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Ozone and C₂–C₅ hydrocarbon observations in the marine boundary layer between 45°S and 77°S

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ABSTRACT

During the austral summer of 1993, measurements of surface ozone (O₃), non-methane hydrocarbons (NMHC), lead-212 and radon-222 activity were performed on board the vessel ANTARCTICA between 43°S and 77°S. The latitudinal variations of light C₂–C₅ alkanes reflect the relatively short photochemical lifetime of these compounds and their intensive photochemical destruction during summer. Average mixing ratios of ethane, propane and acetylene were 291 ± 76 pptv, 61 ± 53 pptv and 48 ± 35 pptv respectively, in good agreement with published measurements previously undertaken in the Antarctic region.

O₃ mixing ratios ranged from 8.5 ppbv to 22.2 ppbv. The few relatively high values of ozone that have been observed during EREBUS94 campaign occurred simultaneously with high Rn-222 activities and possibly indicated continental influence through transport of air masses in the free troposphere. With the exception of these high O₃ events, the O₃ and NMHC observations, in conjunction with air mass back trajectory analysis, radon-222 observations and a global 3-D model calculations, suggest that the troposphere/stratosphere exchanges play an important role on ozone budget at the high latitudes of the southern hemisphere.

1. Introduction

In the troposphere, ozone (O₃) is photochemically produced in air rich in nitrogen oxides (NO_x) and is also transported from the stratosphere. Ozone is destroyed by photochemical reactions in poor NO_x environments and by deposition to surfaces (Logan, 1985). The photochemical production and destruction of ozone is mainly controlled by the natural and anthropogenic sources of its precursors, namely nitrogen oxides (NO_x = NO + NO₂), methane (CH₄), non-methane hydrocarbons (NMHC) and carbon monoxide (CO).

Indeed, oxidation of the above carbon containing compounds can lead to formation or destruction of ozone depending on the levels of NO_x (Crutzen, 1995). NMHC have both natural and anthropogenic sources which include vegetation, soil and ocean, industrialized activities, engine exhausts, and biomass burning (Bonsang and Lambert, 1985; Blake and Rowland, 1986; Singh and Zimmerman, 1992; Rudolph, 1995; Plass-Dülmer et al., 1995; Boissard et al., 1996).

While measurements of ozone precursors in the northern hemisphere are quite well documented, southern hemisphere measurements, and particularly NMHC measurements, are still sparse and relatively limited (Khalil and Rasmussen, 1986; Singh and Salas, 1982; Singh et al., 1988; Bonsang et al., 1990; Rudolph and Johnen, 1990; Koppmann

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et al., 1992; Rudolph, 1995; Clarkson et al., 1997), especially in the Antarctic Ocean region (Rudolph et al., 1989; 1992). In the Antarctic region, the only known natural local source of NMHC is the surrounding ocean, although the mixing ratios of saturated NMHC can be affected by both local and regional sources depending on their atmospheric lifetimes, which range from hours for the most reactive to several months for ethane (C_2H_6), the most abundant (Rudolph and Ehhalt, 1981; Atkinson, 1994). Due to a highly variable distribution of NMHC, a more extensive database for the southern hemisphere is required to improve our knowledge on their spatial variability, seasonal cycle, source localization and strength to evaluate their impact on ozone budget.

To understand the temporal and spatial variations of ozone in Antarctica, measurements of surface ozone have been performed for many years (Oltmans and Komhyr, 1976, 1986, Schnell et al., 1991; Murayama et al., 1992; Winkler et al., 1992; Gruzdev et al., 1993; Oltmans and Levy, 1994). All these measurements have highlighted a seasonal variation in O_3 mixing ratios, with a pronounced summer minimum (around 15 ppbv in January) and a winter maximum (around 30 ppbv in July). Such a seasonal cycle of ozone has not only been observed in the high latitudes of the southern hemisphere, but also in tropical areas (Samoa, 14°S, Oltmans and Levy, 1994) and in the mid latitudes of the southern hemisphere (Cape Grim, 41°S, Ayers et al., 1996; Cape Point, 34°S, Scheel et al., 1990; Amsterdam Island, 37°S, Gros et al., 1997). It has been suggested that this O_3 seasonal variation mainly reflects enhancement of the photochemical destruction of ozone during summer in NO_x -poor air (Ayers et al., 1992) and increased contribution of stratospheric O_3 during winter (Roelofs and Lelieveld, 1997).

The aim of this paper is to help improving knowledge of ozone budget over the Antarctic ocean by complementing the existing data set with atmospheric measurements of ozone and C_2 – C_5 hydrocarbons. The observed space- and time-variability of O_3 and NMHC and the importance of transport processes relative to photochemistry in the Antarctic ocean, are analysed on the basis of radon-222 and lead-212 measurements, of air mass back trajectories and by using the 3-dimensional transport-chemistry global model MOGUNTIA (Zimmerman, 1988).

