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Technical Report Series on the Boreal Ecosystem-Atmosphere Study (BOREAS)

Forrest G. Hall and Sara K. Conrad, Editors

Volume 240

BOREAS TGB-9 Above-canopy NMHC at SSA-OBS, SSA-OJP, and SSA-OA Sites

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BOREAS TGB-9 Above-canopy NMHC at SSA-OBS, SSA-OJP, and SSA-OA Sites

B.N. Kieser, V.L. Young, H. Niki

Summary

The BOREAS TGB-9 team collected data in order to inventory and quantify the anthropogenic and biogenic NMHCs over the BOREAS study areas. This data set contains concentration and mixing ratio values for several NMHCs collected at the BOREAS SSA from 27-May-1994 to 15-Sep-1994. The data are provided in tabular ASCII files.

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1. Data Set Overview

1.1 Data Set Identification

BOREAS TGB-09 Above-canopy NMHC at SSA-OBS, SSA-OJP, and SSA-OA Sites

1.2 Data Set Introduction

The BOREal Ecosystem-Atmosphere Study (BOREAS) Trace Gas Biogeochemistry TGB)-09 team measured nonmethane hydrocarbon (NMHC) data at the Southern Study Area (SSA)-Old Black Spruce (OBS), Old Jack Pine (OJP), and Old Aspen (OA) sites.

1.3 Objective/Purpose

The mission objective was twofold: 1) to provide a quantitative inventory of NMHCs, both anthropogenic and biogenic, at the SSA-OBS, SSA-OJP, and SSA-OA tower flux sites; and 2) to provide ambient concentration data for biogenic hydrocarbons suitable for calculating the flux of biogenic hydrocarbons at the tower flux sites using the gradient method.

1.4 Summary of Parameters

Concentrations in the parts per trillion by volume (pptv) - parts per billion by volume (ppbv) range are reported for a variety of biogenic and anthropogenic NMHCs. Local sources and transport from distant sources contribute to the NMHCs inventory in the boreal forest region. A quantitative inventory of ambient hydrocarbon concentrations can aid in identification of sources important to the boreal atmosphere. In particular, gradient measurements allow biogenic emissions from the forest itself to be quantified.

1.5 Discussion

Each sample was analyzed on two separate Gas Chromatograph (GC) Flame Ionization Detector (FID) systems. In one, the column and temperature program were chosen to optimize quantitation of C2-C6 hydrocarbons. In the other, the column and temperature program were chosen to optimize quantitation of C5-C10 hydrocarbons.

Samples collected at the SSA sites were transported to the laboratory in Toronto for analysis. The time between collection and analysis varied greatly over the course of the study. The earliest samples were analyzed within 1 month of collection, whereas some of the latest samples were not analyzed until 6 months after collection. Extensive experience with such samples has demonstrated that these samples are stable over such long periods of time.

1.6 Related Data Sets

BOREAS TGB-10 Oxidant Concentration Data over the SSA

BOREAS TGB-10 Oxidant Flux Data over the SSA

2. Investigator(s)

2.1 Investigator(s) Name and Title

Professor Hiromi Niki (deceased April 1995)

2.2 Title of Investigation

Ambient Measurements of Nonmethane Hydrocarbons

2.3 Contact Information

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3. Theory of Measurements

Estimates of the hydrocarbon flux above the canopy by the gradient method require measurement of the hydrocarbon concentration gradient. To accomplish this, simultaneous samples were collected at two heights above the canopy and analyzed for a range of hydrocarbons. The flux of any particular hydrocarbon (HC) can then be determined by the following relationship:

$$\text{FLUX(HC)} = k(z) \int ([\text{HC}]'' - [\text{HC}]') / (z'' - z')$$

where $([\text{HC}]'' - [\text{HC}]')$ is the difference in [HC] between the two heights z'' and z' . The eddy diffusivity coefficient $k(z)$ should be obtained from other researchers performing simultaneous measurements at the same sites. Measurements of the hydrocarbon concentrations are made by collecting whole air samples over a 30-minute period in evacuated, electropolished stainless steel canisters that are then transported to the laboratory for analysis. Before being shipped to Saskatchewan for sample collection, the canisters were heated to 80 °C and evacuated to 10⁻⁶ Torr for 2 hours.

