PRODUCTION MECHANISM OF C2-C4
HYDROCARBONS IN SEAWATER: FIELD
MEASUREMENTS AND EXPERIMENTS

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Abstract. The production mechanism of light nonmethane
hydrocarbons (NMHC) in seawater was investigated during
the North Atlantic atmospheric chemistry program
(NATAC) in April and May 1991 in the European coastal
seas and the North Atlantic. A significant alkene production
occurred in the presence of light only. Under conditions of
negligible NMHC emissions (low wind velocity) increasing
hydrocarbon concentrations were observed during daytime,
whereas the concentrations remained constant during night.
NMHC formation experiments were carried out with
seawater filled in quartz glass bottles and showed the same
dependence of light. Experiments with differently pre-
treated seawater samples indicated that the presence of
dissolved organic material (DOM) is also necessary for
alkene production. We suggest a two-step production
mechanism for alkenes: first DOM is released, probably
from algae, then part of this material is photochemically
transformed into alkenes. The production rates in the quartz
glass bottles were comparable to the production rates in the
ocean surface. This indicates that the processes occurring in
the experimental setups represent the processes occurring in
the field. Since the production - and emission rates were in
the same range it can be concluded that the budget of light
alkenes in the remote marine environment is determined by
the production in seawater as the dominant source and the
flux into the atmosphere as the main loss process.

1. INTRODUCTION

Because of their high reactivity toward OH radicals light
non methane hydrocarbons (NMHC) play a significant role
in tropospheric chemistry. Most of the NMHC in the
atmosphere originate from anthropogenic emissions or
vegetation [Hanst et al., 1980; Zimmerman et al., 1978].
Nevertheless, for reactive NMHC in the remote marine
environment the impact of these sources is generally small
and recent investigations have focused on the oceans them-
selves as a source for these compounds [Rudolph and
Ehhalt, 1981; Bonsang et al., 1988; 1990; Plass et al., 1990;
1992; Koppmann et al.; 1992]. The presently available
estimates of global hydrocarbon emissions from the oceans
are based on extrapolations from regionally and seasonally
limited data sets and therefore are highly uncertain. For
more reliable global emission estimates a reasonable under-
standing of the factors determining the NMHC concen-
trations in seawater is essential. However, in spite of an
increasing number of NMHC measurements in seawater the
production mechanism of these substances is not yet under-
stood.

As early as 1970, Linnenbom and Swinnerton suggested a
relationship between hydrocarbon concentration in sea-
water and biological activity. This was supported by
laboratory experiments of Wilson et al. [1970]. They used
either cultures of the algae Chaetoceros or cell-free water to
which dissolved organic material (DOM) from various
phytoplankton cultures had been added. In the case of
illumination they found a production of carbon monoxide
and C_2 to C_4 hydrocarbons in the Chaetoceros cultures,
whereas in the cell-free setup only CO and the unsaturated
hydrocarbons were produced with the production rates
depending on initial DOM - concentrations. From these
results, Wilson et al. [1970, p. 1579] suggested that the
dissolved organic material in the ocean is "one source from

which unsaturated hydrocarbons might be produced in the illuminated zone" and that "additional production by organisms is also possible." However, they finally stated, that "the situation has yet to be clarified."

As far as we know, no further systematic investigations of the NMHC production mechanism were done, except some simultaneous measurements of NMHC concentrations and several biological parameters [Zsolnay, 1973; 1977; Swinnerton and Lamontagne, 1974; Lamontagne et al., 1976; Swinnerton et al., 1977; Bonsang et al., 1989; Plass et al., 1992]. Up to now from these measurements no clear correlations between hydrocarbon concentration and biological parameters were obtained.

As a part of the joint German-Soviet ship campaign North Atlantic atmospheric chemistry (NATAC) in April and May 1991 we conducted experiments concerning the production mechanism of NMHC in seawater. In these experiments the change of NMHC concentrations in isolated seawater samples was measured as a function of physical and biological parameters. Additionally, we measured diurnal variations of NMHC concentrations in the upper ocean. Generally, the alkene concentrations exceeded the alkane concentrations by factors of 3 to 5. In the following we will concentrate on the alkenes. On the basis of the experimental results the alkene production rates for limited ocean areas are estimated and compared with the corresponding local emission rates.