2. Experiment

2.1. The cruise

The EREBUS94 French expedition (Etienne and Averous, 1994) was designed at the end of 1993 to perform oceanographic, volcanological and atmospheric measurements. Surface ozone and non-methane hydrocarbon (NMHC) mixing ratios, radon-222 and lead-212 activities in the atmosphere were measured on board the vessel ANTARCTICA. The ANTARCTICA voyage took place between 12 December 1993 and 25 February 1994 from Hobart (Tasmania: 43°S, 147°E) to the Antarctic coast (near Ross Island, 77°S, 168°E) and then northward to Christchurch (New Zealand: 43°S, 172°E). The followed route is shown in Fig. 1. Four periods have been distinguished for data analysis. During the first period from 12 December to 22, 1993, hereinafter referred to as the “North–South route”, the vessel followed a southwards route on its cruise from Hobart (43°S, 147°E) to Antarctica (66°S, 175°E). During the second period from 23 December 1993 to 20 January, 1994, called “pack” because of the pack ice encountered, the vessel proceeded very slowly from 66°S, 175°E to 77°S, 166°E. Then it was stationed in the Ross sea (77°S, 166°E) during the third stage named “Ross sea” (from 21 January to 9 February 1994). Finally, from 10 to 25 February 1994, the ANTARCTICA navigated northward to New Zealand following the “South–North” route, (from 77°S, 166°E to 45°S, 173°E).

2.2. Ozone boundary layer measurements

Atmospheric surface ozone volume mixing ratios were monitored on board with a Thermo-Electron model 49 UV analyser and recorded every 10 s. This instrument had been calibrated by the manufacturer prior to the voyage against a Thermo-Electron model 49 003, itself calibrated against a Thermo-Electron model 49 PS. The accuracy of the measurements was about ± 1 ppbv. Air samples were collected through a 27 m long, 1/4" internal diameter Teflon FEP sample line, with the inlet located at the top of the bow mast at an elevation of about 30m above sea level. Johnson et al. (1990) applied a correction of 5% for the loss of ozone in such a Teflon sample line. Tests performed at Amsterdam island, in the remote marine atmosphere of the southern hemi-

Fig. 1. Route followed during the voyage. Open circles correspond to the North–South route, open triangles to the period in the pack ice, open squares to the Ross sea and solid circles to the South–North route. Points correspond to 4-hour intervals. Example of air mass back trajectories for “oceanic”, “Antarctic continent” and “Ross sea” types are represented by crosses spaced every 2 hours.

sphere, showed that the influence of a 15m Teflon sample line was less than 1 ppbv for ozone levels below 30 ppbv. Thus, in the experimental conditions of low ozone mixing ratios, the underestimation concerning our ozone data was lower than the instrument accuracy. Consequently, no correction factor was applied to the measurements. The analogue signal of the analyser was both digitized and recorded with a microcomputer system, and plotted on a graphic recorder. Pressure and temperature variations were automatically taken into account by the analyser. The data were then aggregated into hourly arithmetical averages.

2.3. NMHC measurements

During the experiment, air samples were collected at the bow and upwind in 0.85 l evacuated

stainless steel canisters for the analysis of NMHC. During the “North–South route” 10 samples were collected with the frequency of 1 sample per day. Eight additional canister samples were collected during the “pack” period of the voyage and two others during the “South–North route”. The canister samples were analysed 3 months later in the laboratory at Gif-sur-Yvette. Tests performed by Kanakidou (1988) and Boissard (1992) to check the stability of NMHC in the canisters over a 6 month period demonstrated that alkanes were only slightly affected by the long term storage with changes in their mixing ratios within the uncertainty of the analytical procedure, whereas alkenes showed a slight increase over this period. Indeed, other experimental studies of the stability of nonmethane hydrocarbons in steel canisters, or

direct comparison of "in situ" measurements and "delayed" measurements of canister samples have shown substantial differences for alkenes (Donahue and Prinn, 1993). Therefore, only the results of alkanes and acetylene are presented here.

C₂ to C₆ hydrocarbons were measured by gas chromatography using a capillary column and a FID detector according to a previously described technique (Bonsang et al., 1995; Boissard et al., 1996) that has a detection limit of 5–10 pptv for these species and an accuracy of 6%. The short sampling time of few seconds allowed for the selection of wind conditions, thereby eliminating the possibility of contamination by exhaust fumes emitted from the power supply of the vessel. Furthermore, the quality of the sampling was checked using acetylene as a tracer of combustion engine fumes.

2.4. Radon-222 and lead-212 measurements and air mass back trajectories

Radon-222 (half-life 3.8 days) and lead-212 (half-life 10.6 h) were monitored by measuring the decrease of the alpha radioactivity of atmospheric aerosols collected on filters as already described by Lambert et al. (1970) and Polian et al. (1986). Aerosol filter samples were collected from air sucked through a stainless steel line located at the ship's stern. Samples were collected for a period of two hours, twice per day during the North–South route and once per day during the other periods.

During the cruise, meteorological data, latitude, longitude and atmospheric pressure were recorded every 4-hours. Moreover, 10-day back trajectories of air masses ending at the 925 hPa level and corresponding to the ship position have been calculated twice a day, for 00 UT and 12 UT using the wind field analysis of the ECMWF. The vertical motions of the air parcel trajectory are calculated using the initialized vertical wind fields. The method for calculating back trajectories has been described in detail by Martin et al. (1987).