4. Equipment

4.1 Sensor/Instrument Description

- The sample collection system filled two sample canisters simultaneously over 30 minutes. The system consists of:
 - Two electropolished stainless steel sample canisters (Biospherics Research Corp., Oregon, U.S.A.), 3- or 6- liter volume, evacuated, sealed by a Nupro metal bellows valve, and having a Swagelock connection on the inlet.
 - Two mass flow controllers, Tylan FC-260V, 0 - 500 sccm.
 - 12V DC 1.5 A KNF Neuberger metal bellows pump UN05 ATI.
 - Stainless steel tubing and fittings between components.
- The sample analysis system for identification and quantification of hydrocarbons. The system consisted of:
 - Hewlett Packard (HP) 5890II GC-FID with DB-1 100 m x 0.25 mm ID x 0.5 micrometer film column, electronically programmable pressure control inlet, and HP PC-ChemStation v. 1.01 software, primarily for C5-C10 hydrocarbons.
 - HP 5890II GC-FID with Al2O3/KCl PLOT 50 m x 0.32 mm ID column and HP PC-ChemStation v. 1.01 software, primarily for C2-C6 hydrocarbons.
 - HP 5890 GC with SPB-5 30 m x 0.25 mm ID x 0.25 micrometer film column, HP 5970 MSD, HP 5970 GC-MS Workstation v. 3.2 software, and in-house constructed cryogenic sample prefocusing system.
 - Cryogenic sample preconcentration system, one per GC system, constructed in-house.
 - Modified Tekran Cryotherm-100 cryogenic sample prefocusing system, one per GC-FID system. Tekran cryofocusers were modified by replacing all internal nickel tubing with stainless steel tubing. The prefocusing system for the GC-MSD was constructed in-house.

4.1.1 Collection Environment

Samples were collected at each of the SSA-OBS and SSA-OJP sites during Intensive Field Campaign (IFC)-1, IFC-2, and IFC-3. Samples were collected at the SSA-OA site during IFC-2 and IFC-3. Samples were collected regardless of the prevailing weather conditions.

4.1.2 Source/Platform

- A portable sampling system mounted on a backpack frame and placed at the base of the tower. Sampling was through Teflon lines mounted on the tower. Full sample canisters were shipped to the laboratory for analysis.
- Benchtop systems in the laboratory at York University as described above.

4.1.3 Source/Platform Mission Objectives

The objective of the tower was to provide a place to mount instrumentation for measurements. The objective of the backpack was to allow transport of equipment to measurement sites. The lab benchtop provided an area to use to analyze the samples.

4.1.4 Key Variables

Concentration of individual NMHCs in air. Compounds that are measured (not all are included in this data set): ethylene, acetylene, ethane, propene, propane, propyne, isobutane, iso-butene, 1,3-butadiene, n-butane, t-2-butene, 2,2-dimethylpropane, 1-butyne, c-2-butene, 2-methylbutane, 1-pentene, 2-methyl-1-butene, n-pentane, isoprene, t-2-pentene, c-2-pentene, 2-methyl-2-butene, 2,2-dimethyl-butane, 4-methyl-1-pentene, 3-methyl-1-pentene, cyclopentane, 2,3-dimethyl-butane, c-4-methyl-2-pentene, 2-methylpentane, t-4-meth-2-pentene, 3-methylpentane, 2-ethyl-1-butene, 1-hexene, n-hexane, t-2-hexene, c-3-methyl-2-pentene, c-2-hexene, t-3-methyl-2-pentene, 2,2-dimethylpentane, methylcyclopentane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, benzene, cyclohexane, 2-methylhexane, 2,3-dimethylpentane, 3-methylhexane, 1-heptene, 2,4,4-trimeth-pentan, t-3-heptene, heptane, t-2/c-3-heptene, c-2-heptene, methylcyclohexane, 2,2-dimethylhexane, 2,5-dimethylhexane, 2,4-dimethylhexane, 2,3,4-trimethylpenta, toluene, 2-methylheptane, 4-methylheptane, 3-methylheptane, c-1,3-dimethylcycloh, t-1,4-dimethylcycloh, 2,2,5-trimethylhexane, 1-octene, n-octane, t-2-octene, t-1,3-dimethylcycloh, c-2-octene, c-1,2-dimethylcycloh, ethylbenzene, m-xylene, p-xylene, styrene, o-xylene, 1-nonene, n-nonane, iso-propylbenzene, benzaldehyde, alpha-pinene, 3,6-dimethyloctane, n-propylbenzene, camphene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenze, sabinene, 2-ethyltoluene, b-pinene, myrcene, 1,2,4-trimethylbenze, t-butylbenzene, n-decane, 2-carene, iso-butylbenzene, sec-butylbenzene, 3-carene, a-terpinene, 1,2,3-trimethylbenze, p-cymene, limonene, indan, 1,3-diethylbenzene, 1,4-diethylbenzene, n-butylbenzene, g-terpinene, 1,2-dieth-benz, undecane

