mid-Atlantic

From our data we calculated actual and mean local emissions, as defined in section 4.2, for the investigated ocean areas. First, we will focus on the actual emissions. Table 5 lists the emission rates averaged for the various latitude ranges. For comparison, the emission rates given by Plass et al. [1992] are included. The averaged actual emissions for the light alkenes are almost constant in the three regions for the 1989 cruise. When we take into account the results by Plass et al. [1992], the regionally averaged alkene emissions from the mid-Atlantic vary by one order of magnitude from  $3.8 \times 10^7$  molecules cm<sup>-2</sup> s<sup>-1</sup> for 1-butene to  $47 \times 10^7$  molecules cm<sup>-2</sup> s<sup>-1</sup> for ethene. The emissions of the alkanes are generally lower than those of the alkenes and the variability covers 2 orders of magnitude with a maximum of  $39 \times 10^7$  molecules cm<sup>-2</sup> s<sup>-1</sup> for ethane.

The mean local emission rates are calculated by use of the 5° latitudinal averages of both concentrations and transfer velocities. Averages for the various latitude ranges are listed in Table 6. The uncertainty caused by the use of 5° averages is less than 10 %; it cannot be avoided due to the reduced spatial

resolution of the wind velocity charts. Comparing the emission rates from Tables 5 and 6, differences are observed when the mean actual transfer velocities are not representative on the scale of emission times. This is obviously the case for the regions 8°N-3°S and 3°S-30°S in 1988 and 2°S-35°S in 1989 where the averages of the transfer velocities (e.g., for ethene in Tables 5 and 6) differ by up to a factor of 3. However, as discussed above these deviations might be considerably higher for local emission rates (cf. Figure 7).

Table 7 presents the mean oceanic NMHC emissions for the area and season of our investigation. They are calculated from the mean local emissions of Table 6. The emissions sum up to a total of about  $6 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup>. The major contribution to the total emissions is from the alkenes at about 70 %, with ethene contributing with 42 %. The ethene and propene emission rates are close to the values of  $3.6 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup> and  $2.0 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup>, respectively, estimated by Rudolph and Ehhalt [1981] for a limited area of the north Atlantic. These authors used previously published concentrations in seawater [Swinnerton and Lamontagne, 1974] and calculated the emissions according to the gas exchange formulation of Liss and Slater [1974]. Donahue and Prinn [1990] calculated total emissions of light NMHC from previously published concentrations in seawater and a fixed transfer velocity of  $(22 \pm 11)$  cm hour<sup>-1</sup>. They obtained  $(1.3 \pm 1.2) \times 10^9$  molecules cm<sup>-2</sup> s<sup>-1</sup> based on the concentrations published by Lamontagne et al. [1974] for the central Pacific and a considerably larger mean value of  $(5.9 \pm 5.7) \times 10^9$  molecules cm<sup>-2</sup> s<sup>-1</sup> from the concentrations reported by Bonsang et al. [1988] for an area of the Indian Ocean. However, the large uncertainties conservatively estimated by Donahue and Prinn make the above difference insignificant. In the latter estimate also some heavier hydrocarbons were considered, but they contribute less than 15 % to the total emissions.

TABLE 6. Regional Averages of the Mean Local Emission Rates of C<sub>2</sub>-C<sub>4</sub> Hydrocarbons

Compound	1988				1989			
	35°N-30°S	35°N-8°N	8°N-3°S	3°S-30°S	38°N-35°S	38°N-23°N	23°N-2°S	2°S-35°S
ethene	27 (18)	46 (13)	13 (0.5)	13 (4)	21 (6)	22 (4)	26 (7)	17 (4)
propene	12 (9)	21 (7)	5.4 (0.2)	5.7 (1.9)	7.4 (1.8)	7.2 (1.5)	8.3 (2.2)	6.9 (1.4)
1-butene	6.6 (4.9)	11 (4)	2.7 (0.01)	3.1 (1.3)	5.2 (1.4)	5.1 (1.2)	6.0 (1.8)	4.7 (1.1)
ethane	18 (20)	38 (15)	5.3 (0.5)	3.4 (1.7)	3.0 (1.2)	2.0 (0.7)	2.8 (0.8)	3.7 (1.1)
propane	5.0 (5.1)	10 (4.0)	1.5 (0.3)	1.2 (0.5)	1.4 (0.6)	1.5 (0.6)	1.8 (0.6)	1.2 (0.4)
i-butane	0.4 (0.3)	0.7 (0.3)	0.2 (0.05)	0.2 (0.06)	0.2 (0.1)	0.2 (0.1)	0.1 (0.05)	0.3 (0.2)
n-butane	2.2 (2.2)	4.5 (1.5)	0.7 (0.2)	0.5 (0.2)	0.8 (0.7)	0.4 (0.2)	0.8 (0.5)	0.6 (0.2)
acetylene	1.7 (3.2)	0.3 (0.3)	0.1 (0.1)	0.1 (0.3)	1.8 (0.6)	1.3 (0.2)	1.5 (0.5)	2.3 (0.2) <sup>a</sup>
ethene <sup>b</sup> k <sub>w</sub> , cm/h	11 (6)	14 (7)	5 (1)	12 (3)	15 (5)	13 (5)	13 (4)	18 (4)

