In situ measurements of butane and pentane isomers over the subtropical North Pacific

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(Received February 25, 2002; Accepted March 1, 2004)

Butane and pentane isomers were measured in situ in the remote marine atmosphere at the Bellows Beach, on the east side of the Island of Oahu, Hawaii during July and August 1998. Air masses arriving at Bellows Beach site originated mainly from the eastern North Pacific, and sometime polluted air masses of island origin arrived at the sampling site. The median mixing ratios were 11 pptv (i-butane), 18 pptv (n-butane), 1 pptv (i-pentane), and 3 pptv (n-pentane) in clean marine air, which were 3–12 times lower than those encountered in the polluted island air. The observed mixing ratios of the alkanes in marine air are within the range of those previously reported in the Atlantic and Pacific Ocean. The concentration ratios of pentane isomers suggest that the sources of the observed pentanes in marine air were not only derived from the ocean but also from the unidentified anthropogenic sources. Based on the comparison with values in the literature on sea-to-air fluxes, oceanic emissions of these alkanes were estimated to account for less than 30% of the observed mixing ratios. Continental emissions are not the important anthropogenic source due to the air mass trajectory analysis, suggesting that there are unidentified anthropogenic sources associated with ship activity and oceanic oil pollution.

Keywords: nonmethane hydrocarbon, marine boundary layer, back trajectory, long-range transport, oceanic emission

INTRODUCTION

Light hydrocarbons play an important role in atmospheric chemistry due to their reactivity with OH radicals. Thus, they serve as precursors of tropospheric ozone and oxygenated hydrocarbons in the presence of sufficient concentrations of NOx. Measurements of various light hydrocarbons have been reported in the marine atmosphere (e.g., Rudolph and Ehhalt, 1981; Singh and Salas, 1982; Greenberg and Zimmerman, 1984; Bonsang et al., 1988; Donahue and Prinn, 1993; Blake et al., 1996; Yokouchi et al., 1999; Saito et al., 2000; Lewis et al., 2001). Although anthropogenic and natural emissions on the continents are dominant sources for the light hydrocarbons, these studies also suggest that the ocean is an alternative source of volatile hydrocarbons because the ocean surface water is, in most cases, supersaturated with volatile hydrocarbons in respect to the atmospheric concentrations. It is well known that ethylene and propylene are the most abundant hydrocarbons in surface sea water (e.g., Plass et al., 1992). Due to the relatively short lifetime of the alkenes (<a few days), their emissions from the ocean are an important source in the remote marine atmosphere. In contrast, ethane and propane derived of a continental origin are dominant in the marine atmosphere due to their longer lifetimes (>a few weeks), although they are also emitted from the ocean.

Higher alkanes have structural isomers such as normal, iso and anteiso, whose lifetimes are much shorter. These isomers have been used as molecular markers to understand the sources, sinks, and mixing processes of light hydrocarbons (e.g., Jobson et al., 1994). However, their behaviors are still poorly understood in the remote marine atmosphere partly due to the limited numbers of data sets. It has been demonstrated that oceanic fluxes of butanes and pentanes are not large enough to explain the observed concentration levels over the ocean, suggesting that continental sources contribute to these alkanes in the marine atmosphere (Koppmann et al., 1992). On the contrary, Lewis et al. (2001) claimed that these alkane abundances over the North Atlantic and the Southern Ocean are consistent with the reported sea-to-air fluxes. The relatively high reactivity of the alkanes and their inhomogeneous distribution in ocean waters could lead to a large spatial variability of their mixing ratios in the marine atmosphere. More information on the spatial and temporal distributions of these alkanes is obviously needed.

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Measurements of light hydrocarbons have rarely been carried out in the remote marine atmosphere over the North Pacific (Greenberg and Zimmerman, 1984; Greenberg et al., 1992; Atlas et al., 1993; Donahue and Prinn, 1993). In this study, we conducted in situ measurements of butane and pentane isomers in July and August 1998 at the Island of Oahu, Hawaii, which located in the subtropical North Pacific Ocean, several thousand kilometers away from the nearest continent. The dominant trade winds over the island are easterlies. Automated in situ measurements provided hourly mixing ratios of hydrocarbons. So far, in situ measurements have rarely been performed at such a high time-resolution for the variation of trace levels of hydrocarbons in clean marine air (e.g., Rudolph et al., 1990). Here, we report the results of ca. 200 measurements of hydrocarbons. The origin of these alkanes will be discussed in terms of oceanic emissions and long-range atmospheric transport from continental anthropogenic sources.