Other compounds may be identified at a later date. Contact the investigators for further information.

4.1.5 Principles of Operation

a. Sample collection system

Whole air samples were simultaneously collected at constant flow rates for 30 minutes (typically) into stainless steel canisters, from two heights on a flux tower during IFC-1, IFC-2, and IFC-3 at each of the SSA-OBS, SSA-OJP, and SSA-OA sites. Air was pumped from the sampling site on the tower through a Teflon line into a sample canister. The mass flow controller held the pumping rate constant as the can filled to a final pressure of about 20 pounds per square inch (psi). Two pumping systems (mounted on the same backpack) with inlets at different points on the tower were used in order to fill two cans simultaneously with air from different heights above the canopy.

b. Sample analysis

The collected samples were transported to the laboratory for analysis using GC techniques. Permissible injection volumes for capillary GC are below 1 cc (gas). Typical concentrations for the hydrocarbon species being measured are in the range of 10 pptv to 10 ppbv, which, for isoprene as example, gives an analyte range of 0.06 to 60 fg/cc. The constraint on injection volume for capillary GC combined with the low concentrations of analyte requires that the samples be preconcentrated prior to GC analysis. Sample preconcentration is accomplished by passing a known volume of the air sample through a trap filled with fine glass beads cooled to -180 °C. Volatile hydrocarbons are retained on the beads. The bulk air constituents (nitrogen and oxygen) are collected in an evacuated reference

volume. From the final pressure of the reference volume, the total volume of air that passed through the preconcentration system may be calculated. This volume is used to calculate the mixing ratio of each compound in the original air sample after GC analysis. The sample trapped cryogenically on the glass beads is thermally desorbed into a stream of ultrapure helium and retrapped on the surface of a fine stainless steel capillary cooled to -180°C . This second cryogenic trapping stage "focuses" the sample into a small linear section of tubing. Electrical resistance ballistically heats the cold stainless steel capillary, and the cryofocused sample quickly desorbs into the helium stream and is transferred to the chromatographic column.

The volatile components of the sample are carried through the GC column by the mobile phase, the ultrapure helium. Capillary GC columns are typically a long (10-100 m) section of fused silica capillary (0.18-0.53 mm inner diameter, I.D.). The inside surface of the column has a thin (0.05-5 m) coating of a stationary phase designed to interact with the components of a mixture passing through the column. For any individual hydrocarbon, the amount of time taken to traverse the length of the column (retention time) is determined by the component's affinity for the stationary phase, which, in turn, is a function of the chemical nature of the component. This differential affinity of various species for the stationary phase makes it possible for the GC column to separate a complex mixture as it travels through the column. Controlled variation of column temperature over the course of the analysis (temperature program) also affects the separation of the compounds, the retention time for each compound, and the total analysis time for the sample. Compounds are identified by their characteristic retention times.

Compounds eluting from the end of the column are detected using an FID, in which the column effluent is introduced into a hydrogen-air diffusion flame. An electrical charge applied a potential across the flame collects species formed through radical reactions in the flame and the current is amplified by a sensitive electrometer. The FID displays a linear response to carbon atoms over a large dynamic range. The FID is very sensitive to hydrocarbons, but is insensitive to water or carbon dioxide.