2.5. Chemistry-transport global description

Observations performed during the EREBUS94 expedition were compared to the results of the climatological chemistry transport global model MOGUNTIA (Zimmermann, 1988; Zimmermann

et al., 1989; Crutzen and Zimmermann, 1991; Kanakidou and Crutzen, 1993; Poisson, 1997). MOGUNTIA is an Eulerian model able to simulate the spatial and temporal variation of chemical compounds with a 10° latitude × 10° longitude horizontal resolution and 10 vertical layers between the surface and 100 hPa, spaced every 100 hPa. The chemical scheme of the model contains about 150 reactions involving 80 chemical species and is able to describe the photochemistry of O₃, NO_x, HO_x radicals, carbon monoxide (CO), methane and C₂–C₅ NMHC (including isoprene). The model is described in detail by Poisson (1997). It takes into account anthropogenic and natural emissions of NO_x, CH₄, CO and NMHC (C₂H₆, C₂H₄, C₃H₈, C₃H₆, C₅H₈ and other NMHC). Methane emissions of 530 Tg/yr, as suggested by Lelieveld and Van Dorland (1995), have been adopted in the model. Emissions of the other trace gases are summarized in Table 1. The monthly distribution of biomass burning emissions compiled by Hao et al. (1990) has been used for this study. For natural hydrocarbon emissions by vegetation, the spatial and temporal distributions of isoprene emissions calculated by Guenther et al. (1995) have been adopted. Technological sources of NMHC are taken into account as suggested by Olivier et al. (1996). NMHC oceanic emission estimates taken from Bonsang (1993) are distributed proportional to the ocean surface between 60°N and 60°S. The distributions of NO_x emissions by technological sources and by soils available in the GEIA database (Benkovitz et al., 1996; Yienger and Levy II, 1995) have been adopted. Production of NO_x by lightning with 8 Tg-N/yr is considered to occur in the parametrized form according to Price and Rind (1992). The concentrations of HNO₃ at 100 hPa are fixed according to observations (Gille et al., 1987) and these of NO_x to 2-dimensional model calculations (Brühl, 1987; Valentin, 1990), corresponding to a global tropospheric influx through the 100 hPa layer of the model of about 0.4 Tg-N/yr (HNO₃) and 0.2 Tg-N/yr (as NO_x).

The global exchange of mass through the tropopause estimated by Holton (1990) and the O₃ mixing ratios at 100 hPa measured by Komhyr et al. (1989) have been used to define the O₃ upper boundary conditions as a flux of O₃ into the model domain through the 100 hPa layer. These exchanges correspond to a global tropospheric

Table 1. *Natural and anthropogenic annual emissions of NMHC and NO_x adopted in the MOGUNTIA model (see text)*

(Tg-C/yr or Tg-N/yr)	NO _x	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	C ₅ H ₈	Other NMHC
<i>Biogenic sources:</i>							
soils	5.5	0.3	0.2	3.7	0.9		0.1
vegetation		1.6	1.6	11.8	7.7	353	63.1
oceans		1.5	1.4	7.1	6.4		4.4
lighting	8						
sub-total biogenic	13.5	3.4	3.2	22.6	15.0		67.6
<i>Anthropogenic sources:</i>							
biomass burning	6	2.3	0.8	7.7	2.6		3.3
urban areas	21	4.0	4.7	4.7	2.1		70
sub-total anthropogenic	27	6.3	5.5	12.4	4.7		73.3
total	40.5	9.7	8.7	35.0	19.7	353	140.9

influx through the 100 hPa layer of the model of about 500 Tg-O₃/yr, 68% of which is occurring in the Northern Hemisphere (Dentener and Crutzen, 1993).

3. Results and discussion

3.1. Meteorological conditions — air mass origin

Atmospheric pressure variations along the track are given in Fig. 2a. Three characteristic regions with deep low cells have been encountered during both the North–South and the South–North routes. The first one appeared around 50°S on 15 December and on 22 February; the second one occurred around 61–62°S on 20 December and on 18 February and the last one happened around 67°S on 27 December and on 16 February.

Air mass back trajectories can be used to detect variations of the concentrations of the trace constituents measured during EREBUS94. This back trajectory study, based on 80 trajectories, concerns the periods of the North–South route and the pack, when most of the NMHC samples have been collected. During the North–South route, oceanic air masses dominated (76% of the cases) and were characterized by an eastward zonal flux. During this period, most of the air masses were coming from the free troposphere (62% of the cases), suggesting transport through the middle or high troposphere.

During the “pack” period, and especially near the Antarctic coast, the atmospheric circulation

was utterly different with most of the air masses coming from the Ross Sea area (56%) and was strongly influenced by the surrounding relief. These air masses came principally from the Antarctic continent and seemed to have passed to the east of mountains then circulated round the Ross sea. Concerning the vertical history of the air masses during the “Pack” period, air masses originated equally from the boundary layer (33%) and from the free troposphere (38%). The remaining 29% of the air masses were of mixed origin.

In general, during these two periods of the EREBUS 94 cruise, sampled air masses have been weakly influenced by continents other than Antarctica, which is a priori exempt of pollution sources. However, it should be kept in mind that, because of the limited number of observations to constrain meteorological models at the mid and high latitudes of the southern hemisphere, important uncertainties could be associated with trajectory calculations (see for instance discussion in Pickering et al., 1996 and Fuelberg et al., 1996). These uncertainties do not affect the data analysis further presented since it does not exclusively rely on back trajectories of air masses but also uses Radon-222 and NMHC measurements and a chemistry/transport model results.

