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Analysis of atmospheric hydrocarbons during winter MONEX

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ABSTRACT

The distribution of gaseous atmospheric hydrocarbon compounds, halocarbons, and nitrous oxide were studied. Whole air samples were collected aboard the NCAR Electra aircraft platform during the Monsoon Experiment (MONEX) flights in Kuala Lumpur, Malaysia, and on ferry flights to and from the United States. Foliage emission rates were also measured on some tropical plants.

The average free tropospheric TNMHC (total non-methane hydrocarbon) levels from both the transit flight and mission flights were low (2.5 $\mu g/m^3$). TNMHC just above the forest canopy over Borneo but within the mixing layer was higher and the concentrations over land were higher than those obtained over the ocean. The fluorocarbons showed a small latitude gradient or a difference between continental and oceanic air masses or (possibily) both. Methyl chloroform also showed a significant latitude profile. Nitrous oxide was uniformly distributed in the atmosphere. The C_2 hydrocarbons, ethane and acetylene, also showed latitudinal gradients.

The emission rates of foliage in the tropics were higher than those reported by other investigators for the mid-latitudes. The species sampled indicated that most tropical vegetation emits predominantly isoprene, rather than terpenes.

1. Introduction

The Monsoon Experiments (MONEX), which were carried out in 1978–1979, are a multi-national attempt to study and understand the meteorological events which lead to the tropical summer monsoon rains and the winter dry seasons in south and southeast Asia. The knowledge gained from these studies will lead to more accurate forecasts of the beginning, the duration, and the severity of the precipitation in the monsoon seasonal cycle.

The study of the air mass movements which initiate and sustain the monsoon circulation across the China Sea were an important aspect of the winter MONEX program. A small air chemistry program was an adjunct to the larger meteorological program. Sampling equipment was installed aboard the National Center for Atmospheric Research (NCAR) Electra aircraft and was used to collect whole air samples during the MONEX flights based out of Kuala Lumpur, Malaysia, as well as the ferry flights to and from the United States.

In addition, samples were collected of the emissions from a few tropical plants and the foliage emission rates were estimated for these species. Several ground-level samples were collected in conjunction with the foliage samples. An analytical laboratory was shipped to Malaysia and set up in Kuala Lumpur to analyze for the gaseous hydrocarbon species (C2 to C10) in the samples. A limited number of the samples were returned to the Washington State University laboratories in Pullman, Washington, following the winter MONEX field work for analyses of the samples for individual C_2 hydrocarbons and the halocarbons and nitrous oxide.

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2. Experimental description

2.1. *Sampling techniques*

The NCAR Electra aircraft was employed for sample collection during the winter MONEX program. Canister racks which held a combination of 6-liter and 1-liter canisters were mounted in the Electra. After at least a 5 to 10 minute flush of a canister with sample air, the container was pressurized to about 30 psia, to provide several liters of positive-pressure sample for analysis. The details of the sampling method are described elsewhere (Cronn and Nutmagul, 1980). A map of the individual flight tracks from Palo Alto to Kuala Lumpur (round trip) is shown in Fig. 1. Sample numbers collected during ferry flights to and from the United States are also given. Twenty-eight samples (sample numbers 30 to 57) were collected during MONEX flights originating out of Kuala Lumpur, Malaysia. Six of these mission flights were flown in which whole air sampling was accomplished; two flights in the South China Sea, two flights on so-called cold-surge missions, one flight in the Java Sea, and a low-level flight over the jungles of Borneo. Cruising altitudes were typically in the 5500 m range except for the jungle flight when the altitude was mainainted 30 to 100 m above the forest canopy to allow for collection of samples within the mixing layer near tropical vegetation.