2. METHODS

The NMHC concentrations were measured in - situ using a gas chromatographic system installed in a laboratory container. Seawater was pumped continuously from a stainless steel inlet at the hull of the ship to a degassing device in the container. The depth of sampling was 2.5 m below the water surface. Before analysis the tubes and the degassing device were flushed with seawater. Then filtered samples of 1 L volume were transferred into a stripping chamber and purged with helium. Subsequently, the NMHC were cryogenically concentrated from the purge gas at liquid nitrogen temperature and analysed by FID/GC (flame ionisation detector gas chromatography). All materials in contact with the sample were stainless steel or glass. The whole process worked automatically with a processing time of about 2 hours per analysis (for details, see Rudolph et al. [1989] and Plass et al. [1991]). The stripping efficiencies for C_2-C_4 hydrocarbons exceeded 97% (exept acetylene with a lower limit of 80%). The detection limits were 2 to 8 pmol L^{-1}. For 1-butene high blank values increased the detection limit to 20 pmol L^{-1}. The reproducibility of the measurements was 4% to 8% for C_2 and C_3 hydrocarbons and about 10% for 1-butene.

Diurnal variations of NMHC concentrations in the surface layer were measured in the North Sea. These measurements were conducted under conditions of very low wind velocity (about 4 m s^{-1}, see Table 1) and thus low NMHC emission rates. Samples from the ocean surface layer were collected with a stainless steel bucket of two liters volume from the bow of the ship. Within 15 min the samples were transferred into the stripping chamber and analyzed as described above. Before sampling the bucket was mechani-

TABLE 1a. Conditions of the NMHC Formation Experiments and the Diurnal Variation - Measurements

Measurement	NMHC Formation Experiment		Diurnal Variation
	E1	E2	
Area of Sampling	57°3'N 15°9'W	57°3'N 15°9'W	56°1'N 5°0'E
Time	May 3-11	May 10-16	May 16-18
Average wind Velocity, m s^{-1}	8.7 $\pm$2.5	10.4 $\pm$3.7	4.4 $\pm$2.5

TABLE 1b. Experimental Subsets

	Number of Bottles	
	E1	E2
Illuminated		
Unfiltered	4	3
0.2 μm	-	3
0.6 μm	-	3
Dark		
Unfiltered	3	3

cally cleaned and heated at 373 K in a nitrogen atmosphere for at least 2 hours.

Hydrocarbon formation experiments were conducted in the North Atlantic using seawater from the inlet system. For this purpose quartz glass bottles were filled with seawater of known hydrocarbon content and exposed to sunlight or kept dark. The change in hydrocarbon concentrations was measured as a function of exposure time. The bottles were kept on deck in an open container, which was continuously flushed with seawater. Thus the exposure temperature was very close to the actual seawater temperature with differences less then 1.5 K. By using filters of different pore sizes when filling the bottles organisms could be removed depending on their size class: by passing the seawater through filters with a pore size of 0.2 μm the algae and most of the bacteria were removed, by filtering through a nominal pore size of 0.6 μm mainly the algae were removed. In order to prevent contamination with organic compounds the filter materials were aluminium oxide (0.2 μm) (Anotec Separations, Anodisc) and glass fiber (0.6 μm) (Macherey & Nagel, GF/3). The material of the bottles was quartz glass HSQ 300, the volume of each bottle was 2 L. The bottles were cleaned with purified water (Millipore) and by ultrasonics; subsequently, they were heated at 423 K and flushed with pure nitrogen for at least 5 hours.

In order to prevent hydrocarbon losses into a head space the bottles were filled completely. However, due to even a small temperature increase, a closed glass bottle filled with water would break as a result of overpressure. To solve this problem, a pressure release was allowed by means of a capillary glass tube inside each bottle (30 cm, 2 mm i.d.), which extended from the top to close to the bottom, and was connected to an open stainless steel tube (15 cm, 4 mm i d) outside at the top of the bottle.

In Figure 1 the scheme of the experimental procedure is shown. Before the start of an experiment the initial NMHC concentrations in seawater from the inlet line were determined. For each experiment, different subsets of several bottles were filled with identically treated seawater. Subsequently, the bottles were either exposed to sunlight or kept dark by covering them with aluminium foil. At different exposure times the samples were analyzed as described above. Details of the experimental conditions are summarized in Table 1.

In order to determine the number of bacteria in the quartz glass bottles samples of 100 mL were taken from each bottle, fixed with 10 mL 17% formalin and stored at 6°C. The bacteria were counted by epifluorescence microscopy.

During the whole cruise every morning water samples from different depths were taken with Niskien samplers. From these samples the chlorophyll a concentration was measured and the phytoplankton density and species composition were determined aboard the ship as described by Parsons et al. [1984]. Meteorological parameters like wind speed and solar irradiation were measured every hour.

