VERTICAL DISTRIBUTION OF NON METHANE HYDROCARBONS IN THE REMOTE MARINE BOUNDARY LAYER

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Abstract. The marine production and vertical atmospheric distribution of light nonmethane hydrocarbons (NMHC) from C_2 to C_6 in the marine boundary layer was studied at the Hao atoll, in the intertropical South Pacific. NMHC vertical profiles were performed up to 1600 m altitude by using balloon and remote controlled aircraft-borne devices simultaneously with surface air and seawater samplings. Seawater was found to be supersaturated in NMHC. Despite the concentration variations of the seawater its relative composition is well reproducible, within a factor of 2. The average NMHC atmospheric composition at sea level is similar to that of seawater. However, the results obtained display a very large short time variability of the NMHC atmospheric concentrations, which seems to result mainly from variations in the marine emission rates and/or advective processes of transport. It was initially expected that the proportions of short-lived species should rapidly decrease in altitude, because of their chemical decay, mainly by oxidation by OH radicals. However, it appeared that the proportions of the different NMHC measured remained relatively constant up to the maximum altitude sampled during the campaign, i.e., about 1600 m. This suggests that transport processes in the atmosphere were always very rapid, relative to the chemical processes, even for short-lived NMHC. However, for reactive species, simple calculations based on the hypothesis of a steady state in thin atmospheric layers show that the photochemistry involved is consistent with usual OH concentrations varying from 1.6×10^7 rad cm^{-3} at noon to 4×10^4 rad cm^{-3} at sunset.

Introduction

Non methane hydrocarbons (NMHC) are produced by multiple sources and released into the atmosphere where they are destroyed by homogeneous chemical reactions involving OH radicals and, to a lesser extent, O_3 oxidation. Despite their low mixing ratios in the remote troposphere of a few hundred parts per trillion, i.e. 3 or 4 orders of magnitude lower than methane, they can be of importance for the chemistry of the troposphere, and particularly for the ozone and odd hydrogen radicals budgets.

C_2 - C_3 NMHC have been detected in the surface seawater in concentrations similar to that of methane [Swinnerton and Linnenbon, 1967; Lamontagne et al., 1973]. More recently, Bonsang et al. [1988,1989] have found that a wider range of NMHC from C_2 to C_6 were supersaturated in surface

seawater by 2 or 3 orders of magnitude with respect to the atmosphere. Both long-lived and short-lived NMHC are produced by the ocean surface, but, whereas the long-lived species are assumed to mix in the whole troposphere [Aikin et al., 1987], short-lived species are expected to decrease rapidly versus altitude. However, the few vertical profiles obtained over the ocean [Ehhalt et al., 1985; Dickerson et al., 1987; Singh et al., 1988; Greenberg et al., 1990] have shown that the short-lived NMHC are actually transported in altitude, likely by fast vertical advective processes.

In order to investigate the importance of NMHC in the photochemistry of the marine atmosphere the vertical distribution of light hydrocarbons from C_2 to C_6 in the marine atmospheric boundary layer was studied in a remote oceanic site in the intertropical South Pacific. NMHC vertical profiles were performed up to 1600 m altitude by using balloon and remote controlled aircraft-borne devices simultaneously with surface air and seawater samplings.

Experimental Procedure

The measurements were performed in 1987 from May 31 to June 11 on the Hao atoll ($18^\circ 04'S$, $140^\circ 58'W$) in the Pacific Ocean (Figure 1). This site was selected for its isolation at the east of the Tuamotu Archipelago, far from the usual anthropogenic sources of pollution.

Owing to the general circulation of air masses at this latitude, the sampling site was located on the north part of the atoll at 5 km northwest the small village of Hao (Figure 1). However, a variability in the wind direction was observed during the experiment, therefore in order to avoid any contamination by human activities the samplings were conducted only when the sampling site was upwind the village. At the sampling place the width of the atoll between ocean and lagoon was about 100 m, and the influence of the local scarce vegetation was negligible. In addition, three seawater samples were collected at 5 nautical miles northerly of the atoll, and one sample was collected in the lagoon.

Grab air samples were collected in 6 L-stainless steel electropolished canisters, manually opened at sea surface level or automatically opened in altitude. For this purpose, automated valves were fitted on the canisters. Samples were collected with meteorological balloon carrying a load of three canisters. Each sample was collected by opening the valve at a preselected altitude measured with a pressure sensor. Once the last sample collected, the load was automatically disconnected and dropped with a parachute in the lagoon where it was recovered. A tethered balloon was also used in order to take samples at low altitudes. Occasionally, the sampling cylinders were adapted on a remote piloted aircraft (SAM for "Sonde Aérologique Motorisée") used for micrometeorological measurements. NMHC atmospheric concentrations measured by using this device were comparable to those obtained by using the other sampling systems. Low acetylene concentrations indicate the absence of any pollution effect on the air samples collected by using the remotely controlled aircrafts; moreover, as shown by Kanakidou et al. [1988], this acetylene was probably entirely released from the sea.