<sup>a</sup> Measurements of acetylene in 1989 were carried out only north of 31°S; thus this emission value only represents the range 2°S-31°S.

<sup>b</sup> Transfer velocities for ethene (cf. footnote c Table 5).

Rates are in 10<sup>7</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>. Standard deviations are in paranthesis.

The emission rates calculated from our data are on the lower side of published estimates. Deviations between the above emissions arise from differences in the NMHC concentrations in seawater and the assumed transfer velocities. According to Plass et al. [1992] the average concentrations of the available data sets cover a range of one order of magnitude for the alkenes and a factor of 25 for the alkanes. The transfer velocity used by Donahue and Prinn [1990] is about a factor of 2 higher than our mean value. Thus it is not surprising that emission estimates based on different data sets differ by an order of magnitude or even more. However, based on the budget presented in the forgoing sections the NMHC concentrations in seawater depend on the prevailing transfer velocities. It is essential for the calculation of emission rates to use NMHC concentration and transfer velocities which are consistent in space and time. Such calculated emission rates should give a more consistent picture.

Oceanic emissions of NMHC obtained by other methods have been reported. Bonsang et al. [1988] used a global

approach and estimated global oceanic emissions of C<sub>2</sub>-C<sub>6</sub> hydrocarbons corresponding to emission rates of  $9 \times 10^9$  molecules cm<sup>-2</sup> s<sup>-1</sup>. Several authors used another approach for hydrocarbons with short atmospheric lifetimes: they estimated oceanic emissions from the atmospheric NMHC removal rates by demanding a balance [Penkett, 1982; Ehhalt and Rudolph, 1984; Donahue and Prinn, 1990]. The resulting emission rates for light hydrocarbons range from  $3 \times 10^9$  molecules cm<sup>-2</sup> s<sup>-1</sup> to some  $10^{11}$  molecules cm<sup>-2</sup> s<sup>-1</sup>. Thus the atmospheric budget approaches above generally yielded substantially larger emission rates than the diffusive microlayer approach. In the next section we will compare the two approaches for our data.

#### 4.5. Budget of NMHC in the Marine Atmosphere

Koppmann et al. [1992] estimated the contribution of oceanic emissions to the atmospheric budgets of NMHC for the data of the 1988 cruise with a simple one-dimensional eddy-diffusional model of the marine atmosphere. The model calculates the atmospheric NMHC concentrations from actual oceanic emissions as the sole source of NMHC and atmospheric removal by reaction with OH-radicals and ozone. Prescribed relative vertical profiles of OH-radicals, ozone, eddy-diffusion coefficients, temperature, and pressure are used. Absolute values of surface OH were calculated based on measured parameters (T. Brauers, private communication, 1989) and ozone profiles were measured [Smit et al., 1990]. The model does not include fast convective transport in clouds. Thus it is not appropriate for the ITCZ. Since during both cruises latitude ranges and seasons were comparable, as a first approximation the same OH-radical and ozone concentrations as used by Koppmann et al. [1992] were assumed for the 1989 data.

In Figure 10 the atmospheric NMHC concentrations calculated from the model are compared with the measured concentrations (R. Koppmann, unpublished data, 1991). The relative patterns of the measured atmospheric concentrations

TABLE 7. Emission Rates for the Mid-Atlantic (35°N - 35°S)

Compound	Emission Rate <sup>a</sup>
ethene	24
propene	9.8
1-butene	5.9
ethane	11
propane	3.2
i-butane	0.30
n-butane	1.5
acetylene	0.97

<sup>a</sup> Mean values calculated from the 5° latitudinal averages of concentrations and transfer velocities.

Rates are in 10<sup>7</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>.