3 RESULTS

In a first experiment (E1) the effect of solar radiation was investigated. The results are shown in Figure 2. In the illuminated samples alkene concentrations increased, whereas in the dark samples the concentrations remained nearly constant. The initial concentrations were 55 pmol L^{-1} for ethene, 27 pmol L^{-1} for propene and 29 pmol L^{-1} for 1-butene. In the illuminated samples the concentrations increased within 6 days by a factor of 7 for ethene, of nearly 9 for propene, and of 3 for 1-butene (not shown). The corresponding production rates (calculated from linear regression) were 59.5 pmol L^{-1} d^{-1} for ethene, 25.4 pmol L^{-1} d^{-1} for propene, and 11.5 pmol L^{-1} d^{-1} for 1-butene with correlation coefficients of 0.99 (ethene), 0.87 (propene) and 0.95 (1-butene) (Table 2). In the dark samples the concentration of propene and 1-butene remained constant, only for ethene a statistically significant increase (5.3 pmol L^{-1} d^{-1}, r=0.98) was observed. This observation was confirmed in a second experiment (E2) (see Table 2).

In experiment E2 differently pretreated, illuminated subsets were investigated in addition to an unfiltered, dark experimental subset. The results for ethene are plotted in Figure 3, propene and 1-butene showed a similar pattern. In the illuminated unfiltered subset an average ethene production of 50.9 pmol L^{-1} d^{-1}, a propene production of 34.3 pmol L^{-1} d^{-1} and a 1-butene production of 14.6 pmol L^{-1} d^{-1} was found (Table 2). In the filtered samples the alkene concentrations generally increased at a lower
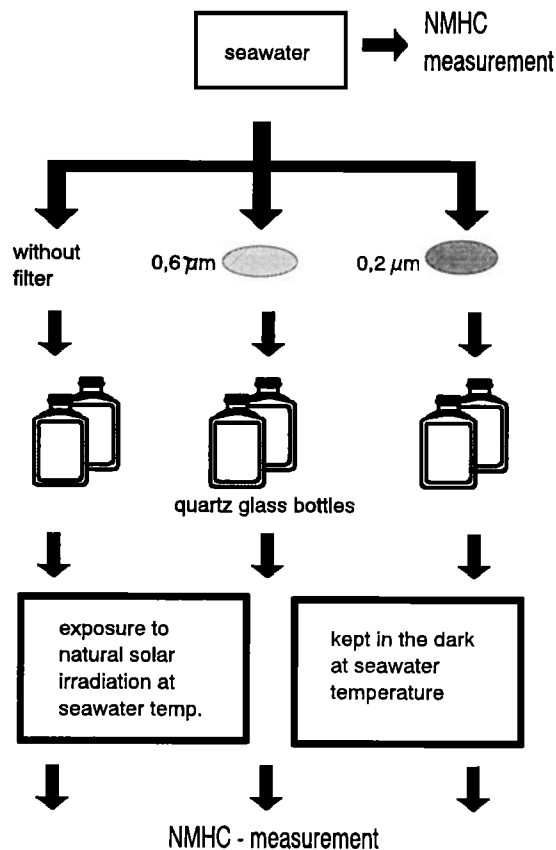

Fig. 1. Scheme of experimental setups with seawater in quartz glass bottles. The bottles were filled with differently pretreated water and then exposed to different conditions.

rate. The regression coefficients of the unfiltered, and the different filtered subsets (calculated up to 96 hours exposure time) differ significantly from each other. The lowest alkene production was observed in the 0.6-μm filtered samples for exposure times up to 96 hours. However, after longer exposure times the alkene concentrations in some of the filtered samples increased with a higher rate than in the unfiltered samples (Table 2, Figure 3).

The corresponding bacteria densities are shown in Figure 4. The bacteria densities in the unfiltered and the 0.6-μm filtered samples were identical (t-test, p>0.05). In contrast to this, in the 0.2 μm-filtered samples the number of bacteria was reduced by a factor of about 15 immediately after filtration. Subsequently, the number of bacteria slightly increased but was always significantly lower than in the unfiltered and 0.6 μm-filtered samples (t-test, p<0.05).