In addition to the FID detector, some of the samples are analyzed using the MSD, which produces mass spectra of the species eluted from the column. The MSD is less sensitive than the FID, but provides a more certain identification of the species eluted by relying not only on the retention time, but also on the mass spectrum of the effluent. The column separates components, they are introduced to a high-energy stream of electrons, and a fraction of the molecules are converted to ions. The ions are electrically accelerated into a quadrupole mass filter and passed to an electron multiplier. The electron multiplier counts the number of ions that strike it. By scanning a range of mass-charge ratios, the MSD can construct a mass spectrum for each compound exiting the column. The pattern and abundance of ions produced are characteristic of the chemical structure of a compound, and thus may be used to identify species eluting from the column. The MSD results are used to qualitatively identify unknown compounds, while the FID results provide quantitative data.

Unlike the FID, the MSD is sensitive to water and carbon dioxide. Water and carbon dioxide are present in ambient air in amounts several orders of magnitude larger than any of the NMHCs. Although small amounts will not affect FID operation, typical ambient concentrations do pose chromatographic problems and problems with the MSD operation. Water and carbon dioxide have a detrimental effect on the chromatographic separation of hydrocarbons. Because of its polar nature, water interferes with the interaction between the hydrocarbons and the stationary phase of the column. Water can also clog the glass bead trap, cryo-focuser, or column during the analysis, and may extinguish the FID flame. In the MSD, high water and carbon dioxide signals increase the background signals for other ions such that the detection limit is raised to an unsuitable level. In order to avoid these problems, water and carbon dioxide are removed from the air samples prior to preconcentration. A cold trap (-20 to -60°C) removes water in sufficient amounts to allow chromatographic analysis to proceed without any clogging or FID quenching. A potassium carbonate trap at 80°C removes carbon dioxide. These traps were tested extensively to ensure that the concentrations of the hydrocarbons of interest are not affected.

4.1.6 Sensor/Instrument Measurement Geometry

The Teflon sampling tubes are mounted on the main tower at each site. The height of the inlet above the ground, in meters, is given for each sample. Both inlets are above the mean canopy height.

4.1.7 Manufacturer of Sensor/Instrument

a. The sampling system was assembled by the investigators. All tubing was chromatographic-grade stainless steel.

(i) Stainless steel canisters were manufactured by:

Biospherics Research Corp.
1121 N.W. Donelson Street
Hillsboro, OR 97124
(503) 690-1077

(ii) Mass flow controllers were manufactured by:

Tylan Corporation
Torrance, CA 90501

(iii) The metal bellows pump was manufactured by:

KNF Neuberger, Inc.
Princeton, NJ
(609) 799-4350

b. Analysis system

(i,ii,iii) GC and GC-MSD was manufactured by:

Hewlett-Packard (Canada)
5150 Spectrum Way H80
Mississauga, ON L4W 5G1
(905) 206-4725

(iv) The cryogenic sample preconcentration system was assembled by the investigators.

(v) The cryogenic sample prefocusing system for the GC-FIDs was manufactured by:

Tekran, Inc.
Toronto, ON

The cryogenic sample prefocusing system for the GC-MSD was assembled by the investigators.

4.2 Calibration

a. Sampling system

The sampling system flow rate was calibrated using a soap bubble flow meter.

b. Hydrocarbon analysis

GC-FID systems were calibrated with standard mixtures from Environment Canada, National Center for Atmospheric Research (NCAR), Scott Specialty Gases, as well as standard mixtures prepared in the laboratory (Dr. Daniel Wang, Environment Canada, 351 St. Joseph Blvd., Hull, PQ K1A 0H3; Dr. Eric Apel, NCAR, 1850 Table Mesa Drive, Boulder, CO 80303; Scott Specialty Gases, 6141 Easton Road, Plumsteadville, PA 18949-0310), and checked with secondary standards mixed in the laboratory.