**EXPERIMENTAL**

Light hydrocarbons were measured using an automated pre-concentration/capillary gas chromatography (GC) system which was set up in the University of Hawaii special studies laboratory at the Bellows Air Force Station, Waimanalo, Oahu (Fig. 1). The Bellows Beach site is located on the northeast side of Oahu directly facing to the trade winds from the eastern North Pacific. Measurements were performed over the period of three weeks from 23 July to 12 August, 1998. BARONS, a study of organic nitrogen in aerosols and rain (Cornell et al., 2001), was taking place at the same time and place as these measurements.

About 200 hourly measurements of light hydrocarbons were performed using an automated pre-concentration/GC system (see Fig. 2), which was modified from Saito et al. (2000). Air was drawn from the top of a tower (ca. 20 m) built on the site through 1/4 inch OD FEP Teflon tubing at a flow rate of ca. 30 L/min. Part (50 ml/min) of this airflow was supplied to the analytical system. Sample air was dried using a magnesium perchlorate trap. The hydrocarbons in 0.5 to 1.5 liters of air were collected in a 1/8 inch OD stainless steel tube packed with a combination of Carboxene 1000 (carbon molecular sieve, 60/80 mesh) and Carbopack B (graphitized carbon, 60/80 mesh) maintained at 10°C using liquid CO2. Following thermal desorption, this air was injected onto an alumina PLOT column (0.53 mm ID, 30 m long) installed in a HP 6890 GC. The GC column oven temperature was maintained at 30°C for 5 min and then increased to 200°C at a rate of 10 °C/min. Although this system was designed to analyze C2–C6 hydrocarbons, the system was severely damaged at an early stage of the campaign. Only data on C4 and C5 alkanes were of sufficient quality to report here.

The alkane mixing ratios were calculated by comparison with a standard gas containing 10 ppbv of C2–C6 hydrocarbons. Analysis of the standard gas was performed once every day or two. Calibration of the measurement system was also performed with diluted standard down to levels of 10 pptv (parts per trillion by volume). The accuracy of the final mixing ratios was estimated to be better than 10%. The detection limits for a 500-ml sample are 4 pptv for i-butane, 2 pptv for n-butane, and 1 pptv for pentanes. The reproducibility of the hydrocarbon measurements in the analytical procedure was tested from pre-concentration procedure to GC analysis using the marine air collected in stainless steel canisters at the
Measurements of butane and pentane isomers in the marine atmosphere

Bellows Beach site. The results showed that reproducibilities were 3% for i-butane, 3% for n-butane, and 8% for pentanes. A Teflon-coated glass fiber filter was installed at the sample inlet for the removal of aerosol particles. The filter was replaced every week. System blanks were run periodically with ultra pure grade helium introduced to the inlet of the pre-concentration system to insure that there was no cross contamination among samples and to determine any other artifacts of the analyses. Blank levels were below the detection limits (1 pptv) for all constituents except for the periods of 25 to 27 July, 7 and 8 August. In these periods, blank levels of several pptv were obtained for all the constituents; the data obtained in the periods were not used in this study. Acceptable blank levels were achieved by the conditioning of the pre-concentration trap.

Fig. 3. Five-minutes average meteorological data for (a) wind speed, (b) wind direction, (c) ambient temperature, and (d) relative humidity.

Fig. 4. Temporal variation of (a) i-butane, (b) n-butane, (c) i-pentane, and (d) n-pentane. Solid and open circles mean “marine air” and “island air”, respectively. For more details, see the text.
RESULTS AND DISCUSSION

Local meteorological conditions

Figures 3(a)–(d) present wind speed and direction, temperature, and relative humidity as a function of date. Relatively strong northeasterly winds originating from the marine atmosphere dominated during this campaign. The prevailing winds were interrupted by the weak winds that came from the west and northwest (island air) on August 1 and 8 through 12. During the periods of northeasterly flow (marine air) the meteorological parameters remained almost constant. When the wind speed was greater than 4 m/s, the wind came only from the northeast and the ambient temperature was around 24.5°C. The relative humidity generally stayed high at around 80%. However, during several episodes of island air, the relative humidities increased up to 95%.