Some exploratory, ground-level foliage sampling was accomplished during the field project in Malaysia. The technique used was a simplified version of the methodology developed by Zimmerman (1979a, b). The choice of six genera (and specific species) to be sampled were selected on the recommendation of Dr. Gordon Smith of the University of Malaya botany faculty to provide the widest selection of the most common natural and cultivated plants on the Malaysian peninsula. The

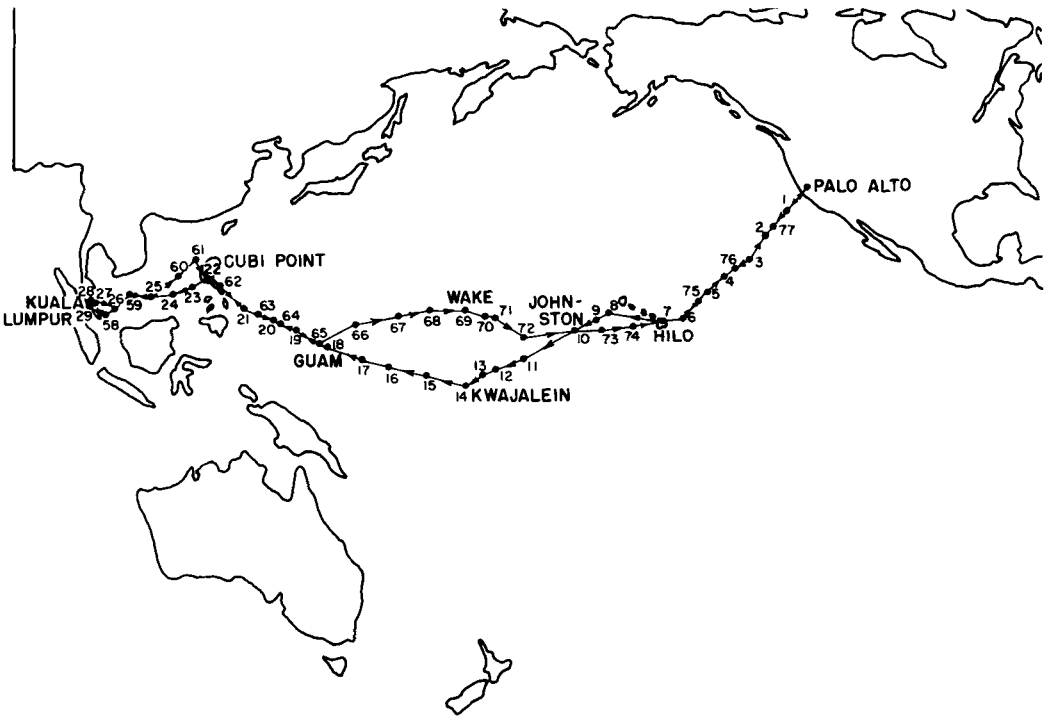

Fig. 1. Flight path from Palo Alto to Kuala Lumpur (round trip). Samples 1–7 were collected on November 18, 1978, 8–10 on November 20, 1978, 11–14 on November 21, 1978, 15–18 on November 22, 1978, 19–22 on November 23, 1978, 23–29 on November 24, 1978, 58–61 on January 3, 1979, 62–65 on January 4, 1979, 66–69 on January 6, 1979, 70–72 on January 7, 1979, and 73–77 on January 8, 1979.

two widely cultivated, commercially important species grown on the Malaysian peninsula, namely rubber tree (*Hevea brasiliensis*) and oil palm (*Elaeis guineensis*), were chosen for sampling. In addition, one major plant from each of the four most-commonly represented genera occurring on the Malaysian peninsula were also selected for sampling.

The details of the sampling method are described elsewhere (Cronn and Nutmagul, 1980). Briefly, after plant selection, the Teflon bag enclosure was turned inside out, the unsealed edge was opened, and the bag alternately filled and deflated with ambient air to insure that any car exhaust components accumulated during transit were flushed out. The foliage was enclosed in the Teflon bag with great care taken not to crush, bend, or damage the foliage. The base of the bag was held closely around the branch during sampling. After 5 minutes, an evacuated 6-liter canister was attached directly to the sampling port of the enclosure and the valve opened. Subsequently, fifteen 100-ml aliquots from the enclosure were transferred through septa via a ground-glass syringe to pressurize the sample container. This generally required up to an additional 10 minutes enclosure time. Estimates of ambient temperature, wind speed, shadiness of enclosed branch, enclosure volume, plant location, etc. were noted. Ambient air samples were also collected within minutes of the foliage sample. After sampling, the branch was clipped at the point at which the bag was sealed and returned to the University of Malaya to be dried and weighed. Branches, leaves and fruit were weighed separately after 24 to 48 hours drying time.