Calibration of the GC systems was accomplished using prepared gas mixtures in air of known concentration to determine the characteristic retention time and FID response for each compound in the mixture. Measured FID responses were checked against the expected response based on the number of carbon atoms in each compound, since the FID response is linear over a large range, and is essentially mass responsive to carbon atoms.

4.2.1 Specifications

4.2.1.1 Tolerance

a. Sampling system: Constant flow rate of 500 ± 50 sccm air at STP.

b. Hydrocarbon analysis: Detection limits and precision:

NMHC analysis detection limit: 5 pptv

NMHC Precision:

+/-5pptv for [HC] < 0.1ppbv

+/-5% for $0.1\text{ppbv} < [\text{HC}] < 1.0\text{ppbv}$

+/-1% for [HC] > 1.0ppbv

NMHC GC-MSD analysis detection limit: 0.1-0.5 ppbv (depending on compound)

Precision: not used for quantitative analysis

4.2.2 Frequency of Calibration

a. Sample collection system calibration was checked weekly.

b. NMHC analysis system was checked weekly for all components reported using standards from NCAR and/or Environment Canada and/or laboratory- prepared mixtures.

4.2.3 Other Calibration Information

For NMHC analysis, the two samples in each pair were run consecutively on the same day by the same operator on the same GC. Before the project began, each operator demonstrated that he could achieve the precision quoted in Section 4.2.1.1 for multiple runs of the same sample. Each day, one sample was repeated by another operator on the same GC to test reproducibility between operators. The concentration of isoprene obtained from the two GCs was compared for each sample. Several samples from each IFC were analyzed more than once to monitor the system performance, as well as track any sample stability problems.

5. Data Acquisition Methods

The two outlets of the pumping system were connected to evacuated stainless steel canisters. The inlets of the pumping system were connected to Teflon lines mounted on a tower so that air could be sampled simultaneously from two heights above the forest canopy. The flow rate for the mass flow controllers was set such that each can would fill to a pressure of about 20 psi during 30 minutes of sampling. The cans were sealed by shutting the valve, and the full cans were then shipped to the laboratory for analysis.

Approximately 500 - 700 mL (at standard temperature and pressure) of sample was used for GC-FID analysis. The sample handling procedure is described in more detail in Section 4.

6. Observations

6.1 Data Notes

None given.

6.2 Field Notes

SSA-OBS: The mean canopy height was 9 m. Sampling inlets were placed at 12.4 m and 23.3 m above ground level. A path about 50 m wide was made from the road to the tower. Data taken when the wind was from the direction of the road may be suspect because of the removal of trees to create the path.

7. Data Description

7.1 Spatial Characteristics

7.1.1 Spatial Coverage

Samples were collected only from the tower at each site. Each sample may be considered as an ambient sample whose spatial coverage could be determined by back-trajectory analysis for the 30-minute sampling period. The North American Datum of 1983 (NAD83) coordinates of the measurement sites are:

SSA-OBS: 53.98717N, 105.11779W

SSA-OJP: 53.91634N, 104.69203W

SSA-OA: 53.62889N, 106.19779W

7.1.2 Spatial Coverage Map

Not available.

7.1.3 Spatial Resolution

The resolution, for gradient calculations, is no better than the footprint of forest considered in flux measurements. As ambient measurements, the spatial resolution is subject to the meteorological conditions at the time the measurements were made.

7.1.4 Projection

Not applicable.

7.1.5 Grid Description

Not applicable.

7.2 Temporal Characteristics

7.2.1 Temporal Coverage

Samples were collected at the three SSA tower flux sites during the IFCs from 27-May to 15-Sep-1994.

7.2.2 Temporal Coverage Map

Note: Sample refers to a pair of upper- and lower-level samples.