The results of the measurements of diurnal variations are presented in Figure 5. Increasing alkene concentrations were found during daytime, whereas the concentrations remained constant at night. Ethene showed the most distinct pattern of diurnal variations. The initial ethene concentration of 68 pmol L^{-1} increased up to 150 pmol L^{-1} within 42
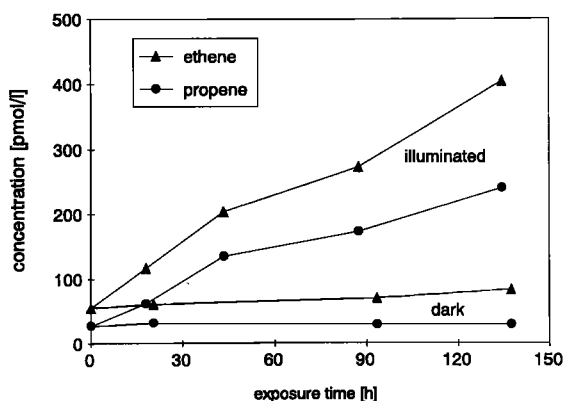
Fig. 2. Concentrations of ethene and propene in illuminated and dark unfiltered samples of experiment E1 up to an exposure time of 138 hours.

hours. From this an average production rate of 47 pmol $L^{-1} d^{-1}$ was calculated. For propene the average production rate was found to be 18 pmol $L^{-1} d^{-1}$, for 1-butene 11 pmol $L^{-1} d^{-1}$ (Table 2).

The biological parameters in seawater concerning the experiments and the diurnal variations are summarized in Table 3. The results indicate that the experiments took place during a period of a considerable phytoplankton bloom, which was dominated by diatoms, especially the species Chaetoceros and Nitzschia. During the measure-

ments of diurnal variation a dinoflagellate bloom accompanied with coccolithophores was observed, but generally with much lower densities.

4. DISCUSSION

4.1. Production Mechanism of Alkenes in Seawater

The comparison between illuminated and dark samples indicates that a substantial alkene production only occurred in illuminated samples. In addition, the alkene concentrations in filtered samples were significantly lower than in unfiltered samples. In the following we investigate whether our measurements support the hypothesis of a two step production mechanism for alkenes in seawater: first dissolved organic material (DOM) is released, probably from algae, then the DOM is photochemically transformed into alkenes.

In case of a direct alkene production by organisms no alkene increase should occur in the filtered samples (experiment E2). However, in the filtered samples an alkene production was still observed, although at a significantly lower rate. There are two possible explanations for this finding. The first is that a few organisms remained in the samples in spite of filtering, which account for a photobiological alkene production. The second possibility is that both the filtered and the unfiltered samples provided precursors for a photochemical alkene production - probably dissolved organic material (DOM). In the following we will present evidence supporting the latter explanation.

First we have to concern the efficiency of filtering. We have experimental evidence that bacteria were still present

TABLE 2. Alkene Production Rates Obtained in the NMHC Formation Experiments and the Diurnal Variation Measurements

Measurement		Ethene Production Rate[a] r+		Propene Production Rate[a] r+		1-Butene Production Rate[a] r+	
E1 Unfiltered	0-135h	59.5+/-4.3	0.99	25.4+/-7.2	0.87	11.5+/-2.4	0.95
Dark	0-138h	5.3+/-0.7	0.98	n.s.		n.s.	
E2 Unfiltered	0-136h	50.9+/-3.6	0.99	34.3+/-3.4	0.99	14.6+/-2.2	0.98
0.6 μm	0-93 h	17.3+/-4.3	0.97*	17.3+/-6.5	0.82*	7.2+/-2.2	0.96*
	93-140h	107		364		-	
0.2 μm	0-96 h	27.4+/-3.8	0.99	18.2+/-6.0	0.95	n.s.	
	96-143h	30		67		41	
Dark	0-140h	4.3+/-0.7	0.98	n.s.		n.s.	
Diurnal Variation		47		18		11	