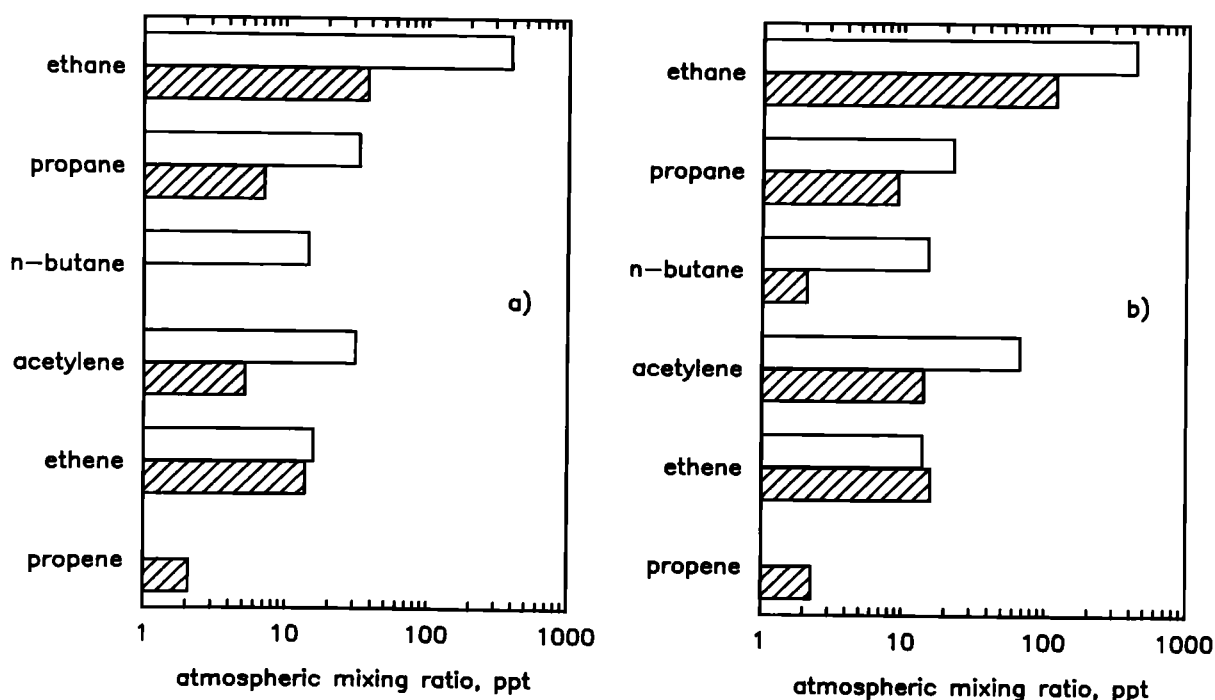


Fig. 10. Comparison of the calculated mixing ratios (hatched bars) and the measured mixing ratios (open bars) of the 1989 cruise: (a) 5°N to 35°N; and (b) equator to 30°S. (The calculated n-butane mixing ratio (5°N-35°N) was 1 ppt.)

are similar for the northern (35°N-5°N) and the southern latitude range (0°-30°S). However, the absolute concentrations measured at northern latitudes are nearly a factor of 2 higher. For the light alkanes and acetylene, about 10 % to 40 % of the atmospheric removal are balanced by the oceanic emissions with higher oceanic contributions at southern latitudes. Thus the major source for these compounds in the remote Atlantic atmosphere is long-range transport from the continents. For ethene the calculated and measured concentrations are in good agreement, for propene no atmospheric measurements are available. However, from the budget calculations propene mixing ratios below 10 ppt can be expected. These results are in general agreement with previous findings for the 1988 cruise [Koppmann et al., 1992]. Different from the 1989 findings, in 1988 the atmospheric removal of ethane was nearly balanced by the oceanic emissions for the range 35°N-5°N. The acetylene emissions in 1989 were on average a factor of 10 higher than in 1988, but still contribute less than 20 % to atmospheric acetylene concentrations.

In contrast to our consistent results for the atmospheric budgets of short-lived NMHC, Donahue and Prinn [1990] pointed out that a serious discrepancy exists between NMHC emissions calculated from exchange models and emissions derived from model calculations of the atmospheric removal rates. Their calculations were based on atmospheric and oceanic NMHC observations taken from literature which, in general, were not measured simultaneously. Compared with an atmospheric ethene concentration of 75-300 ppt used by Donahue and Prinn [1990], a substantially lower concentration of 15-30 ppt was measured by R. Koppmann (unpublished

data, 1991). Despite the different NMHC data sets, the used OH-radical concentrations are similar at ground level, although the shapes of the vertical profiles differ.

## 5. CONCLUSIONS

The concentrations of C<sub>2</sub>-C<sub>4</sub> hydrocarbons in seawater presented in this paper are in the range of some pMol/L to several 100 pMol/L. The concentrations generally decrease with increasing molecular weight and the alkenes are the predominant compounds within the NMHC.