Seawater samples were outgassed with ultra pure helium, by an head space equilibration technique. Dissolved NMHC in seawater were then analyzed by gas chromatography with the same technique as for air samples [Bonsang et al., 1987].

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Fig.1. Map of atoll of Hao and location in the Pacific Ocean (18°04'S-140°58'W).

Sample analysis was performed in the laboratory within 2 months after the experiment. For this purpose a gas chromatograph equipped with a flame ionisation detector was used. 0.5 to 1 L of air sample was dried by a potassium carbonate trap and cryogenically enriched in a tenax trap cooled at -120°C. After this first enrichment step the sample was transferred into the chromatographic column (porous layer open tubular column, KCl /Al₂O₃) cooled at -80°C, and temperature programmed to 120°C according to a technique described elsewhere [Kanakidou et al., 1988]. Interferences

with ozone during the enrichment step have not been checked, because they are unlikely owing to the trapping temperature (-120°C). The accuracy of the analysis was estimated at 5 to 10 %, the minimum detectable limit was 5 pptv for most of the C₂-C₅ NMHC.

The meteorological data used to interpret the NMHC profiles have been provided by the French meteorological weather service as well as by the European Center of Medium Range Weather Forecast (ECMWF, Reading, United Kingdom). The data include daily radiosoundings of Rapa

(27°37'S; 144°20'W), Tahiti-Faa (17°33'S; 149°37'W), and Hao (18° 04'S; 140° 58'W), performed for the world meteorological network. Infrared satellites images from the National Oceanic and Atmospheric Administration (NOAA-GOES) have also been used when they were available. Furthermore, detailed pressure, temperature, and humidity profiles (PTU) up to about 1000 m height were measured over the atoll, by using the remote piloted aircraft [Martin, 1980]. These PTU profiles were obtained just when the NMHC airborne samplings were completed. Moreover, ten days backward trajectories have been computed for three ending levels (925, 850, and 700 hPa) at Hao. Trajectories calculations were made by taking into account the synoptic vertical motions, particularly important in tropical regions, as described and discussed by Martin et al. [1987, 1990].

The period from May 31 to June 11, 1987, was characterized by successive perturbations associated with the proximity of the intertropical convergence zone (ITCZ). ITCZ was oscillating northern and southern of the sampling site

leading to unusual precipitations and inducing variable wind in strength and direction. The wind velocity at 10 m altitude was generally of the order of 3-5 m/s during the campaign and reached a maximum of 15 m/s on June 7.

Results and Discussion

Seven atmospheric NMHC vertical profiles were obtained in the marine boundary layer from May 31 to June 11, 1987: four profiles during daytime or at twilight up to an altitude of 1600 m; three profiles at night at lower altitudes, up to 300 m. Ten air samples were collected at sea level; three seawater samples were collected in the open ocean and one additional in the lagoon.

The NMHC concentrations in seawater, expressed in ppbv (10^{-9} cm³ gas / cm³ of water at 30°C) are reported in Table 1. The atmospheric mixing ratios for the seven flights are reported in Table 2.

TABLE 1. Concentrations of Dissolved Hydrocarbons in Seawater and Ratios to Ethene

	Date							
	June 4, 1987		June 7, 1987		June 11, 1987		June 5, 1987	
Local Hour	1430		0925		0605		1410	
Water temperature	28°C		28°C		28°C		30°C	
Air temperature	27°C		24°C		26.3°C		27°C	
Wind speed	9.5 m/s		13.5 m/s		5 m/s		7.5 m/s	
	Concentration		Concentration		Concentration		Concentration*	
	ppbv	Ratio	ppbv	Ratio	ppbv	Ratio	ppbv	
C ₂ H ₂	0.52	0,190	9.32	0,159	2.20	0,058	2.20	
Alkanes								
C ₂ H ₆	1.50	0,549	21.81	0,373	39.62	1,051	4.81	
C ₃ H ₈	1.39	0,509	13.55	0,232	17.94	0,476	3.06	
i C ₄ H ₁₀	0.29	0,106	3.62	0,062	2.53	0,067	0.40	
n C ₄ H ₁₀	0.65	0,238	7.44	0,127	9.60	0,255	1.10	
i C ₅ H ₁₂	0.44	0,161	11.42	0,195	3.29	0,087	1.26	
n C ₅ H ₁₂	0.71	0,260	11.68	0,200	4.33	0,115	1.19	
n C ₆ H ₁₄	0.38	0,139	7.65	0,131	1.66	0,044	0.93	
Alkenes								
C ₂ H ₄	2.73	1,000	58.44	1,000	37.69	1,000	230.4	
C ₃ H ₆	5.87	2,150	74.51	1,275	70.21	1,863	9.55	
trans-2-C ₄ H ₈	0.30	0,110	3.92	0,067	2.84	0,075	0.46	
1 C ₄ H ₈	1.78	0,652	22.19	0,380	28.06	0,744	1.85	
i C ₄ H ₈	4.02	1,473	38.53	0,659	21.80	0,578	5.52	
cis-2-C ₄ H ₈	0.26	0,095	3.12	0,053	4.70	0,125	0.36	
1 C ₅ H ₁₀	1.33	0,487	13.01	0,223	10.65	0,283	1.06	
1 C ₆ H ₁₂	0.43	0,158	3.70	0,063	4.30	0,114	0.49	

Concentrations in parts per billion by volume (ppbv) (10^{-9} L of gas per liter of water at 28°C)
Ratios are to ethene.