[a] Production rate and error in pmol*L-1*d^{-1}; E1 and E2: calculated from linear regression; except the rates after 93 hours, which are calculated from initial and final concentrations. Diurnal variations: calculated from initial and final concentrations. If not marked otherwise, the samples were illuminated. The value r+: correlation coefficient of linear regression; without an asterisk: significant, α=0.05; asterisk means significant, α=0.1; n.s. means not significant;
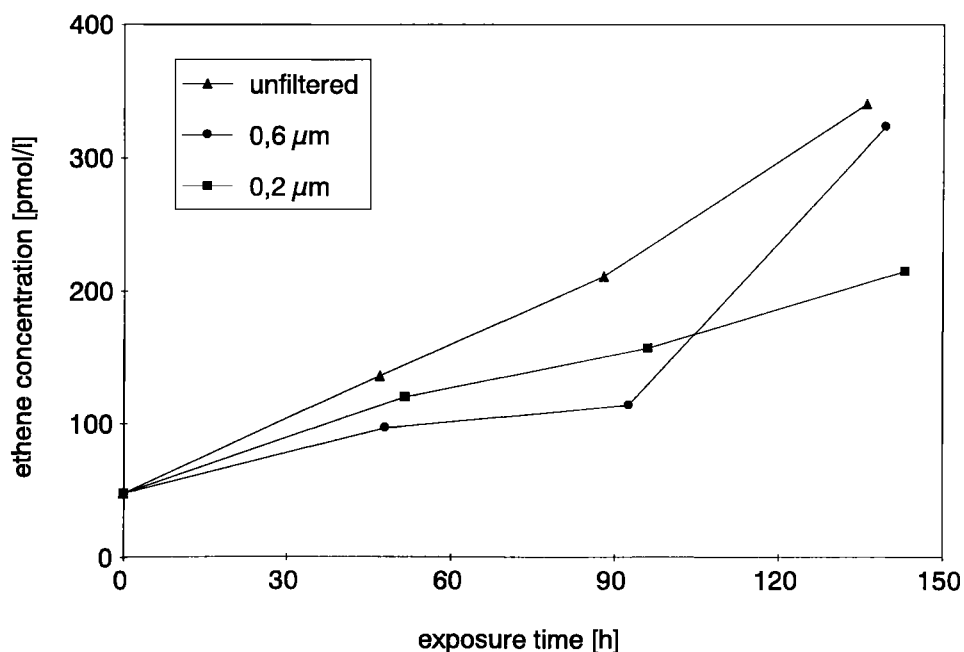
Fig. 3 Concentrations of ethene in illuminated samples of experiments E2, depending on pretreatment: the water was exposed either unfiltered or after passing a filter of a pore size of 0.6 and 0.2 μm respectively.
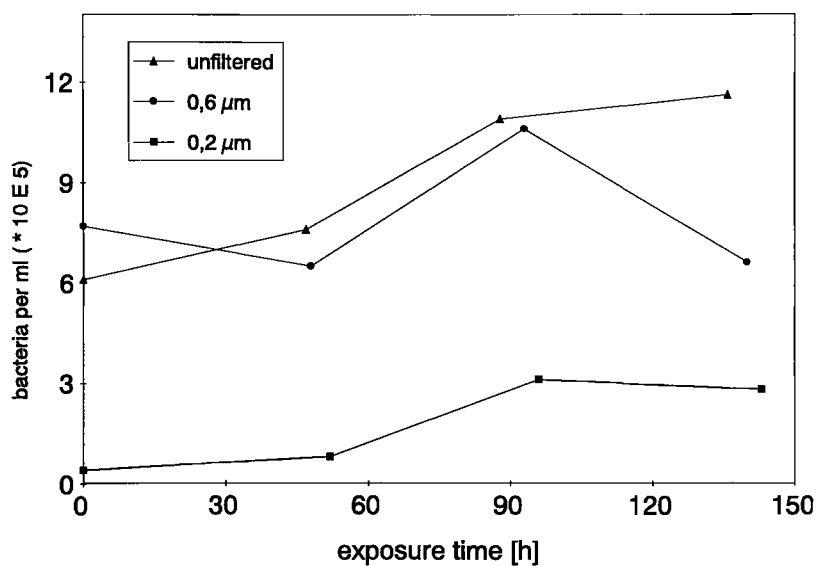

Fig. 4 Numbers of bacteria in the illuminated samples of experiment E2 as a function of filter pore size used and exposure time.

in the 0.2-μm filtered samples, although their density was drastically reduced, whereas filtering through a pore size of 0.6 μm did not affect the number of bacteria (Figure 4). What's about the number of algae? Considering the pore sizes of 0.6 and 0.2 μm, diatoms (> 50 μm) are not expected to pass through the filters. However, it seems possible, that part of the small coccolithophores or flagel-