Vertical profiles indicate homogeneously distributed alkenes and acetylene in the upper 20 m. In this layer the concentrations of alkanes appear to be uniform only when substantial mixing due to wind stress occurs. At low wind stress the alkane concentrations at the surface may exceed the concentrations in 11 m depth by a factor of 5. This points toward a net alkane production in the surface adjacent layer. Different alkenes are linearly correlated and a production mechanism similar for all alkenes seems reasonable. For the alkenes we have no indications for the existence of destruction processes in seawater, the dominant loss process seems to be the emission into the atmosphere. As a consequence, the concentrations of NMHC in seawater cannot be viewed independent from the local transfer rates into the atmosphere. High transfer rates deplete the oceanic mixed layer with resulting low NMHC concentrations and vice versa. Regarding the production process, we have not observed enhanced production rates for alkenes in regions of high phytoplankton abundance, however, in a region of low



phytoplankton abundance. It can be speculated, that high phytoplankton concentrations attenuate solar light and thus inhibit the photochemical production of alkenes.

The oceanic mixed layer represents a reservoir for atmospheric hydrocarbons with a characteristic time of depletion due to emission into the atmosphere of some 10 days. The emission rates may differ substantially between time scales of several hours and some 10 days, for example, up to an order of magnitude for local emission rates and factors of 2 or 3 in regional averages.

The total emissions of the  $C_2$ - $C_4$  hydrocarbons from our data from the mid-Atlantic are  $6 \times 10^8$  molecules  $cm^{-2} s^{-1}$  with a contribution of more than 70 % from the alkenes. Our calculated emission rates are clearly on the lower side of previously published emission rates. Estimates based on diffusive microlayer approaches are between  $9 \times 10^8$  molecules  $cm^{-2} s^{-1}$  and  $6 \times 10^9$  molecules  $cm^{-2} s^{-1}$  with a range of uncertainty between  $1 \times 10^8$  molecules  $cm^{-2} s^{-1}$  and  $1 \times 10^{10}$  molecules  $cm^{-2} s^{-1}$  [Rudolph and Ehhalt, 1984; Donahue and Prinn, 1990]. However, the above estimates differ in the assumed transfer rates and the used NMHC concentration data sets taken from literature. Additionally to possible seasonal and regional variations in NMHC concentrations a further uncertainty in reported emission rates arises from neglecting the relation between the NMHC concentrations in seawater and the transfer rates.

Oceanic emission rates estimated from NMHC measurements in the marine atmosphere and the assumption of a balance between atmospheric removal and oceanic emissions are between  $3 \times 10^9$  molecules  $cm^{-2} s^{-1}$  and some  $10^{11}$  molecules  $cm^{-2} s^{-1}$  [Penkett, 1982; Ehhalt and Rudolph, 1984; Donahue and Prinn, 1990]. Donahue and Prinn pointed out that such estimates are generally larger and thereby inconsistent with those obtained from diffusive microlayer approaches. However, Donahue and Prinn [1990] used concentrations from literature, which were generally not measured simultaneously in atmosphere and seawater. Also, the atmospheric alkene concentrations they used were probably too high for the marine atmosphere, for example, larger by factors of 5 to 20 than those found by Koppmann et al. [1992], Rudolph and Johnen [1990], and R. Koppmann (unpublished data, 1991). From simultaneous measurements we calculate atmospheric removal rates for ethene which are consistent with the oceanic emission rates. For the  $C_2$ - $C_4$  alkanes, continental sources play a significant role. Here the oceanic source of alkanes on average contributes with 10 % to 40 % to the atmospheric budgets. Similar results are found by Koppmann et al. [1992]. Our atmospheric budget gives strong evidence for the reliability of our oceanic emission rates. Furthermore, we have no indications for increased emission rates in areas close to coast lines and in areas of enhanced biomass abundance. This is different from distributions of dissolved carbonyl sulfide, which are substantially enhanced in coastal areas [Andreae, 1990; Mihalopoulos et al., 1992]. Thus we think our emission rate for  $C_2$ - $C_4$  hydrocarbons of  $6 \times 10^8$  molecules  $cm^{-2} s^{-1}$  is representative for the mid-Atlantic at the season of our investigation. On the basis of these emissions and according to the model by Donahue and Prinn [1990], the impact of  $C_2$ - $C_4$  hydrocarbons on ozone and

OH-radical levels in the marine atmosphere seems to be much weaker than often assumed.

However, despite of some general features the production mechanism of NMHC in seawater is not yet understood. Investigations concerning the production mechanism and the seasonal and regional distribution of areas with high NMHC emissions are needed in order to better quantify the impact of oceanic emissions on local and global budgets of atmospheric NMHC.

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- H. Kuosa, Tvärminne Zoological Station, SF-10900 Hanko, Finland.

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