3.2. Ozone

The shipboard measurements of ozone mixing ratios are shown in Fig. 2b for the different legs

Fig. 2. Latitudinal variations of (a) atmospheric pressure (hPa) and (b) ozone (ppbv) and radon-222 (pCi m^{-3}) during the EREBUS94 voyage. Solid diamonds correspond to the North–South route, open squares to the pack period and open triangles to the South–North route.

of the EREBUS94 voyage. The highest ozone mixing ratios were observed between 50°S and 65°S and were slightly higher during the “North–South route” (December 1993) than during the “South–North route” (February 1994). The arithmetical average and standard deviation of ozone mixing ratios were 16.4 ± 1.8 ppbv and 13.9 ± 1.3 ppbv for the North–South and South–North routes, respectively. This slight difference could be attributed to the seasonal variation of surface ozone in the marine boundary layer of the southern hemisphere, with summer minimum generally in January–February (see references in the introduction).

During the “pack” period, when the vessel was slowly moving through the ice, ozone mixing ratios were more variable than during the North–South and South–North routes, especially around 67°S (12–22 ppbv) and around 71°S (8–16 ppbv). The ozone variability could be explained by atmospheric transport, likely to have involved the injection of air from the middle troposphere at these latitudes. This hypothesis is supported: (i) by the air mass back trajectory analysis for the “pack” period that showed a mixing of free tropospheric and marine boundary layer air masses, and (ii) by the radon-222 levels. Radon-222 is commonly used as a tracer of continentally influenced air masses

since it has almost exclusively continental sources and a short radioactive decay half-life of 3.8 days. Typical surface air activities over continents are of the order of 80 to 200 pCi m⁻³ (Lambert et al., 1982) and of about 0.5 pCi m⁻³ in the marine atmosphere (Polian et al., 1986). The latitudinal variation of radon-222 during the EREBUS94 campaign, as shown in Fig. 2b, presents relatively constant values between 40°S and 65°S lower than 1 pCi m⁻³, and therefore characteristic of a marine atmosphere that has not recently been affected by air of continental origin (Polian et al., 1986).

Between 65°S and 77°S, radon-222 mixing ratios increased drastically and reached, in some cases, 5 pCi m⁻³. As shown in Fig. 2b, the highest variations in ozone at 67°S and at 71°S corresponded to simultaneous increases in radon-222, indicating that the sampled air masses have been somewhat influenced by continental emissions the week before sampling. During the EREBUS94 cruise, the short-lived continental tracer lead-212 was always lower than 0.25 pCi m⁻³ (i.e., twice the detection limit of the measuring technique) and the wind speed was always greater than 5 m s⁻¹ thereby excluding a local impact on the sampled air mass. Enhancement of radon-222 mixing ratio close to the Antarctic coast has been observed previously between Hobart (Tasmania) and Dumont d'Urville (on the east coast of the Antarctic continent) by Polian et al. (1986). Polian (1984) suggested that the high mixing ratio of radon-222 observed during summer resulted from rapid vertical motions of air masses over the continents due to convective processes, followed by latitudinal transport due to large scale dynamics and then subsidence over the Antarctica due to the high cell over this area. Thus, the highest mixing ratios of radon-222 observed during the EREBUS94 expedition could be attributed to transport of continental air through the middle or the high troposphere.

Fig. 2 also seems to indicate that each of the low pressure readings was associated with an increase in the ozone mixing ratio. Frontal systems are generally associated with these low cells. It has been observed at Point Arena (California) by Singh *et al.* (1988) that ozone concentrations are strongly influenced by the transport in such mesoscale atmospheric circulations, in particular, ozone increases after the frontal passage. Furthermore, Gedzelman (1985), has shown that prior to the

passage of a cold front, in the warm and wet sector, ozone-poor air is moved upward by convection from the marine boundary layer to the upper layers of the troposphere. On the opposite, in the cold sector, ozone-rich air from the free troposphere is mixed into the marine boundary layer. Thus, we can argue that such transport processes directly affected ozone.

Hourly mean ozone mixing ratios showed no diurnal variation during the whole EREBUS94 campaign. This is in agreement with observations of surface ozone in Antarctica by Gruzdev et al. (1993). The absence of ozone diurnal cycle is consistent with the absence of a photochemical cycle during summer. The role played by photochemistry on ozone budget at the high latitudes of the southern hemisphere will be discussed further in Subsection 3.4 in conjunction with NMHC observations and transport/chemistry model results.

3.3. Non-methane hydrocarbons

Volume mixing ratios of the main measured NMHC are reported in Table 2 according to sampling time, latitude, longitude, air mass origin, radon-222 and ozone. For each compound, arithmetical means, standard deviations and median values have been calculated. Medians and arithmetical means are quite similar for ethane, propane and acetylene, while medians are always lower than arithmetical means for higher alkanes. This is consistent with the shorter lifetime of butanes and n-pentane which therefore present higher scatter than C₂ and C₃ hydrocarbons. Indeed, the respective standard deviations of butanes and n-pentane are always higher than their arithmetical means on contrary to the other NMHC.