The major differences between the sampling technique as used for this work and that reported by Zimmerman were: (1) the bag enclosure was not deflated around the branch and subsequently re-filled with zero air. Instead, ambient air samples were collected immediately after, and in near proximity to, the foliage samples, and the background hydrocarbons were subtracted from the emission sample; (2) the Zimmerman method allows for withdrawal of sample aliquot at the same rate that zero air replaces it. In this study, sample was withdrawn as described above.

The emission rates were calculated from the chromatographic results for the foliage emission samples, and the ambient air samples collected near the folliage sampling sites. The method chosen to eliminate ambient air hydrocarbons before calculation of emission rates was as follows. The concentration of a given component in the ambient air sample was subtracted from the concentration of the same component in the foliage emission sample. Negative values were set to zero. After the foliage emission sample results had been thus corrected for ambient air influence, the remaining concentration of each component was summed to obtain the TNMHC. The calculations of total (or isoprene or terpenes) emission rates were obtained by using the following formula:

$$\text{Emission Rate} = \frac{[\text{TNMHC}][V\,\text{bag}]}{[W][T]} \times 60\,\mu\text{g/g-h}$$

where TNMHC = total concentration of non-methane hydrocarbons (μg/m^3) (or isoprene or terpenes),

V bag = estimated volume of the sampling bag (m^3),

W = weight of dry leaves (g),

T = average sampling time (min).

The volume of the sampling bag was estimated to be 0.06 m^3 for all samplings with the exception of 0.045 m^3 for sampling of the rubber tree. Sampling time was estimated from the average time of enclosure during the sampling procedures (6 liters sampled at 5 minutes and fifteen 100-ml aliquots each sampled at 40-second intervals thereafter gave an average enclosure time of 6.5 minutes).

It should be stressed that the calculated emission rates from this study are only estimates. The accuracy is probably not as accurate as the data reported by Zimmerman (1979a, b) due to the simplification of the sample collection procedure. The accuracy is estimated to be a factor of two worse due to these changes.

Emission rates in this study were not standardized to 30°C or 35°C because estimated ambient temperatures were 30 °C to 35 °C, in contrast to the work of Zimmerman (1979b) who standardized to 30 °C or Tingey et al. (1978) who standardized to 35 °C.

2.2. *Analytical techniques*

A Hewlett-Packard Model 5700 A gas chromatograph equipped with dual sample inlets, columns, and flame ionization detector systems

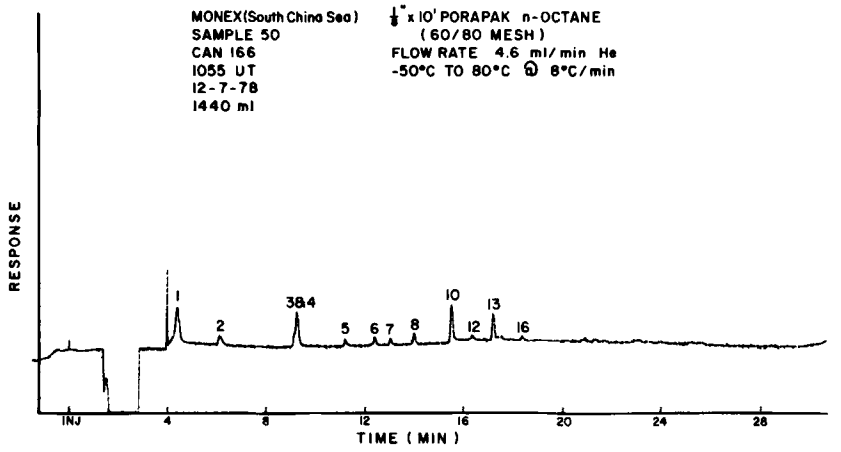

Fig. 2. An example chromatogram for a light hydrocarbon analysis of a free tropospheric air sample. 1 = ethane; 2 = ethylene; 3 = acetylene; 4 = propane; 5 = F-12; 6 = propene; 7 = isobutane; 8 = *n*-butane; 10 = methyl chloride; 12 = 1-butene and propyne; 13 = 1,3-butadiene, isobutene and F-11; 16 = *n*-pentane. (December 7, 1978.)