* Lagoon sample

TABLE 2. CH₄ and NMHC Mixing Ratios Above the Hao Atoll

	Flight Number											
	1	1	1	1	-	2	2	3	3	-	-	4
Date	May 31	May 31	May 31	May 31	May 31	June 2	June 2	June 3	June 4	June 5	June 7	June 8
Local hour	1450	1430	1200	1200	2100	2250	2230	2240	0010	1400	1030	1705
Altitude, m	0	100	400	1000	0	0	100	300	0	0	0	0
Wind direction	340					360			320	240	80	80
Wind speed, m/s	5					8.5			5	7.5	13.5	11
UV, mW/cm ²	3.6	3.6	4.2	4.2	0	0	0	0	0			0.1
Sampling mean	MAN	T.B.	B.	B.	MAN	MAN	T.B.	T.B.	MAN	MAN	T.B.	B.
CH ₄ , ppmv	1.651	1.640	1.662	1.657	1.640	1.648	1.654	1.661	1.633	1.658	1.625	1.646
NMHC, ppbv												
C ₂ H ₂	0.117	0.023	0.084	0.090	0.168	0.227	0.115	0.054	0.056	0.139	0.125	0.092
Alkanes												
C ₂ H ₆	0.625	0.491	0.498	0.423	1.128	1.465	1.088	1.155	0.753	0.854	1.294	0.814
C ₃ H ₈	0.448	0.242	0.238	0.195	1.228	1.333	0.972	0.869	0.496	0.878	1.096	0.714
iso-C ₄ H ₁₀	0.040	0.017	0.028	0.036	0.069	0.062	0.054	0.164	0.055	0.045	0.049	0.061
n-C ₄ H ₁₀	0.197	0.128	0.129	0.091	0.422	0.447	0.325	0.476	0.205	0.238	0.389	0.281
iso-C ₅ H ₁₂	0.040	0.017	1.560	0.290	0.093	0.116	0.222	1.852	0.056	0.043	0.131	0.036
n-C ₅ H ₁₂	0.401	0.099	0.132	0.102	0.727	0.753	0.641	0.517	0.154	0.408	0.617	0.701
néopentane	nd	nd	0.035	0.004	0.008	0.009	0.006	0.013	0.011	0.005	0.009	nd
2methyl-pentane	nd	0.023	0.067	0.022	0.031	0.046	0.059	0.259	0.053	0.011	0.030	0.011
3methyl-pentane	0.012	0.012	0.033	0.013	nd	0.022	0.040	0.238	0.016	nd	<0.01	nd
n-C ₆ H ₁₄	0.056	0.078	0.123	0.062	0.185	0.181	0.173	0.672	0.086	0.096	0.147	0.093
Alkenes												
C ₂ H ₄	1.225	0.865	0.171	0.244	2.030	3.852	2.306	1.973	4.833	1.651	1.893	1.504
C ₃ H ₆	1.465	0.732	0.936	0.056	2.424	2.978	2.249	1.718	3.573	2.220	2.035	1.993
trans-2-C ₄ H ₈	0.047	0.033	0.023	0.017	0.037	0.045	0.036	0.058	0.138	0.032	0.031	0.056
1-C ₄ H ₈	0.390	0.237	0.221	0.182	0.480	0.640	0.506	0.710	0.736	0.357	0.477	0.412
iso-C ₄ H ₈	0.376	0.415	0.390	0.280	0.453	0.561	0.559	0.778	0.785	0.401	0.371	0.412
cis-2-C ₄ H ₈	0.046	0.028	0.025	0.016	0.034	0.040	0.036	0.054	0.116	0.027	0.028	0.054
1-C ₅ H ₁₀	0.701	0.152	0.235	0.202	0.973	1.236	1.079	0.686	0.366	0.584	0.855	0.970
1-C ₆ H ₁₂	0.089	0.099	0.070	0.082	0.122	0.150	0.106	0.935	0.161	0.085	0.107	0.100
Dienes												
propadiène	0.005	nd	nd	nd	0.012	0.009	0.007	nd	nd	0.006	0.007	0.003
1.2butadiène	0.048	nd	nd	0.006	0.054	0.061	0.028	0.007	0.012	0.039	0.042	0.011
1.3butadiène	0.022	0.014	0.030	0.013	0.019	0.025	0.014	0.020	0.021	0.014	0.017	0.010

Supersaturation of the Surface Sea Water In NMHC

In seawater, ethene and propene are the most abundant species with mixing ratios of 2.7 to 58 and 6 to 75 ppbv, respectively. Mixing ratios of 1 and iso-butene (C₄H₈), ethane (C₂H₆), and propane (C₃H₈) are about two times lower than for ethene. The concentrations in the lagoon of the atoll are similar except for ethene which presents a significant higher contribution of 230 ppb against 2 to 10 ppb for the other main species.