Temporal variations of butanes and pentanes

The measured mixing ratios of i-butane, n-butane, i-pentane, and n-pentane are plotted in Figs. 4(a)–(d) as a function of date. At midnight of July 31, mixing ratios of i-butane, n-butane, i-pentane, and n-pentane elevated up to 389, 1666, 1229, 271 pptv, respectively. There are other spikes of the mixing ratios during the period of August 10 to 12. The temporal variations in Fig. 4 clearly show that the mixing ratios of these alkanes co-varied throughout the campaign. The higher mixing ratios of alkanes during the low-wind speed episodes are indicative of local influence as explained above. Thus, the measurements were divided into two categories by a threshold value of wind speed of 4 m/s. The periods when the wind speed was greater than 4 m/s, which include only northeasterly trade winds, are termed as “marine regime”, and the other as “island regime”. Table 1 shows the average, median, maximum, and minimum mixing ratios of alkanes in two regimes. The averaged concentrations observed in the island air are four or more times higher than those of the marine air.

For the alkanes, the averaged mixing ratios are significantly higher than the median values. It should be noted that there were sometimes fishing boats and other combustion sources upwind off Bellows, even during marine regime. Thus the median values are more meaningful than the averaged mixing ratios. The median mixing ratios under marine air condition are within, but slightly lower than those of previously reported results in the marine atmosphere in the Northern Hemisphere (e.g., Singh et al., 1988), reflecting the sampling location far from the continents and the season of highest OH radical concentrations. Considering only the data taken in the remote marine atmosphere in similar latitudes, our measurements are comparable to those made at 400 km northwest of Honolulu in May (Greenberg et al., 1992) and over the equatorial North Pacific in February/March (Atlas et al., 1993; Donahue and Prinn, 1993), indicating that our medians seem to be representative for the background atmosphere at low latitudes in the North Pacific.

Sources of butanes and pentanes in the subtropical marine atmosphere

The photochemical lifetimes of iso and normal alkanes are nearly equal (Atkinson, 1997). Thus their i-/n-alkane ratios for butanes and pentanes should remain nearly constant in the process of photochemical degradation. Figure 5 shows a scatter-plot of normal- and iso-alkanes for the island and marine regimes with their averaged ratios. Good correlations for butanes and pentanes were observed in each regime. The averaged i-/n-butane ratios are similar (0.52 for the marine regime and 0.45 for the island regime). The averaged i-/n-butane ratios are consistent with the comprehensive data sets in continental North America, including urban regions (0.49, Parrish et al., 1998), and with the estimated emission ratios from the ocean (0.2–0.5, from Bonsang et al., 1988; Plass et al., 1992; Plass-Dülmer et al., 1993).

In contrast, the slope of the pentane isomers for the island air is significantly larger than those of marine air. Anthropogenic emissions of pentanes are characterized by the dominance of the iso structure. The averaged ratio of 2.25 is quite similar to that reported in 39 U.S. cities (2.1, Seila et al., 1989), indicating that the air masses encountered during the low-wind speed episodes are heavily influenced by a local anthropogenic emission source.

Table 1. Summary of alkane mixing ratios (pptv) observed at the Bellows Beach site, Oahu, Hawaii

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Wind speed &gt;4 m/s (Marine air, n = 153)</th>
<th>Wind speed &lt;4 m/s (Island air, n = 44)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Median</td>
</tr>
<tr>
<td>i-Butane</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>n-Butane</td>
<td>46</td>
<td>18</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>13</td>
<td>3</td>
</tr>
</tbody>
</table>

n = number of samples; s.d. = standard deviation.
On the other hand, the observed lower ratios (av. 0.66) are consistent with those reported in seawater: 0.2–0.8 (av. 0.6) in the tropical Indian Ocean (Bonsang et al., 1988), 0.5–1.0 (av. 0.6) in the North Sea (Broadgate et al., 1997), and 0.5–1.1 (av. 0.8) in the Southern Ocean (Pszenny et al., 1999). The observed ratios in this study are also consistent with those (around 0.7) reported in the marine atmosphere (Saito et al., 2000; Lewis et al., 2001).