The major observed species are the C₂-C₃ alkanes : ethane (C₂H₆) and propane (C₃H₈) which are usually found at significant levels in background air. A relatively regular decrease of their mixing ratios toward the south pole was observed. Effectively, except the low values for ethane and propane on 13 December at the beginning of the cruise (205 pptv and 50 pptv, respectively, at 44°S), the mixing ratio of ethane showed a regular variation from 466 pptv at 47°S to 171 pptv at 72°S, and that of propane from 242 pptv down to 25 pptv for the same latitudes

Table 2. NMHC (pptv) with corresponding values of Rn-222 (pCi.m^{-3}), ozone (ppbv) and origin of the backward trajectories (O stands for ocean, A for Antarctic continent, RS for Ross sea and NZ for New-Zealand, BL for boundary layer, FT for free troposphere)

Date	Local time	Latitude	Longitude	Trajectory	Radon	Ozone	C ₂ H ₂	C ₂ H ₆	C ₃ H ₈	i C ₄ H ₁₀	n C ₄ H ₁₀	n C ₅ H ₁₂
NS route												
13 Dec 93		44.0		O/FT		14.7	103	205	50	13		28
14 Dec 93	19:50	47.15	151.37	O/FT	0.34	14.3	124	466	242	157		110
16 Dec 93	17:30	52.25	156.33	O/FT	0.17	16.4	106	411	137	34	170	127
17 Dec 93	19:35	54.83	159.25	A/FT	0.34	18.2	40	326	56	64	113	127
18 Dec 93	21:10	57.18	161.97	O/FT	0.5	16.9	30	354	55	13	180	23
19 Dec 93	19:15	59.57	165.18	O/FT	0.39	18.1	24	333	38	9	17	12
20 Dec 93	15:00	61.45	168.95	O/FT	0.61	17.2	46	318	24			
22 Dec 93	18:15	66.9	174.33	O/BL	1.09	14.6	38	288	7	12	11	
Pack												
23 Dec 93	15:45	66.88	175.72	A/FT	1.93	18.3	20	227	21		4	5
24 Dec 93	10:30	66.93	175.72	A/FT	0.93	15.3	14	303	46	7	19	16
25 Dec 93	22:00	66.77	176.42	O/FT	1.17	13.1	20	316	53	9	34	22
18 Jan 94	03:50	71.3	179.03	RS/BL	1.56	9.8		193	19		5	
18 Jan 94	11:50	72.1	178.51	RS/BL	0.68	12.9	17	171	25	7	14	10
18 Jan 94	16:40	72.5	179.45	RS/BL	0.68	13.0	22	294	77	17	46	33
19 Jan 94	16:50	76.46	174.43	RS/BL	0.39	13.0	78	296	59	13	26	17
20 Jan 94	14:35	76.77	168.27	RS/BL	2.43	12.3	64	255	55	12	32	20
SN route												
22 Feb 94	10:40	51.58	173.57	NZ/BL	1.02	12.0	28	286	76	15	35	31
24 Feb 94	10:40	45.08	173.13	NZ/BL	2.83	12.8	49	204	25	9	10	10
			arithmetical		1.00	14.6	48	291	61	26	51	37
			mean									
			standard		0.77	2.5	35	76	53	39	59	45
			deviation									
			median		0.68	14.5	38	295	51	13	29	20

respectively. Then, a slight increase is observed again for both compounds at further southern latitudes (74°S–77°S). In order to better understand these variations, which integrate spatial and temporal variability, we compared our observations with the MOGUNTIA model calculations.

Figs. 3a, b show the latitudinal variations of ethane and propane measured during the

EREBUS94 cruise together with the model results. Measurements between 45°S and 68°S were performed in December 1993, while those between 70°S and 80°S were made in January 1994. For this reason, the calculated mixing ratios for December have been depicted for latitudes northern 65°S whereas those for January have been depicted for latitudes southern 65°S. Finally, for

Fig. 3. Comparison between observations during EREBUS94 and MOGUNTIA model results for (a) ethane, (b) propane (in pptv). Model results correspond to monthly mean values for December northern 65°S and for January southern 65°S.

clarity, the two NMHC measurements performed in February are not reported in this figure.

The calculated NMHC mixing ratios are higher in December than in January when photochemistry in the southern hemisphere is more intensive. Therefore model results suggest that the seasonal variations of NMHC in the high latitudes of the southern hemisphere, reflect mainly that of their photochemical sink (Rudolph et al., 1992). Indeed, observed mixing ratios of ethane decrease from 55°S toward the south pole, whereas the model calculates an almost constant value of 430 pptv for December and 350 pptv for January for these latitudes. Thus, the latitudinal pattern in ethane and propane levels observed during EREBUS94 seem to mainly reflect their temporal variation.