SSA-OJP 27-May-1994, 4 samples

SSA-OJP 07-Jun to 12-Jun-1994, 33 samples

SSA-OJP 27-Jul to 02-Aug-1994, 30 samples

SSA-OJP 09-Sep to 11-Sep-1994, 8 samples

SSA-OJP 15-Sep-1994, 4 samples

SSA-OBS 31-May to 05-Jun-1994, 25 samples
SSA-OBS 20-Jul to 24-Jul-1994, 32 samples
SSA-OBS 01-Sep to 07-Sep-1994, 32 samples

SSA-OA 04-Aug to 08-Aug-1994, 20 samples
SSA-OA 12-Sep to 14-Sep-1994, 21 samples

7.2.3 Temporal Resolution

On the dates listed in Section 7.2.2., samples were typically collected at 1-hour intervals, usually from late morning to evening. On several occasions, samples were collected over a 24-hour period, when there was no precipitation.

7.3 Data Characteristics

7.3.1 Parameter/Variable

The parameters contained in the data files on the CD-ROM are:

```
Column Name
-----
SITE_NAME
SUB_SITE
DATE_OBS
TIME_OBS
CANISTER_NUM
HT_AGL
ISOPRENE_CONC
QA_CODE
ETHANE_MIX_RATIO
PROPANE_MIX_RATIO
N-BUTANE_MIX_RATIO
ISOBUTANE_MIX_RATIO
N-PENTANE_MIX_RATIO
ISOPENTANE_MIX_RATIO
N-HEXANE_MIX_RATIO
2-METHYL-PENTANE_MIX_RATIO
3-METHYL-PENTANE_MIX_RATIO
N-HEPTANE_MIX_RATIO
METHYL-CYCLOHEXANE_MIX_RATIO
ACETYLENE_MIX_RATIO
ETHENE_MIX_RATIO
PROPENE_MIX_RATIO
1-BUTENE_MIX_RATIO
ISOBUTENE_MIX_RATIO
1-PENTENE_MIX_RATIO
1,3-BUTADIENE_MIX_RATIO
ISOPRENE_MIX_RATIO
ALPHA-PINENE_MIX_RATIO
BETA-PINENE_MIX_RATIO
CAMPHENE_MIX_RATIO
3-CARENE_MIX_RATIO
PARACYMENE_MIX_RATIO
D-LIMONENE_MIX_RATIO
BENZENE_MIX_RATIO
TOLUENE_MIX_RATIO
```

FILE_NUM
 REVISION_DATE
 CRTFCN_CODE

7.3.2 Variable Description/Definition

The descriptions of the parameters contained in the data files on the CD-ROM are:

Column Name	Description
SITE_NAME	The identifier assigned to the site by BOREAS, in the format SSS-TTT-CCCC, where SSS identifies the portion of the study area: NSA, SSA, REG, TRN, and TTT identifies the cover type for the site, 999 if unknown, and CCCC is the identifier for site, exactly what it means will vary with site type.
SUB_SITE	The identifier assigned to the sub-site by BOREAS, in the format GGGGG-IIIII, where GGGGG is the group associated with the sub-site instrument, e.g. HYD06 or STAFF, and IIIII is the identifier for sub-site, often this will refer to an instrument.
DATE_OBS	The date on which the data were collected.
TIME_OBS	The Greenwich Mean Time (GMT) when the data were collected.
CANISTER_NUM	Sampling canister number for isoprene data.
HT_AGL	The height above ground at which the measurements were taken.
ISOPRENE_CONC	The ambient concentration of isoprene
QA_CODE	Quality assurance code 1=good, 2=missing, 3=value outside expected range, 4=unexpected reverse gradient.
ETHANE_MIX_RATIO	The ethane mixing ratio in the air sample.
PROPANE_MIX_RATIO	The propane mixing ratio in the air sample.
N-BUTANE_MIX_RATIO	The n-butane mixing ratio in the air sample.
ISOBUTANE_MIX_RATIO	The isobutane mixing ratio in the air sample.
N-PENTANE_MIX_RATIO	The n-pentane mixing ratio in the air sample.
ISOPENTANE_MIX_RATIO	The isopentane mixing ratio in the air sample.
N-HEXANE_MIX_RATIO	The n-hexane mixing ratio in the air sample.
2-METHYL-PENTANE_MIX_RATIO	The 2-methyl-pentane mixing ratio in the air sample.
3-METHYL-PENTANE_MIX_RATIO	The 3-methyl-pentane mixing ratio in the air sample.
N-HEPTANE_MIX_RATIO	The n-heptane mixing ratio in the air sample.
METHYL-CYCLOHEXANE_MIX_RATIO	The methyl-cyclohexane mixing ratio in the air sample.
ACETYLENE_MIX_RATIO	The acetylene mixing ratio in the air sample.
ETHENE_MIX_RATIO	The ethene mixing ratio in the air sample.
PROPENE_MIX_RATIO	The propene mixing ratio in the air sample.
1-BUTENE_MIX_RATIO	The 1-butene mixing ratio in the air sample.
ISOBUTENE_MIX_RATIO	The isobutene mixing ratio in the air sample.
1-PENTENE_MIX_RATIO	The 1-pentene mixing ratio in the air sample.
1,3-BUTADIENE_MIX_RATIO	The 1,3-butadiene mixing ratio in the air sample.
ISOPRENE_MIX_RATIO	The isoprene mixing ratio in the air sample.