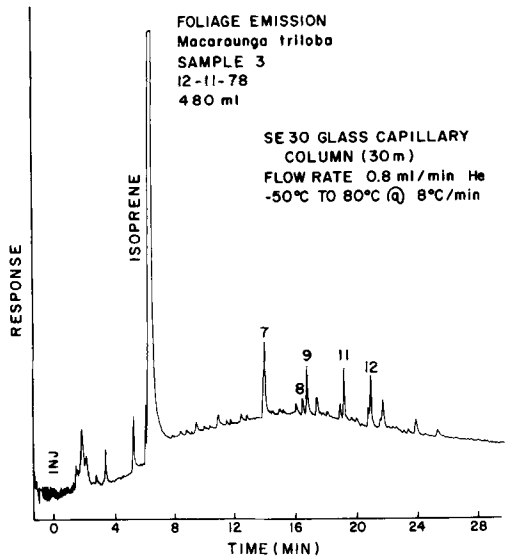

Fig. 3. An example chromatogram for a heavy hydrocarbon analysis of a foliage enclosure sample from an isoprene-emitting plant. 7 = 2,3,4-trimethylpentane and toluene; 8 = ethylbenzene: 9 = m-xylene and p-xylene; 11 = α-pinene; 12 = β-pinene. (December 11, 1978.)

was transported to Kuala Lumpur for analysis of hydrocarbons. A column packed with n-octane on Porasil C (60/80 mesh) was used for analysis of C_2 through C_6 hydrocarbon species and an SE-30 capillary column was used for analysis of C_5 through C_{10} hydrocarbons. Typically 500–1000 ml sample aliquots were used in the analysis. Other details of the analytical technique can be found elsewhere (Cronn and Nutmagul, 1980). The lower limits of detection of this method were 0.02 $\mu g/m^3$ for a 2000 ml sample aliquot or 0.08 $\mu g/m^3$ for a 500 ml sample aliquot. As an example of the results of the hydrocarbon analysis techniques, a typical light (C_2 through C_6) hydrocarbon chromatogram for free tropospheric air is shown in Fig. 2 and a heavy (C_5 through C_{10}) hydrocarbon chromatogram for a foliage emission sample of an isoprene emitting plant is shown in Fig. 3. An isothermal GC analytical technique was used for analysis of N_2O, CF_2Cl_2, $CFCl_3$, and CH_3CCl_3 on samples returned to WSU. A dual-column, dual-detector Perkin Elmer Model 3920 gas chromatograph with an electron capture detector (^{63}Ni foil) was used. A column packed with 10% SF-96 on 100/120 mesh Chromosorb W was used for analysis of $CFCl_3$ and CH_3CCl_3 and a column packed with Porasil B (100/120 mesh) was used for analysis of N_2O, CF_2Cl_2 and $CFCl_3$. A 5 ml sample was used for the first column and a 1 ml sample for the second column. The detection limits have been reported by Cronn and Robinson (1979a) to be 0.3 ppb for N_2O, 0.7 ppt for F-11, 10 ppt for F-12, and 6 ppt for CH_3CCl_3. The precision is shown by the percentage standard deviations for five replicate runs of 0.7% for N_2O, 0.6% for F-11, 0.5% for

F-12, and 4.2% for CH_3CCl_3. The accuracies are estimated to be not any worse than ±20% and probably as good as 5–10% for F-11 and F-12.

Analyses for the C_2 hydrocarbons (ethane, ethylene, and acetylene) were also performed at WSU on a Perkin Elmer Model 3920 gas chromatograph equipped with flame ionization detection. A column packed with Porapak N (80/100 mesh) was used for the analysis. The detection limits as reported by Cronn and Robinson (1979b) are 0.12 $\mu g/m^3$ for ethane (0.1 ppb) and 0.04 $\mu g/m^3$ for acetylene (0.04 ppb) for a 500-ml sample aliquot. The sample aliquot sizes used in this study ranged from 250 ml to 1 liter. The precision is 1.5% S.D. on four replicate analyses for ethane and 10.5% for acetylene. Ethylene is similar to ethane. The accuracy is estimated to be better than ±0.2 $\mu g/m^3$ for ethane and ethylene and better than a factor of two for acetylene.