lates (1-20 μm) can pass through the glass fiber filters (0.6 μm) [Munawar et al., 1982]. To sum up, we should expect the following situations in the quartz glass bottles: (1) unfiltered water: unchanged number of algae and bacteria; (2) 0.6-μm filtered water: reduced number of algae, unchanged number of bacteria; and (3) 0.2-μm filtered water: no algae, reduced number of bacteria.
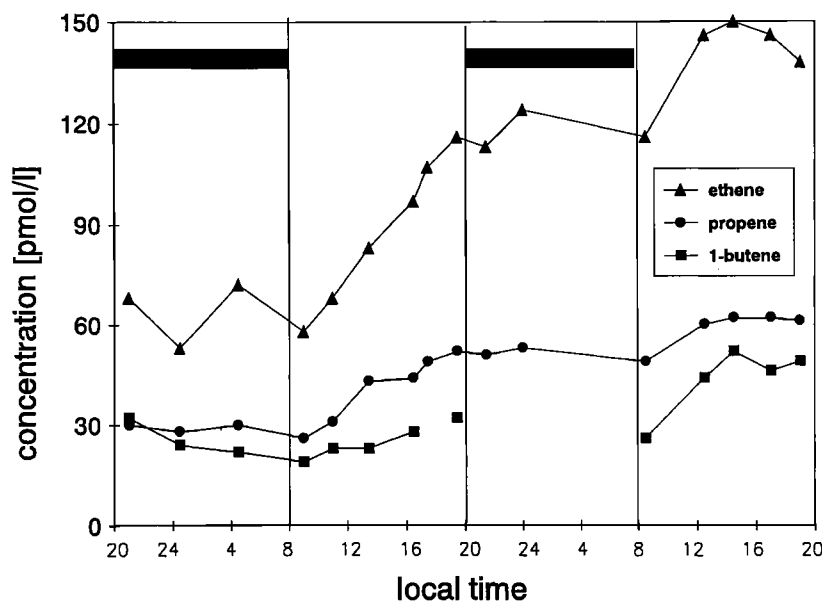
Fig. 5 Diurnal variation of alkene concentrations in surface layer (0-1 m) of the North Sea, samples taken and measured from May 16 to 18, 1991. The dark bars indicate night.

TABLE 3. Phytoplankton species and density and concentration of chlorophyll a in seawater at the regions where the experiments and measurements of diurnal variation took place.

Measurement	NMHC Formation Experiments		Diurnal Variation
	E1	E2	
Dominant phytoplankton	diatoms 1,2,3	diatoms 1,2	dinoflagellates, 4 coccolithophores
Cell density, cells L-1	depth 0 m 1*10⁷ 2 m 5*10⁶	depth 0 m 4*10⁶ 10m 8*10⁶	depth 0 m 1*10⁴ 4 m 1*10⁴
Chlorophyll a, μg L-1	0 m 4.0 2 m 3.6	0 m 5.1 10m 3.4	0 m 0.5 -

Notes 1: Chaetoceros; 2: Nitzschia; 3: Thalassiosira; 4: Gymnodinium (S.A. Gemlitzky et al., unpublished data, 1991).

If the bacteria would account for a direct photobiological alkene production the 0.6-μm filtered and the unfiltered samples should exhibit very similar alkene production rates. This obviously was not the case (Figure 3). In case of a sole photobiological alkene production by algae or by an interaction of algae and bacteria, no alkene production should occure in the 0.2-μm filtered samples, which does not aggree with our experimental findings (Figure 3).

Therefore we can conclude from our experiments that a photochemical mechanism is definitely involved in alkene production, although the existence of an additional photo-biological mechanism cannot be completely excluded. The photochemical alkene production requires the presence of dissolved organic material. Assuming the irradiation to be constant, the alkene production rate therefore should depend on the concentration of DOM. In our experiments the lower production rates in the filtered samples therefore are probably due to reduced availability of DOM in these samples. A lower concentration of DOM can be due to different reasons.

The first is that the DOM is released by algae. Hence a reduced number of algae would lead to a decrease in DOM concentration. There are some hints from experiment E2 that organisms with a diameter > 0.6 μm, probably algae, are a possible source of DOM. In contrast to the very similar bacteria densities in the unfiltered samples and the 0.6-μm filtered samples (Figure 4), there was a significant difference between the alkene production rates in these samples (Figure 3, Table 2). Hence it is likely that the algae are involved in the release of the alkene precursors rather than the bacteria. However, the conclusion concerning the algae in the quartz bottles as the source of DOM is only valid if the DOM is photochemically transformed into alkenes within one or two days. In case of slower turnover rates the photochemical active DOM is not influenced by the presence or absence of organisms at least up to several days, i.e., the duration of our experiments. At present we have no information about the times of DOM turnover.

There is a second explanation for lower DOM concentrations in the filtered samples. One should consider that DOM is defined as organic molecules smaller than 0.45

µm. Thus, in our experiments the DOM concentration perhaps was reduced by adsorbtion at the filter material or even by retaining the macromolecules on the filter. It is conceivable that depending on the chemical structure of the DOM components only part of the DOM can act as alkene precursors. Unfortunately, no DOM measurements - neither before nor after filtering - are available.

There seems to exist even a negative relationship between the presence of bacteria and the alkene production rate. Generally, in samples with reduced number of algae but with unchanged number of bacteria (0.6 µm filtered) the alkene production rate in the first 96 hours of exposition was lower than the production rate in samples containing no algae and only few bacteria (0.2 µm filtered) (Table 2). This may indicate either a direct alkene destruction or, more likely, an uptake of the organic alkene precursors by heterotrophic bacteria.