Seawater samples collected on June 7 and 11 present NMHC concentrations of about 1 order of magnitude greater than the concentrations of the first sample collected on June 4. The origin of this variability of the dissolved NMHC concentrations is not known, however, the study of the NMHC vertical distribution in the seawater by Swinnerton

and Linnenbom [1967] and more recently by Bonsang and Lambert [1990] revealed the presence of maxima in the euphotic zone. It is therefore reasonable to assume that the NMHC present at the sea surface can be produced at least partly in depth. Thus the increase of sea surface NMHC water concentrations could be attributed to a mixing of the superficial water, under the influence of a greater ventilation as occurring during the second period of the experiment.

Despite this great variability it appears that the concentrations of the different NMHC covary, according to our previous observations in the tropical Indian and North Pacific oceans [Bonsang et al., 1988, 1989]. The ratios of the NMHC concentrations to that of ethene used as a reference are constant in the open ocean within a factor of 2 (3 for C₂H₂ and n C₆H₁₄; Table 1).

Taking into account our atmospheric measurements (Table

TABLE 2. (continued)

	Flight Number												
	4	4	4	5	5	6	6	6	-	7	7	7	7
Date	June 8	June 8	June 8	June 10	June 10	June 11	June 11	June 11	June 11	June 11	June 11	June 11	June 11
Local hour	1810	1735	1620	1820	1744	1115	1000	1000	0655	1554	1613	1556	1535
Altitude, m	300	600	850	0	500	0	375	1595	0	200	750	1200	0
Wind direction	80			60		330				340			
Wind speed, m/s	11			11.5		5				5.5			
UV, mW/cm ²	0	0.04	0.23	0	0	3.9	1.7-3.4	1.7-3.4	0	0.96	2.71	1.95	1.45
Sampling mean	S.A.M.	S.A.M.	S.A.M.	MAN	S.A.M.	MAN	B.	B.	MAN	S.A.M.	S.A.M.	S.A.M.	MAN
CH ₄ , ppmv	1.673	1.627	1.657	1.628	1.632	1.652	1.622	1.635	1.619	1.603	1.630	1.662	1.645
NMHC, ppbv													
C ₂ H ₂	0.145	0.051	0.062	0.110	0.119	0.022	0.082	0.087	0.052	0.020	0.025	0.071	0.049
Alkanes													
C ₂ H ₆	1.202	0.454	0.630	0.980	1.258	0.360	0.560	1.834	0.414	0.435	0.407	0.620	0.635
C ₃ H ₈	0.561	0.177	0.321	0.841	0.720	0.102	0.210	0.770	0.127	0.103	0.115	0.231	0.426
iso-C ₄ H ₁₀	0.042	0.028	0.044	0.086	0.100	0.011	0.030	0.060	0.010	0.041	0.011	0.033	0.035
n-C ₄ H ₁₀	0.357	0.071	0.143	0.300	0.297	0.051	0.121	0.295	0.056	0.159	0.033	0.113	0.131
iso-C ₅ H ₁₂	0.049	0.020	0.126	0.044	n.m.	0.010	0.062	0.182	0.013	0.040	0.007	0.069	0.063
n-C ₅ H ₁₂	0.293	0.064	0.112	0.637	0.317	0.065	0.161	0.248	0.082	0.047	0.023	0.299	0.564
néopentane	0.006	nd	0.003	0.002	0.066	nd	nd	nd	nd	nd	nd	nd	nd
2methyl-pentane	0.032	0.010	0.050	0.015	0.509	nd	0.203	0.195	nd	0.032	nd	0.654	1.483
3methyl-pentane	nd	0.005	0.038	nd	0.296	nd	0.093	0.122	nd	0.022	nd	0.290	0.643
n-C ₆ H ₁₄	0.233	0.043	0.125	0.096	0.290	0.026	0.145	0.196	0.034	0.036	0.012	0.386	0.773
Alkenes													
C ₂ H ₄	0.532	2.046	1.134	2.395	3.944	0.225	0.231	0.534	0.172	0.308	0.157	1.661	0.151
C ₃ H ₆	1.498	0.638	0.820	1.779	4.522	0.404	0.582	1.078	0.584	0.606	0.242	0.756	0.286
trans-2-C ₄ H ₈	0.034	0.029	0.040	0.051	0.164	0.019	0.022	0.052	0.015	0.020	0.012	0.024	0.011
1-C ₄ H ₈	0.491	0.193	0.257	0.379	0.975	0.090	0.198	0.377	0.181	0.137	0.069	0.259	0.119
iso-C ₄ H ₈	0.382	0.216	0.467	0.419	1.170	0.170	0.310	0.494	0.220	0.433	0.037	0.381	0.197
cis-2-C ₄ H ₈	0.032	0.028	0.039	0.049	0.140	0.017	0.021	0.062	0.015	0.016	0.009	0.023	0.010
1-C ₅ H ₁₀	0.254	0.139	0.160	0.702	0.501	0.090	0.141	0.193	0.167	0.093	0.039	0.228	0.103
1-C ₆ H ₁₂	0.152	0.082	0.101	0.095	0.208	0.020	0.058	0.082	0.067	0.037	0.020	0.112	0.049
Dienes													
propadiène	0.008	nd	0.003	0.003	0.005	nd	0.009	0.010	nd	nd	nd	0.003	nd
1.2butadiène	0.021	0.006	0.007	0.016	nd	nd	0.011	0.017	0.007	nd	nd	0.006	0.006
1.3butadiène	0.021	0.006	0.010	0.011	0.034	0.004	0.033	0.063	0.020	0.008	0.003	0.029	0.010