3. Discussion

Light hydrocarbon samples from the MONEX flights have been separated into the transit flight samples, the jungle flight, and other MONEX mission samples for interpretive purposes. The free tropospheric total non-methane hydrocarbon (TNMHC) average from the transit flight (excluding the low altitude samples) was 2.4 $\mu g/m^3$ (S.D. = 1.0 or 41%). For the jungle flight, the concentrations of TNMHC were in the range of 0.4–40.3 $\mu g/m^3$. The average concentration of TNMHC just above the canopy and within the mixing layer was 23.8 $\mu g/m^3$ (S.D. = 13.7 or 58%). Two samples were collected low over the ocean on this flight. The concentrations were 2.8 $\mu g/m^3$ at an altitude of 63 m at 2° 30′N and 110°37′E and 0.4 $\mu g/m^3$ at an altitude of 4345 m at 2°49′N and 107°57′E. These results showed that the concentrations of TNMHC over land were higher than those obtained over ocean, presumably due to the greater source strength over land. The TNMHC concentrations obtained from the two ocean samples indicated a higher level within the mixing layer than that obtained in the free tropospheric ocean air samples. For the other MONEX mission samples, higher concentrations of TNMHC often occurred at low altitude near Kuala Lumpur. The average concentration of TNMHC during these missions (excluding the low altitude samples) was 2.5 $\mu g/m^3$ (S.D. = 1.1 or 44%).

The results of the hydrocarbon emission studies of foliage samples in Malaysia are given in Table 1. Each species showed a distinct emission pattern. Five of the six species sampled emitted mainly isoprene. Only *Mallotus paniculatis* emitted primarily terpenes. Zimmerman (1979b) reported the average emission rates for conifers and oaks during daytime in summer at mid-latitudes of 8.9 $\mu g/g$-h and 24.7 $\mu g/g$-h at a leaf temperature standardized to 30 °C, respectively. Tingey et al. (1978) reported an average emission rate from slash pine of 9.38 $\mu g/g$-h (10.6 μg compound/g-h) at a leaf temperature of 35 °C. It should be noted that the emissions from slash pine and conifers consisted mainly of monoterpenes while the emissions from oaks were primarily isoprene. Tingey et al.

Table 1. *Non-methane emission rates of tropical foliage*

Foliage type	Major emission	Individual terpenes or isoprene emission rate ($\mu g/g$-h)	Total non-methane hydrocarbon emission rate ($\mu g/g$-h)
Mallotus paniculatis	Terpenes	0.78	1.02
Eugenia grandis	Isoprene	11.61	11.62
Macaraunga triloba	Isoprene	43.61	45.30
	Terpenes	0.74	
Ficus fistulosa (fig)	Isoprene	25.97	27.27
	Terpenes	0.16	
Elaeis guineensis (palm oil tree)	Isoprene	166.46	166.71
Hevea brasiliensis (rubber tree)	Isoprene	7.18	7.85
	Terpenes	0.53	

(1978) also pointed out that the emission rates from plants that emitted mainly monoterpenes were dependent only on leaf temperature while the emission rate of the hemiterpene, isoprene, depended upon both light intensity and leaf temperature. The sampling in this study was conducted at temperatures estimated to be in the 30 to 35 °C range of ambient temperatures. Therefore, standardization to a leaf temperature was not necessary. The foliage emission rates from this study were higher than those reported by the investigators mentioned above. This is true especially since wintertime emission rates in the mid-latitudes would be even lower, while the measurements reported here were made in December (although a much smaller seasonal change in emission rates would be expected at 5° N latitude).

A vertical gradient of isoprene is observed with values of 12 ± 5 $\mu g/m^3$ at ground level (from the background ambient samples), dropping to 2.7 ± 1.8 $\mu g/m^3$ above the canopy but still within the mixing layer, and further dropping to below the detection limit of the analysis technique (0.02–0.08 $\mu g/m^3$) in free tropospheric air.

These preliminary measurements which indicate (1) high emission rates of tropical foliage and (2) a predominance of isoprene emitters in the mixture of tropical plants, were not unexpected based on the experience gained from the studies of Zimmerman (1979a, b). These results have significant importance relative to the question of the global budget of non-methane hydrocarbons. The potential impact of larger-than-previously-estimated amounts of isoprene being emitted into tropical air masses may help balance the global budgets of O_3, CO and H_2 as discussed by Zimmerman et al. (1978).