Finally, we will compare the experimentally obtained hydrocarbon production rates in unfiltered seawater with the field production rates measured in the diurnal variations (Table 2). Although obtained under different conditions both rates are comparable with the field production rates being always somewhat lower. Part of these differences may be due to the fact that even during low wind velocities a small flux of alkenes to the atmosphere persisted. On the basis of an average wind velocity of 4.4 m s^{-1} and a depth of the mixed layer of 15 m (taken from temperature profiles) fluxes of 7.1 pmol L-1 d^{-1} for ethene, 2.8 pmol L-1 d^{-1} for propene, and 1.7 pmol L-1 d^{-1} for 1-butene were calculated according to Liss and Merlivat [1986] with a Schmidt number correction included according to Plass-Dülmer et al. [1993].

In the North Sea, where the measurements of diurnal variations were made, the phytoplankton density was about two orders of magnitude smaller than in the North Atlantic, where the bottle experiments were conducted (Table 3). If the actually existing algae are considered as the main source for DOM the differences in the production rates should have been much more distinct. Possibly other effects compensated for the lower phytoplankton density. The first effect is the light intensity. In the North Sea, the light intensity indeed exceeded that in the North Atlantic: the average energy irradiation was 248 J m^{-2} s^{-1}, during the experiments in the North Atlantic it was 106 J m^{-2} s^{-1} (E1), and 150 J m^{-2} s^{-1}, respectively (E2). Another aspect to take into account is the stage of the phytoplankton bloom. In the North Atlantic we found an active bloom of diatoms. In contrast to this, in the North Sea the phytoplankton was dominated by dinoflagellates. This indicates a previous bloom of diatoms, since the dinoflagellates usually follow the diatoms. So, although the actual cell density was low, the deceasing diatoms perhaps provided an increased amount of DOM as precursor for alkenes. This however would support the hypothesis of algae as DOM source, but with DOM turnover rates on a larger time scale.

4.2. Comparison of Production Rates and Emission Rates

Plass et al. [1992] concluded indirectly from field measurements that the flux into the atmosphere represents the main loss process for alkenes in the ocean and that other destruction mechanisms - if existing - are of secondary importance. In the following we will test this conclusion for the situations during experiment E1 and E2 (57°3'N; 15°9'W, May 3-11 and May 10-16). If this assumption is correct, the production and emission rates should be of comparable magnitude. In order to calculate the hydrocarbon production rates the following assumptions are made. First, the production is proportional to the light intensity. In a first approximation we assume the euphotic layer to be relevant for photochemical alkene formation. The euphotic layer is defined from a biological point of view as the zone in which light intensity is sufficient for phytoplankton growth. It extends to a depth of 1% intensity of the visible light. Second, in the mixed layer there is a homogenous distribution of DOM. Third, the alkene production rate in the glass bottles on deck is identically to the production rate at the ocean surface.

The column-integrated field production rates per unit surface area can be calculated using equation (1) and subsequent integration over the depth of the euphotic layer:

$$I[d]/I_0 = P[d]/P_0 \qquad (1)$$

with

I_0 light intensity at the ocean surface;
P_0 Production rate in the quartz glass bottles;
$I[d]$ light intensity at the depth d;
$P[d]$ Production rate at the depth d;

According to the extinction law the relation of light intensity in the depth d and the surface can be written as:

$$I[d]/I_0 = e^{-k*d} \qquad (2)$$

with k = extinction coefficient.

For estimating k we used the internationally standardized Secchi-disc and the empirical equation given by Tait [1968]:

$$k = 1.7/S \qquad (3)$$

with S = depth at which the disc becomes invisible (Secchi depth).

The integrated production rate in the euphotic layer of the depth d is

$$\int_0^d P(d) = P_0/k * (1-e^{-k*d}) \qquad (4)$$

For the region of our experiments the Secchi depth was about 6 m. From this an extinction coefficient k of 0.28 m^{-1} and a depth of the euphotic layer of 16 m was calculated. For these conditions the expression $(1-e^{-k*d})$ in equation (4) is near to one. The values for P_0, calculated from the production rates given in Table 2 (E1 and E2, unfiltered, illuminated), as well as the integrated column production rates are summarized in Table 4.