MAN: manual sampling at sea level; T.B.: tethered balloon sampling; B: meteorological balloon sampling; S.A.M.: "Sonde Aérologique Motorisée" or remote piloted aircraft sampling.
Here nd, non detected (<0.005 ppbv)

2) and the Henry's constants, as deduced from the solubility data of McAuliffe [1966], it appears that the seawater is supersaturated with respect to the atmosphere by at least two orders of magnitude and acts as a net source of NMHC. This large supersaturation was previously reported for different oceanic areas [Bonsang et al., 1988].

Because of this large supersaturation the NMHC production by surface seawater is the piston velocity times the seawater concentration. This production is therefore independent on the Henry's constants. According to Deacon [1977] and Liss and Merlivat [1986], the piston velocity is a function of the square root of the Schmidt number of the species. It was shown by Kanakidou [1988] that for the

NMHC measured here, the variations of the piston velocity do not exceed 20 %. Consequently, as a first approximation, the relative magnitude of the marine emissions of the different NMHC reflects their seawater composition.

NMHC Atmospheric Compositions

The main species present in the lower atmosphere are mainly ethene, propene, ethane, and propane. Whereas the CH₄ concentration is extremely constant (± 1.2 %), the NMHC concentrations at surface level vary over 1 order of magnitude from 0.2 to 4.8 ppbv for ethene, 0.1 to 3.5 ppbv for propene, 0.4 to 1.5 ppbv for ethane, 0.1 to 1.3 ppbv for

propane. Other alkanes and alkenes are of the sub parts per billion level.

The average air composition at sea level, using ethene as reference is reported on Figure 2 versus that of seawater. The similarity of these compositions has been already reported by Bonsang et al. [1988, 1990] in the Indian Ocean and particularly at Amsterdam Island. It has been shown that all the NMHC there originate from seawater, except C_2H_6 whose lifetime is about 2 months, and which can partly result from continental advections. It can be similarly assumed that, except may be for C_2H_6 , the NMHC measured in the lower layers over the atoll of Hao originate from the ocean surface, including C_2H_2 , as previously discussed by Kanakidou et al. [1988]. This point is confirmed by the analysis of the 9 day back trajectories ending at 925 hPa (Figure 3).

Similar comparison can be done for the samples taken at altitudes above 500 m (Figure 2). However, in this case it can be seen a slight difference between the seawater

Fig. 2. Average air composition at sea level and 500 m versus the average seawater composition. Ethene is used as the reference (see text). Dark circles: alkanes; open circles: alkenes. 1: C_2H_6 ; 2: C_3H_6 ; 3: iso C_4H_8 ; 4: C_2H_2 ; 5: 1 C_4H_8 ; 6: C_3H_8 ; 7: 1 C_5H_{10} ; 8: C_5H_{12} ; 9: n C_4H_{10} ; 10: iso C_5H_{12} ; 11: C_2H_2 ; 12: n C_6H_{14} ; 13: 1 C_6H_{12} ; 14: cis-2 C_4H_8 ; 15: trans-2- C_4H_8 ; 16: iso C_4H_{10} .

Fig. 3. Nine days back trajectories ending at 925 hPa above the Hao atoll during the experiment. June 1, 3, 4, 6, 9, 11, and 12, 1987, at 0000 UT; May 31, June 5 and 7, 1987, at 0600 UT; and June 2, 8, and 10, 1987, at 1800 UT.

composition and the atmospheric composition which presents a higher contribution of alkanes. This observation is consistent with a faster destruction of alkenes.

NMHC Vertical Profiles

During the experiment the thermal structure of the atmosphere surrounding the atoll was generally characterized by the presence of a thin absolutely unstable layer above the ocean from 100 to 300 m. A dryer layer, generally convectively and selectively unstable, was located between 900 and 700 hPa (1000 to 3000 m). Above this layer, up to the tropopause, a stable layer, generally absolutely stable, was observed.

The obtained vertical profiles are reported in Figures 4a to 4d for the four flights 1, 4, 6, and 7 undertaken during daytime.

During the flight 1 (Figure 4a) a high-pressure cell was marked by a strong temperature inversion located from 850 to 770 hPa (1500 to 3000 m). Below this layer, convection could take place and allowed the development of small cumulus up to the inversion level. The high diffusivity coefficient between 100 and 600 m. was due to the thermal and dynamical instability. The vertical profile of the NMHC is characterized by a strong negative concentration gradient between sea level and 100 m height. Above this level, alkenes are sharply decreasing versus altitude, whereas for the alkanes and acetylene, this general trend is less pronounced. However, the alkanes and alkenes vertical distributions are not directly related to their chemical reactivities. For example, ethane (C_2H_6) and 1-butene (1- C_4H_8) display very similar profiles despite the great difference of their kinetic constants of reaction with OH radicals: $0.26 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $32 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, respectively.