However, i-/n-pentanes ratios reported for the seawaters in the equatorial/subtropical North Pacific are as low as 0.1 in the region near and south of Hawaii (Donahue and Prinn, 1993, these values were read from graph by Pszenny et al., 1999) and around 0.2 in the eastern equatorial Pacific (data are cited in Pszenny et al., 1999 as X. Shi and R. G. Prinn, unpublished manuscript, 1996). Although the origin and production mechanism of pentane isomers in seawater and their spatial distributions are not well understood, similar ratios may be applicable to the summertime seawaters in the subtropical North Pacific as well. Pszenny et al. (1999) found that the isomer ratios show a difference in different ocean regions. These considerations on the pentane isomers and their observed ratios in the marine air suggest at least a part of the measured pentanes were derived from anthropogenic sources with higher i-/n-pentane ratios.

In order to validate the above implication, oceanic emissions of light hydrocarbons were estimated using a simple model with the published sea-to-air fluxes of alkanes into a boundary layer (height of 1 km) and the first-order loss by OH radical reaction. In the model calculation, the OH radical concentration is assumed to be $1.3 \times 10^6$ cm$^{-3}$ (the zonally and monthly averaged concentration of OH for July in 20°N at 1000 hPa, from Spivakovsky et al., 2000). The rate constants at 25°C in the reactions of butanes and pentanes with OH were taken from Atkinson (1997). The sea-to-air fluxes are taken from the western tropical Indian Ocean (Bonsang et al., 1988), the Atlantic Ocean (Plass et al., 1992; Plass-Dülmer et al., 1993), and the North Sea (Broadgate et al., 1997).

Table 2 shows the calculated mixing ratios as well as our median values taken during marine regime. The calculated results from Bonsang et al. (1988) are significantly higher than those of other authors as well as our measurements. The calculated mixing ratios are higher by factors of 2 (butanes) and 10 (pentanes) compared to our measurements. This difference might be reasonable because the former sampling sites are located near the coastline of the Madagascar and Africa, which are upwelling regions, whereas our site is located in the oligotrophic ocean in the North Pacific. Since elevated NMHC concentrations in waters associated with upwelling have been reported (e.g., Lamontagne et al., 1974), we do not consider that the results from Bonsang et al. (1988) which are not reasonable to compare with our results. For i-butane and n-butane, 3–9 and 6–23% of their removal by atmospheric reactions are balanced by the oceanic emissions, respectively. Calculated mixing ratio for i-pentane corresponds to 30% of the measurements, while that for n-pentane corresponds to 13%. These discussion based on the data obtained only for open ocean lead to a conclusion that the calculated mixing ratios are...
Table 2. Comparison of the calculated alkane mixing ratios (pptv) in the marine boundary layer with our measurements

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bonsang et al. (1988)*</th>
<th>Plass et al. (1992)</th>
<th>Plass-Dümler et al. (1993)</th>
<th>Broadgate et al. (1997)</th>
<th>This study median</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-Butane</td>
<td>22 (23)</td>
<td>1.0 (0.9)</td>
<td>0.3 (0.1)</td>
<td>0.4</td>
<td>11</td>
</tr>
<tr>
<td>n-Butane</td>
<td>32 (27)</td>
<td>4.1 (4.7)</td>
<td>1.0 (0.9)</td>
<td>—</td>
<td>18</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>12 (30)</td>
<td>—</td>
<td>—</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>29 (34)</td>
<td>—</td>
<td>—</td>
<td>0.4</td>
<td>3</td>
</tr>
</tbody>
</table>

*Sea-to-air fluxes are calculated from the seawater concentrations and wind speeds in cited paper, using the formulation of Liss and Merlivat (1986).
Standard deviations are given in parentheses except for the data of Broadgate et al. (1997).