The hydrocarbon emission rates can be calculated using the parametrization of the gas transfer according to Liss and Merlivat [1986]:

TABLE 4. Calculated Alkene Production and Emission Rates for the Situations of Experiments E1 and E2

	P_0, molec $cm^{-3} s^{-1}$	c_w, molec cm^{-3}	k_w, cm h^{-1}	Production Rate molec $cm^{-2} s^{-1}$	Emission Rate molec $cm^{-2} s^{-1}$
		Experiment E 1			
Ethene	$4.1*10^5$	$3.3*10^{10}$	10.8	$1.47 * 10^8$	$0.99 * 10^8$
Propene	$1.8*10^5$	$1.6*10^{10}$	9.5	$0.62 * 10^8$	$0.42 * 10^8$
1-Butene	$0.8*10^5$	$1.7*10^{10}$	8.7	$0.29 * 10^8$	$0.41 * 10^8$
		Experiment E 2			
Ethene	$3.5*10^5$	$2.9*10^{10}$	14.2	$1.25 * 10^8$	$1.14 * 10^8$
Propene	$2.4*10^5$	$1.5*10^{10}$	12.6	$0.85 * 10^8$	$0.52 * 10^8$
1-Butene	$1.0*10^5$	$1.6*10^{10}$	11.5	$0.36 * 10^8$	$0.51 * 10^8$

Table is based on P_0, which is production rate in quartz glass bottles, c_w is the NMHC concentration in seawater, and k_w is the transfer velocity (see equation (4) and (5)).

$$E = k_w * (c_w - c_a/H) \qquad (5)$$

with
E emission rate;
k_w transfer velocity;
c_w concentration in seawater;
c_a concentration in the atmosphere;
H Henry coefficient (dimensionless)

Since seawater is supersaturated with alkenes by several orders of magnitude the expression c_a/H is very small compared to c_w and can be neglected. The values for c_w were derived from the initial concentrations of E1 and E2. They are given in Table 4.

The transfer velocity k_w is a function of the wind velocity [Liss and Merlivat 1986]. For a simple estimation we used the average wind velocity measured for the time period of experiment E1 (8.7 $\pm$2.5 m s^{-1}) and E2 (10.4 $\pm$3.7 m s^{-1}), respectively. The corresponding transfer velocities were calculated according to Liss and Merlivat [1986]. A Schmidt number correction according to Plass-Dülmer et al. [1993] was used.

In Table 4 the calculated alkene emission rates are given and compared to the column-integrated production rates. For ethene and propene the calculated production rates slightly exceed the emission rates, for 1-butene the pattern is reversed. However, regarding the calculation of both rates, it is likely that the differences at least in part are due to uncertainties of the used parameters. A possible alkene destruction in the ocean cannot be ruled out; however, the results of the comparison between production and emission rates demonstrate that in the investigated area the flux to the atmosphere is the dominant loss process for alkenes.

5. CONCLUSIONS

The experimentally determined production rates in unfiltered samples (quartz glass bottles) and those from field measurements (diurnal variations) were very similar. Although the interaction of the biological, chemical and physical parameters is not yet fully understood, the comparison of the productions rates indicate that the experimental findings in principle seem to describe the processes in the open ocean. The production of alkenes depends on the presence of light. Additionally there is strong evidence that the presence of dissolved organic material (DOM) is necessary, which may be released from algae, and then is photochemically transformed into alkenes. These results agree with the observations Wilson et al. [1970] obtained in the laboratory using phytoplankton stock cultures. Our presented results extend the findings of Wilson et al. [1970] to the open ocean. However, we have no experimental evidence for a direct hydrocarbon production by organisms. Moreover, it is still not clear which kind of biological activity (photosynthesis, excretion, decomposition) is the main source for the alkene precursors. The source and photochemical turnover rate of DOM should be investigated in further experiments.

There is increasing evidence from literature for trace gas production mechanisms via biological activity and/or photochemistry in the ocean. A very well known example of a substance produced indirectly from phytoplankton is dimethyl sulfide [Andreae et al., 1983; Andreae and Barnard, 1984; Nguyen et al., 1988]. Photochemical production mechanisms were established for carbonyl sulfide (COS) [Ferek and Andreae, 1984] and for CO [Conrad and Seiler, 1980; Redden and Gordon, 1982]. For low molecular weight substances such as formaldehyde, acetaldehyde, or acetone a production by photochemical degradation of DOM was suggested [Mopper, 1985; Mopper and Stahovec, 1986; Mopper and Zhou, 1990].

We found a reasonable agreement between alkene production and emission rates, both calculated for a restricted oceanic region. This supports the suggestion of Plass et al. [1992] that emission to the atmosphere is the dominant loss

mechanism for alkenes from the ocean. It also means that the knowledge of the alkene production rates would provide a first basis for emission estimates.

Obviously, the production rates obtained in the experiments and diurnal variations only represent a limited oceanic region with a special phytoplankton community, chemical composition, and irradiation conditions. Therefore an extrapolation from these data to other oceanic regions is unwarranted until a more precise and quantitative description of the alkene production mechanism in seawater is available.

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