The results of the halocarbon and nitrous oxide analyses indicated that the average mixing ratio of F-12 (280 ± 14 ppt) was lower than the approximately 286 ± 13 ppt observed at the same time period at a long-term continuous background monitoring site in eastern Washington. However, the data sets were not significantly different as shown by a *t*-test. Although the average is not statistically significantly lower than the eastern Washington average, a latitudinal gradient is indicated by this data, especially in light of the much lower median (275 ppt) for the MONEX data. This is in keeping with the fall/winter gradient observed in October 1977 by Robinson (1978) but differs from the well-mixed Northern Hemispheric distribution reported by Singh (1979b). F-11 showed an apparently constant mixing ratio between 2° N and 34° N latitude with an average of 165 ± 5 ppt which was less than the average mixing ratio of 172 ± 5 ppt observed during the same time period in eastern Washington. The mixing ratios of F-11 from the two data sets were significantly different by a *t*-test ($P = 0.01$). There are two possible reasons to consider in explaining this difference: (1) a latitudinal gradient; or (2) elevated levels of F-11 in continental air masses (eastern Washington) relative to oceanic air masses (MONEX samples). Such differences between oceanic and continental air masses have been observed by Heidt (private communication, 1979) for halocarbons. A spread of values with an average mixing ratio of 117 ± 9 ppt was indicated for methyl chloroform which is less than the average value (134 ± 14 ppt) at the higher latitude observed during the same time period in eastern Washington. This result is in agreement with the latitude profiles reported by various investigators (Cronn, 1980; Cronn and Robinson, 1978; Robinson, 1978; Rowland, private communication, 1978; Singh et al., 1979a). The distinct latitudinal gradient for this compound is explained by the shorter lifetime (estimated at 6.4 years by Campbell, 1980) due to attack by hydroxyl radical, coupled with the existence of the majority of emissions in the mid-latitudes of the northern hemisphere.

Nitrous oxide showed an apparent constant mixing ratio with an average of 333 ± 4 ppb, which was about the same mixing ratio as the 331 ± 3 ppb observed at the same time period in eastern Washington. The results show no latitudinal gradient and are in agreement with other investigators (Robinson, 1978; Singh et al., 1979a).

The results of background tropospheric levels of ethane, ethylene and acetylene indicate the existence of latitudinal gradients for ethane and acetylene. Measurements of background tropospheric levels of ethane, ethylene and acetylene are not abundant. The data reported here are the average values for the high altitude samples (5000–7000 m) at 4°N–34°N. The range of values, the average, the standard deviation (S.D.), the relative standard deviation (% S.D.) and number of samples (*N*) are given in Table 2. Cronn and Robinson (1979) reported average upper tropospheric concentrations, between 20,000 ft (6 km) and 35,000 ft (11 km) near 37°N–123°W of

Table 2. *Average tropospheric levels of ethane, ethylene and acetylene*

	Concentration ($\mu g/m^3$)					
	$\bar{X}$	S.D.	% S.D.	N	Min.	Max.
C_2H_6	0.78	0.19	24	25	0.55	1.28
C_2H_4	1.01	1.25	124	25	0.10	4.31
C_2H_2	0.086	0.034	40	24	0.034	0.170

1.2 $\mu g/m^3$ for ethane and 0.24 $\mu g/m^3$ for acetylene, and 0.95 $\mu g/m^3$ near 9° N–80° W for ethane and 0.09 $\mu g/m^3$ for acetylene; Singh et al. (1979b) also reported a total burden in the northern hemisphere for ethane of 1.1 ppb (1.55 $\mu g/m^3$) and 0.22 $\mu g/m^3$ for acetylene for flights over the Pacific Ocean. The results of this study indicate the existence of latitudinal gradients for ethane and acetylene, i.e., low concentrations at low latitudes and high concentrations at high latitudes, when compared with the results of other investigators above. For ethylene, the data is largely scattered. The scatter is most likely due to sample contamination as reported previously by Cronn and Robinson (1979b).

4. Acknowledgment

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