During the flight 4 (Figure 4b), the Hao atoll was under the influence of a large anticyclonic subtropical cell centered far at the South East at 850 hPa. At this level, the flux was north-east. At the surface a large subtropical high-pressure

Fig. 4a. Flight 1: vertical distribution of acetylene, alkanes, micrometeorological parameters and vertical eddy diffusivity coefficient. Left panels: hydrocarbons profiles. Right panels: dotted line, potential temperatures (degrees Celsius); dashed line, horizontal wind gradient ($\text{m s}^{-1}/100\text{m}$); full line, eddy diffusivity coefficient ($\text{m}^2 \text{s}^{-1}$).

Fig. 4b. Flight 4 vertical profiles.

Fig. 4c. Flight 6 vertical profiles.

Fig. 4d. Flight 7 vertical profiles.

cell kept up the north-east trade wind, a cold front separating the equatorial air from the tropical air remained near the atoll. This frontal system was associated with a cloudy sky. Locally, a thermal instability was observed up to 200 m height. Above this level the turbulence was only due to dynamical instability induced by wind gradient. Under these conditions, we can generally observe a very slight decrease of the NMHC concentrations from 0 to 600 m height with no systematic difference between alkanes and alkenes. All species present a relatively regular decrease up to 600 m and then an opposite trend from 600 to 850 m. However, the vertical distribution of C_2H_4 appears more irregular than the others.

Both flights 6 and 7 were performed on the same day (June 11, 1987). The temperature profile remained constant during the day. As for the previous flights, an unstable layer was observed up to 200 m.

For the flight 6 (Figure 4c) a very significant increasing trend versus altitude was found for all NMHC. The vertical gradient seems to be independent on the species. The analysis of the corresponding meteorological situation indicates that the sampling site was at this time in the vortex of a low pressure system.

For the flight 7 (Figure 4d), performed in the afternoon, we can note a similarity with the previous flight for the alkanes distribution. On the opposite, the alkenes distribution presents now a complex vertical structure with a maximum at 750 m.

Nighttime flights 3 and 5 do not present any systematic trend versus altitude. On the opposite, the nocturnal flight 2 shows a systematic decrease of the concentrations between 0 and 100 m with a concentration ratio practically constant of about 0.75, whatever the species (Figure 5).

Discussion of the Results

It may be concluded from the seven preceding studies that, even in the center of a very large ocean, the emission and transport processes of NMHC are much too variable to lead to a reproducible typical vertical profile. This observation agrees with the conclusion of a similar study by Greenberg et al. [1990]. Such an effect is mainly due to the fact that for the considered NMHC the atmospheric dynamical processes are dominant relative to their chemical destruction.

However, it appears on the whole that anticyclonic situations are generally associated with a slight decreasing trend of the NMHC versus altitude. On the opposite, low-

pressure systems result in the formation of enriched layers aloft, even for the most reactive species such as butenes or pentenes. For a given flight the profiles of alkanes and acetylene are similar, whereas some alkenes can significantly differ. As no systematic difference can be related to the chemical reactivity of the alkenes, it is clear that the emissions and transports are very variable in space and time. These subgrid processes are not well quantified by meteorological synoptic models in which they are only parametrized. However, some peculiar profiles were obtained in which the vertical gradients appear to be slightly different for different NMHC. They can be tentatively analyzed in term of chemical evolution.

In effect, the meteorological parameters measured during the experiment have shown that, between sharp inhomogeneities, the atmospheric layers actually displayed a strong stratification during vertical and horizontal transport. It may be assumed that inside a well-characterized layer, the concentration gradient of NMHC should result from both vertical transport (upward and downward) by eddy diffusion and simultaneous chemical decay, essentially due to the NMHC reaction with OH radicals. The vertical distribution of the NMHC within an atmospheric layer should reflect the average OH mixing ratios existing in this layer. Assuming a steady state, a continuity equation can be written for the concentrations of each species between two levels where the eddy diffusivity coefficient K_z has a low variability: see appendix. With this hypothesis we have

$$\frac{\ln(C_b/C_a)}{(z_a - z_b) \cdot \sqrt{k_{OH}}} = \sqrt{[OH] / \langle K_z \rangle}$$

where C_a and C_b are the mixing ratio of an NMHC at the levels z_a and z_b , k_{OH} its kinetic constant of oxidation by OH radicals, and $\langle K_z \rangle$ the average value of the vertical eddy diffusivity coefficient between z_a and z_b . The OH concentration and K_z being the same for all NMHC, the first term of this equation must be found constant.