Fig. 6. Ten-days backward trajectories calculated for every two days at heights of 500 m between 24 July, 0000 UTC (trajectory #1) and 9 August, 0000 UTC (trajectory #9). The symbols on each trajectory indicate locations at daily intervals. The trajectory was calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT-4) model (http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, Maryland).

too low to explain our measurements only from oceanic sources. This suggest that there is additional source for the light hydrocarbons.

In contrast to our results for the atmospheric budgets of the alkanes, Pszenny et al. (1999) pointed out that the estimated sea-to-air fluxes in the Southern Ocean are generally consistent with the atmospheric mixing ratios of butane isomers, which were measured simultaneously (Blake et al., 1996). Lewis et al. (2001) have also reported consistent C₄–C₆ alkane mixing ratios at a North Atlantic coastal site (Mace Head, 53°N) and a coastal site in the Southern Ocean (40°S) with the previously published fluxes. However, in the low and mid latitudes of the Northern Hemisphere, the oceanic emissions of short-lived alkanes (including n-butane) were estimated to account for only less than 10% of the atmospheric mixing ratios from the simultaneous measurements of both air and seawater samples (Koppmann et al., 1992; Plass-Dümler et al., 1993). Donahue and Prinn (1993) also reported that the flux of alkanes including both butanes and pentanes is insufficient to support the observed atmospheric mixing ratios in the tropical Pacific, although the authors reported no quantitative difference.

Continental is a potential source of relatively high concentrations of alkanes. In order to assess the influence of continental emissions, we conducted 10 days backward trajectory analysis for the air samples taken during marine wind regime (Fig. 6). Most of the air masses circulated around the eastern North Pacific then came over the Bellows, although only a few trajectories just touched the western coast of North America. Atmospheric lifetimes are approximately 5 days for butanes and 3 days for pentanes. Therefore, it is not likely that the light hydrocarbons measured during marine wind regime in this study were transported long distances from the North America. These considerations further suggest that there is a missing source of light hydrocarbons in the North Pacific. Potential source of such hydrocarbons may be associated with ship activity over the ocean. Although there is no estimates of light alkane emissions from ships, ship has been reported as a significant source of NOₓ in the Atlantic (Lawrence and Crutzen, 1999). Another possible interpretation is the contribution of sea-to-air flux from polluted ocean. About 440 gallons of aviation fuel was accidentally discharged from a Marine Corps helicopter into seawater about 7 km northeast of Bellows on July 24. In the early studies by Brooks et al. (1973) and Swinnerton and Lamontagne (1974) a clear correlation between oceanic oil pollution and abundance of C₁–C₄ alkanes in seawater was reported. To our knowledge, however, concentrations of butanes and pentanes in aviation fuel are not reported.

**SUMMARY AND CONCLUSIONS**

Two hundred GC measurements were performed on the Island of Oahu for three weeks in the summer of 1998. Temporal variations of C₄–C₅ alkanes in the subtropical North Pacific atmosphere were obtained. Very high concentrations of all the alkanes were observed during the weak-wind episodes whereas lower concentrations were
observed during the episodes of maritime air. The mixing ratios of i-butane, n-butane, i-pentane, and n-pentane co-varied during the campaign. Concentrations of these alkanes in the marine atmosphere were generally within the ranges observed by other investigators over the world ocean. The calculated atmospheric mixing ratios from the published sea-to-air fluxes suggest that oceanic emissions of butanes and pentanes correspond to 3–23% and 13–30% of our median concentrations during marine regime, respectively. The concentration ratios of pentane isomers suggest that the sources of the observed pentanes in marine air were not only derived from the ocean but also from some anthropogenic sources. However, air mass trajectory analysis showed that continental emissions are not the important anthropogenic source of the hydrocarbons.

We consider that there are anthropogenic sources including ship activity and oil pollution.

Acknowledgments—We would like to thank Steve Howell and Liangzhong Zhuang in the Department of Oceanography, University of Hawaii for their cooperation throughout this field campaign. Further we are grateful to Bernd Simonet for constructive comments on the manuscript. This study was supported in part by the Japanese Ministry of Education, Science, Sport and Culture through a Grant-in-Aid (No. 10144101) and by the CREST project of the Japan Science and Technology Corporation. We also appreciate the Research Fellowship from the Japan Society for the Promotion of Science for Young Scientists to T.S.

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