Furthermore, it can be seen that the model results are very close to observations around 50°S whereas they overestimate C_2H_6 by about 50–100 pptv south of 55°S. This overestimation by the model of the C_2H_6 mixing ratios in the southern hemisphere has also been reported by Kanakidou et al. (1992). It might be linked to the absence of seasonality in the marine source parametrisation in the model or to the adopted oceanic emissions. The sensitivity of the model results to these parameters will be discussed elsewhere (Touaty et al., unpublished data). It should be noted that ethane mixing ratios measured previously in Antarctica (Rudolph et al., 1989; Khalil and Rasmussen, 1986) are in good agreement with our measurements (Table 3). For propane, both measured and calculated mixing ratios decrease with latitude between 45°S and 75°S but this decrease is much higher for our observations than for the calculations. This difference is due to the samples collected on 14 and 16 December which present relatively high NMHC values suggesting the influence of a local source. Excluding these two elevated concentrations, the observed latitudinal gradient is as low as the calculated one which is in agreement with the observations by Clarkson et al., 1997. As the corresponding back trajectories show southward oceanic origin, the probability of being influenced by the Australian continent is weak. Since the area has a non negligible traffic, it is likely that a close located point source, such as a commercial ship, is the origin of these relatively high NMHC values. Such an hypothesis is supported by the relatively low ozone levels in

these air masses which do not indicate any photochemical induced change in ozone.

With the exception of the samples collected during the first days of the experiment between 47°S and 54°S, heavier alkanes for which observations were performed ($i-C_4H_{10}$, $n-C_4H_{10}$, $n-C_5H_{12}$), were all in the range of < 10 to 40 pptv. All of these species were more variable than the C_2 – C_3 alkanes as a consequence of their shorter lifetimes, and also of the greater uncertainty on the measured mixing ratios which were often close to the detection limit of our analytical method of 5 to 10 pptv.

Table 3 compares our results with earlier published measurements of NMHC for the austral summer and for December only in the southern hemisphere. For ethane, the average levels of 291 (± 76) pptv and 322 (± 74) pptv, for summer and December only respectively, agree well with the measurements reported by other authors for the same periods. For propane, levels of 61 (± 53) pptv and 73 (± 49) pptv (respectively for summer and December only) are in the range of previous measurements, although higher than the 15 pptv reported by Clarkson et al. (1997). Note that our data include also the high values obtained at the beginning of the campaign. Only the results from Bonsang et al. (1990) at Amsterdam Island (37°S) seem significantly higher. This difference is reasonable when taking into account the location of the sampling site of Amsterdam Island, partly influenced by continental emissions from Africa (Touaty et al., 1996).

For butanes ($n-C_4H_{10}$ and $i-C_4H_{10}$) our results are respectively of 51 and 26 pptv (all summer months) and 69 and 35 pptv (December only). Only $n-C_4H_{10}$ data have been reported in literature, and our results agree with the averages of 53 pptv and 55.5 pptv reported by Rudolph et al. (1992) for Antarctica and Bonsang et al. (1990) for Amsterdam island. The agreement on this background level is consistent with the short lifetime of butanes preventing any significant variability due to transport from the continents. Other alkanes levels are in the range of 5–20 pptv, but they can not be compared with previously published data because their levels, close or below the usual detection limits, are usually not reported.

Acetylene (C_2H_2) has mainly anthropogenic sources (engine exhaust fumes and biomass burning) with a negligible marine component

Table 3. NMHC observed mixing ratios (pptv) in remote areas of the southern hemisphere during summertime. “±” stands for error of the mean and number in parenthesis is the standard deviation

Refs.	Summer				December only			
	Khalil and Rasmussen (1986)	Singh and Salas (1988)	Bonsang et al. (1990)	This work	Rudolph et al. (1989)	Rudolph et al. (1992)	Clarkson et al. (1997)	This work
location	South Pole	0–47°S	Amsterdam Island (37°S)	43°S–77°S	Antartica Antartica (70°S)	New-Zealand (41°S) (70°S)	43°S–77°S Antartica (70°S)	
date	summer 1979–1985	Nov–Dec 1984	summer 1984–1986	summer 1993–1994	Dec 1982–1985	Dec 1982–1989	Dec 1991–1996	Dec 1993
sampling	flasks	in situ	flasks	flasks	flasks	flasks	flasks + in situ	flasks
alkanes				mean median				mean median
C ₂ H ₆	161 (10)	310	376	291 (76) 295	332 ± 40	362	248 ± 5	322 (74) 318
C ₃ H ₈		40	124	61 (53) 51	93 ± 24	84	15 ± 1	73 (49) 64
iso—C ₄ H ₁₀		20	23	26 (39) 13				35 (50) 13
n-C ₄ H ₁₀		10	55.5	51 (59) 32		53		69 (74) 27
n-C ₅ H ₁₂			72	37 (45) 20				51 (56) 22
alkynes								
C ₂ H ₂	70.5 (0.7)	30	25	48 (35) 38	10 ± 5	12		51 (40) 38

Table 4. Comparison between the theoretical and the observed values of the slope of the natural logarithms: $\ln(X/C_2H_6)/\ln(C_3H_8/C_2H_6)$, see text Subsection 3.4 for details. Number in parenthesis gives the correlation coefficient for the respective measurements

	n-butane	i-butane	n-pentane
Theoretical value	2.66	2.74	4.40
Rudolph and Johnen (1990)	1.66 (0.84)	—	—
Parrish et al. (1992)	1.47 (0.95)	—	—
Jobson et al. (1994)	1.44 (0.96)	1.47 (0.95)	0.89 (0.97)
This work	1.84 (0.94)	1.44 (0.89)	1.33 (0.96)