Only five couples of samples were obtained under such conditions. Some situations with negative vertical concentration gradients, corresponding to a source located at the lower level, are observed for flight 1 between 0 and 100 m, and flight 7 between 0 and 200 m and between 750 and 1200 m. During flight 4 there was no systematic trend versus altitude. This observation can be accounted for by the previously described structure of the atmosphere surrounding the Hao atoll. However, an enriched layer was observed at 600 m height. Consequently, assuming that diffusion occurred from both sides of this layer, the continuity equation can be applied for the two couples of samples respectively collected at 300 and 600 m, and 600 and 850 m.

In Figure 6 are plotted the numerical values of OH/K_z versus the kinetic constant of oxidation by OH radicals for the five considered cases. It can be seen that, except for the flight 4 (300-600 m), the steady state hypothesis is a reasonable assumption for those alkenes with a kinetic constant greater than $20 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ i.e., species whose lifetimes are short enough to allow an equilibrium between vertical transport and chemical decay. On the opposite, long-lived species, and all the considered NMHC for flight 4 (from 300 to 600 m), were unable to reach such a steady state. For these cases, the decrease of OH/K_z versus the chemical reactivity is in agreement with the theoretical analysis of McKeen et al. [1990]. In the same way the work of these authors would lead to conclude, from OH/K_z constant versus k_{OH} that we deal with puff emissions from patchy sources.

The OH/K_z values and the OH radical concentrations deduced from these gradients are reported in Table 3. The calculation of K_z was performed from the temperature and

Fig. 5. Flight 2: ratios of the concentrations measured at 100 m over the concentrations measured at sea level versus the sea level concentrations. Dark circles: alkanes; open circles: alkenes and dienes. 1: C_2H_6 ; 2: C_3H_8 ; 3: iso C_4H_{10} ; 4: C_2H_4 ; 5: 1 C_4H_8 ; 6: C_3H_6 ; 7: 1 C_5H_{12} ; 8: C_5H_{12} ; 9: n C_4H_{10} ; 10: iso C_5H_{12} ; 11: C_2H_2 ; 12: n C_6H_{14} ; 13: 1 C_6H_{12} ; 14: cis-2 C_4H_8 ; 15: trans-2- C_4H_8 ; 16: iso C_4H_{10} ; 17: 1,2 Butadiène; 18: 1,3 Butadiène.

TABLE 3. Determination of OH Radicals Concentrations from the Vertical Gradients of NMHC

	Flight Number			
	1	4	7	7
Date	May 31	June 8	June 11	June 11
Local Hour	1200-1450	1620-1735	1535-1554	1556-1613
Altitude, m	0-100	600-850	0-200	750-1200
UV, mW/cm ²	3.6 to 4.2	0.04-0.23	1.0-2.7	1.45-1.95
Average [OH]/K _z , molec cm ⁻⁵ s	213	5.00	74.1	8.8
Average K _z , cm ² s ⁻¹	7.65x10 ⁴	8.6x10 ³	4.95x10 ⁴	1.22x10 ⁴
Average [OH], rad cm ⁻³	1.6 x 10 ⁷	4.3 x 10 ⁴	3.7 x 10 ⁶	1.1 x 10 ⁵

wind velocity profiles according to the parametrization defined by Louis [1979]. The calculated diffusion coefficients and the corresponding OH concentrations are also shown in Table 3, together with the corresponding hour of the day and the UV flux at 310 nm. A low OH concentration of 4×10^4 rad/cm³ is observed at about 5 p.m., whereas at noontime we calculate OH concentrations up to 1.6×10^7 rad/cm³. These estimations are consistent with the expected values of OH radical concentrations for the latitude and season computed by Logan [1981] and Crutzen [1982], on a global scale.

Conclusion

The relative composition of the superficial seawater in this part of the Pacific ocean is well reproducible within a factor of 2, as previously pointed by Bonsang et al. [1989]. This accounts for an atmospheric relative composition at sea level similar to that of the seawater.

The atmospheric concentrations of NMHC obtained during the experiment at the Hao atoll display a very large short time variability even in this place located in the open ocean and free of any natural and anthropogenic continental

Fig. 6. OH/K_z versus the kinetic constant of oxidation by OH radicals deduced from the vertical gradients of NMHC in the five considered cases.

sources. This observation agrees very well with the previous results of Bonsang et al. [1989] and Singh et al. [1988], and more particularly with the measurements of Kanakidou during the cruise of the R/V Researcher, about 400 km NE from Oahu island [Carsey et al., 1988].

For the experiment over the Hao atoll this variability could be attributed partly to the heterogeneity of concentrations in the superficial seawater, all around the atoll and partly to discontinuous marine emissions followed by a rapid transport. The irregular vertical distributions observed prevent of interpreting the results in terms of OH concentrations by assuming a simple continuous one-dimensional model. However, as previously pointed out, for five couples of samples, the vertical gradients were found slightly different for different NMHC. In these particular cases it was possible to assume that the proportions of short-lived species decreased from an enriched layer because of their chemical decay, mainly by OH radicals. Assuming that in thin atmospheric layers (typically 200 m thickness), vertical eddy diffusion and chemical destruction by OH radicals drive the atmospheric gradients of NMHC, a simple diffusion model enables us to calculate average OH concentrations of about $1.6 \times 10^7 \text{ cm}^{-3}$ at noon and $4 \times 10^4 \text{ cm}^{-3}$ at sunset. A test of validity of the steady state assumption is given by the constancy of the ratio OH/K_z versus k_{OH} observed for the most reactive species.

Appendix

Determination of the vertical eddy diffusivity coefficient K_z is based on the link of the dynamical turbulence and the thermal turbulence. Such kind of parametrization was developed by Louis [1979] for medium range forecast models developments, and great care should be taken in field experiment applications. The use of a parametrization for determining eddy flux coefficient K_z is limited to an estimation of the mean value of K_z around the time during which temperature and wind profiles are performed (i.e., 0000 UT or 1400 local time).

The Louis' technique depends on the static stability of the atmosphere so that dynamically as well as thermally forced turbulence is simulated. The temperature and wind vertical profiles are the pertinent input data whereas the roughness length, z_0 , the asymptotic value of the mixing length l_m and the surface layer are the local input parameters. We have performed sensitivity tests in order to examine the effects of the variability of these parameters. The surface layer is arbitrary taken equal to 12 m and according to Justus [1985], the roughness length above the sea is taken equal to 0.02 cm. These parameters are only sensitive for K_z computed in the surface layer. Above the surface layer, only the asymptotic value is sensitive. However, it is obvious that it does not influence the vertical gradient of K_z . A discussion and further recommendations can be found in the work by Tiedke et al. [1979] for the appropriate choice of l_m . We have retained the value of 120 m considering this value as the best compromise between stable and unstable cases.

Above the surface layer the diffusion coefficient K_z depends on height (z), stability, and wind shear according to the relationship:

$$K_z = l_m^2 [dv/dz] F(Ri)$$

where l_m is the mixing length as suggested by Blackadar [1962]:

$$l_m = k z / (1 + k z / \lambda)$$

with k , the Von Karman's constant (0.4), and λ an adjustable parameter.

$F(Ri)$ is the analytical function proposed by J.F. Louis and Ri the Richardson number defined as

$$Ri = g (\Delta\theta/\Delta z) / \theta (\Delta v/\Delta z)^2$$

where θ is the potential temperature, $\Delta\theta/\Delta z$ and $\Delta v/\Delta z$ the potential temperature and the wind velocity vertical gradients respectively.

The function $F(Ri)$ depends on the stability conditions: 1) in stable cases it is given by the relationship:

$$F = 1 / (1 + b Ri)^2$$

with $b = 4.7$. 2) in unstable cases it is given by

$$F = 1 - [b' Ri / (1 + c Ri^{1/2})]$$

with $b' = 9.4$, and

$$c = 7.4 l^2 b' [(z + \Delta z/z)^{1/3} - 1]^{3/2} [z^{-1/2} \Delta z^{-3/2}]$$

However, we have seen that K_z became unrealistic in the stable cases, especially when Ri reached high values. This has been ascribed to the bad behavior of the F function under such conditions. According to Kondo et al. [1978], we let Ri tend toward an asymptotic figure for high Richardson numbers. We chose $Ri_c = 2$ as the highest critical value:

$$Ri = Ri / (1 + Ri/Ri_c)$$

Following the above scheme to compute K_z , the Figures 4a to 4d show the vertical profiles of K_z for May 31, and June 8 and 11. Then, we have calculated arithmetic mean values between levels z_a and z_b :

$$\langle K_z \rangle = 1 / (z_b - z_a) \int_{z_a}^{z_b} K_z(z) dz$$

with $\Delta z = 100 \text{ m}$.

Assuming a steady state, the variation of an NMHC concentration versus altitude would be given by the continuity equation:

$$\partial/\partial z [K_z \partial C_{z,i}/\partial z] - \lambda_i C_{z,i} = 0 \quad (A1)$$

$$K_z \partial^2 C_{z,i}/\partial z^2 + \partial K_z/\partial z \cdot \partial C_{z,i}/\partial z - \lambda_i C_{z,i} = 0 \quad (A2)$$

where z is the altitude, K_z the vertical eddy diffusivity coefficient, and λ_i the kinetic constant of oxidation of the species i .

During daytime the sink due to hydroxyl radicals is dominant, and λ_i is almost entirely related to the OH concentration and the kinetic constant $k_{\text{OH},i}$ of oxidation by OH by the formula:

$$\lambda_i = k_{\text{OH},i} [\text{OH}]$$

the equation (A2) is then integrated as follow

$$C_b = C_a \exp [-\sqrt{(k_{\text{OH}}[\text{OH}])/\langle K_z \rangle} \cdot (z_b - z_a)] \quad (A3)$$

from which we derive

$$\frac{\ln(C_b/C_a)}{(z_a - z_b) \sqrt{(k_{\text{OH}}[\text{OH}])/\langle K_z \rangle}} = 1 \quad (A4)$$

The OH concentration and K_z being the same for all the NMHC, the first term of (A4) must be constant. Using the kinetic constants k_{OH} given by Atkinson [1986], the results

are reported in Figure 6 and Table 3, and discussed in the text.

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