(Kanakidou *et al.*, 1988). Two air samples (collected on 15 and 21 December 1993) presented very high acetylene mixing ratios (greater than 600 pptv) exceeding by one order of magnitude the usual mixing ratios observed in the marine atmosphere. For this reason, these two samples suspected of contamination by the vessel have been discarded. The other observed mixing ratios of C_2H_2 were, in most cases, lower than 50 pptv and as low as 14–20 pptv in the vicinity of 70°S. These levels are in the range of earlier measurements (10–20 pptv) by Rudolph *et al.* (1992) at the Antarctic continent. However, two values of 78 and 64 pptv at 74.5°S and 76.8°S respectively, are above the usual background levels for these latitudes. These two relatively high values can not be simply explained by horizontal air masses back trajectories which definitely originate from the Ross Sea. As the corresponding two trajectories come from the free troposphere, a transport of continental air through the middle or high troposphere might have occurred. For the air sample collected at 76.8°S (64 pptv acetylene), this hypothesis is supported by the relatively high radon-222 levels of 2.43 pCi m⁻³ indicating a remote continental influence. For the sample collected at 74.5°S (78 pptv of acetylene) this is not so evident since it is associated with a background radon-222 figure of only 0.39 pCi m⁻³. Considering the different lifetimes of acetylene (3 weeks) and radon-222, this observation would be consistent

with an older continental influence of several weeks leading only to a significant change in the acetylene level.

3.4. Aging of air masses and relationship with the observed ozone

Considering that alkanes are mainly injected in the atmosphere from a continental and well defined source, typically anthropogenic, and that they are removed in a first approximation by the oxidation with OH radicals, the measured ratios of several alkanes are used in a log-log relationship to derive a linear dependence which reflects the evolution of an aging air mass. This method has been described by several authors (see for example Rudolph and Johnen, 1990 and Parrish *et al.*, 1992).

In Fig. 4 the regression of the natural logarithm of the observed ratio of n-butane to ethane is depicted versus that of propane to ethane. The corresponding slope is 1.84 very close to the 1.66 reported by Rudolph and Johnen (1990) for the Atlantic ocean (open circles in Fig. 4). Average figures calculated from the data reported by Rudolph *et al.* (1992) for the Antarctic troposphere, Singh *et al.* (1988) for the Atlantic and Bonsang *et al.* (1990) for the Indian Ocean are also plotted (open squares labeled respectively 1, 2 and 3). The intercept is dependent on the alkane ratio at the source and therefore varies according to the area investigated. Our observations are consistent with those of Rudolph *et al.* (1992) for the Antarctic troposphere, whereas the data points for the Atlantic and the Indian ocean seem in general agreement and correspond to a different intercept. However the range of variation of the intercept is low and remains within the variability of the data point. For different sets of alkanes (n-butane, iso butane, n-pentane), the logarithm of the ratio $\ln(\text{alkane/ethane})$ has been plotted versus $\ln(\text{propane/ethane})$. The slopes as well as the regression coefficients of the linear relationship are summarized in Table 4. Our experimental results are also compared to the theoretical values and to earlier experimental data obtained by several authors in various environments (Parrish *et al.* (1992) for California coast; Rudolph and Johnen (1990) for the Atlantic Ocean and Jobson *et al.* (1994) for boreal areas). Theoretical values have been calculated at 273° K, but Parrish *et al.*

Fig. 4. Correlation between the natural logarithm $\ln$ (n-butane/ethane) and $\ln$ (propane/ethane). Close circles represent EREBUS94 data, two outliers, represented by crosses, have not been taken into account in the calculations. Open circles are data from Rudolph and Johnen (1990) for the Atlantic ocean. Open squares stand for average values calculated from (1) Rudolph et al. (1992) for the Antarctic troposphere, (2) Singh et al. (1988) for the Atlantic ocean and (3) Bonsang et al. (1990) for the Indian Ocean.

(1992) showed that temperature only slightly affects the slope. Differences between experimental and theoretical slopes are systematically observed due to the occurrence of dilution with tropospheric air, influence of other sources during the transport such as oceanic emissions, and possibly oxidation processes involving mechanisms other than OH attack (McKeen and Liu, 1993). However, the experimental slopes are often very similar and reflect a major contribution of anthropogenic emissions on alkanes budget in most environments as suggested by Parrish et al. (1992) and Rudolph and Johnen (1990). Thus our data, although limited in number, are consistent between them and also with literature data from other marine environments.

In Fig. 5 the observed C_2H_2 and O_3 mixing ratios are plotted versus the natural logarithm of the observed ratio of C_3H_8 to C_2H_6 . This parameter decreases as the photochemical age of the air mass increases. Even if the correlation between C_2H_2 and the natural logarithm of the ratio of C_3H_8 to C_2H_6 is not high, ($R=0.65$), a clear co-variation can be pointed out since the lowest C_2H_2 mixing ratio correspond to air masses photochemically older. This shows the importance of photochemistry on the C_2H_2 mixing ratios over

the oceans. Contrary to the observations of Parrish et al. (1992), no significant correlation has been observed between O_3 levels and the photochemical age of the corresponding air masses during EREBUS94. This indicates that the observed O_3 was not dominated by photochemistry during the campaign. In order to investigate this statement, our observations have been compared with the MOGUNTIA transport/chemistry model results.

3.5. Origin of observed ozone

Fig. 6 depicts the latitudinal variations of ozone measured during the EREBUS94 cruise for (a) North–South route, (b) pack and (c) South–North route cruise. Corresponding model results are given for a) December, b) December and January and c) February. The computed ozone mixing ratios reflect the observed seasonal variation of ozone previously described in Subsection 3.2, with higher values in December during the North–South route than in January–February during the South–North route. The calculated O_3 mixing ratios decrease at $50^\circ S$ from about 20 ppbv in December to 17.5 pptv in January–February and at $75^\circ S$ from 14 ppbv in

Fig. 5. Observed mixing ratios of ozone (ppbv) and of acetylene (pptv) plotted versus the natural logarithm of the propane to ethane ratio, used as indicator of the photochemical age of the air masses.

December to 12 ppbv in January. A mean latitudinal gradient of about 0.2 ppbv/deg is calculated for between 50°S and 75°S. These latitudinal and temporal modeled trends of ozone are in rather good agreement with our observations. As expected, our climatological model cannot reproduce the relatively low O_3 mixing ratios observed close to the Australian continent (45°–50°S), which result from long range transport of marine air masses as shown in Fig. 1. The model considers all possible origins of air masses and not only air masses coming from the south west sector as those sampled during EREBUS94. It also artificially diffuses ozone concentrations in its 10°latitude $\times$ 10°longitude grid box that contains also some land surface. Having these limitations in mind, the model can be used to analyse the observed ozone levels. On the whole, MOGUNTIA is able to reproduce the general trend in the latitudinal distribution of ozone between 50°S and 75°S, by taking into account (i) the exchanges of O_3 between the stratosphere and the troposphere, (ii) the net photochemical production of O_3 over continental areas, (iii) O_3 transport to the open ocean, (iv) O_3 deposition on surfaces and (v) the

net photochemical destruction of O_3 over oceanic areas.

To further analyse the observed ozone distributions, we performed two additional simulations, the first one by neglecting NMHC chemistry (model-CH₄) and the second one by neglecting all chemical processes in the model (model-nochemistry). In this last simulation, ozone is considered as an inert tracer that comes exclusively from the stratosphere, is transported in the troposphere and deposited on surfaces. Note that these calculations represent an upper limit of the stratospheric impact on O_3 values since for the “model-strato” simulation the chemical destruction of O_3 in the troposphere is neglected. For clarity, only the summer mean values calculated by these two additional simulations have been plotted in Figs. 6. The model results depicted in these figures demonstrate that photochemistry loses importance on the observed O_3 levels when moving from 50°S (Figs. 6a and 6c) toward the South Pole (Fig. 6b). Around 50°S about 30% of the observed ozone may originate from photochemistry within the troposphere whereas the remaining 70% is linked to O_3 coming from the stratosphere. Close

Fig. 6. Surface ozone measurements (symbols) and MOGUNTIA calculations (lines) between 45°S and 75°S during: (a) North–South route, (b) pack and (c) South–North route. (see text for explanation of model results).

to Antarctica, most of the observed O_3 originates from the stratosphere, photochemistry might contribute by less than 20% (Fig. 6b). Transport from the stratosphere seems to explain the observed relatively low ozone levels around 45°S, in agreement with the back trajectories shown in Fig. 1 which indicate that the sampled air masses at these latitudes were coming from southern latitudes. The overall analysis of ozone budget on the basis of comparison between observations and model results demonstrates that during EREBUS94 ozone was mostly originating from the stratosphere, in agreement with the absence of correlation between ozone and the photochemical age indicator discussed in the previous section.

4. Conclusions

The EREBUS94 cruise took place from Tasmania (43°S, 147°E) to the Antarctic coast (77°S, 168°E) and then northward to New Zealand (43°S, 172°E) from 12 December 1993 to 25 February 1994. The latitudinal surface variations of ozone, NMHC and radon-222 have been determined in the higher latitudes of the southern hemisphere, where limited experimental data are available. The observed ozone mean mixing ratio was 14.1 ± 2.7 ppbv between 45°S and 77°S. No diurnal cycle was observed on ozone mixing ratios during the austral summer. Acetylene and alkanes mixing ratios seem to reflect the anthropogenic

source of these NMHC and the photochemical aging of air masses during long range transport over the ocean.

The comparison of the observations made during the EREBUS94 cruise with the calculations of the 3-D global model MOGUNTIA partly validates the model results and points out the importance of troposphere/stratosphere exchanges on O_3 budget at the high latitudes of the southern hemisphere. This conclusion is consistent with the NMHC and radon-222 observations, the air mass back trajectory and finally with the absence of correlation of O_3 with the photochemical age indicator. Only during some particular events (at 66°S and 71°S) continental influence via transport of air masses rich in ozone through the mid- or high troposphere, can be detected on ozone observations, in agreement with radon-222 results.

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