ALPHA-PINENE_MIX_RATIO	The alpha-pinene mixing ratio in the air sample.
BETA-PINENE_MIX_RATIO	The beta-pinene mixing ratio in the air sample.
CAMPHENE_MIX_RATIO	The camphene mixing ratio in the air sample.
3-CARENE_MIX_RATIO	The 3-carene mixing ratio in the air sample.
PARACYMENE_MIX_RATIO	The paracymene mixing ratio in the air sample.
D-LIMONENE_MIX_RATIO	The d-limonene mixing ratio in the air sample.
BENZENE_MIX_RATIO	The benzene mixing ratio in the air sample.
TOLUENE_MIX_RATIO	The toluene mixing ratio in the air sample.
FILE_NUM	The file number for the raw data in teams archives.
REVISION_DATE	The most recent date when the information in the referenced data base table record was revised.
CRTFCN_CODE	The BOREAS certification level of the data. Examples are CPI (Checked by PI), CGR (Certified by Group), PRE (Preliminary), and CPI-??? (CPI but questionable).

7.3.3 Unit of Measurement

The measurement units for the parameters contained in the data files on the CD-ROM are:

Column Name	Units
SITE_NAME	[none]
SUB_SITE	[none]
DATE_OBS	[DD-MON-YY]
TIME_OBS	[HHMM GMT]
CANISTER_NUM	[none]
HT_AGL	[meters]
ISOPRENE_CONC	[parts per billion Carbon]
QA_CODE	[unitless]
ETHANE_MIX_RATIO	[unitless]
PROPANE_MIX_RATIO	[unitless]
N-BUTANE_MIX_RATIO	[unitless]
ISOBUTANE_MIX_RATIO	[unitless]
N-PENTANE_MIX_RATIO	[unitless]
ISOPENTANE_MIX_RATIO	[unitless]
N-HEXANE_MIX_RATIO	[unitless]
2-METHYL-PENTANE_MIX_RATIO	[unitless]
3-METHYL-PENTANE_MIX_RATIO	[unitless]
N-HEPTANE_MIX_RATIO	[unitless]
METHYL-CYCLOHEXANE_MIX_RATIO	[unitless]
ACETYLENE_MIX_RATIO	[unitless]
ETHENE_MIX_RATIO	[unitless]
PROPENE_MIX_RATIO	[unitless]
1-BUTENE_MIX_RATIO	[unitless]
ISOBUTENE_MIX_RATIO	[unitless]
1-PENTENE_MIX_RATIO	[unitless]
1,3-BUTADIENE_MIX_RATIO	[unitless]
ISOPRENE_MIX_RATIO	[unitless]
ALPHA-PINENE_MIX_RATIO	[unitless]
BETA-PINENE_MIX_RATIO	[unitless]
CAMPHENE_MIX_RATIO	[unitless]
3-CARENE_MIX_RATIO	[unitless]
PARACYMENE_MIX_RATIO	[unitless]

D-LIMONENE_MIX_RATIO	[unitless]
BENZENE_MIX_RATIO	[unitless]
TOLUENE_MIX_RATIO	[unitless]
FILE_NUM	[unitless]
REVISION_DATE	[DD-MON-YY]
CRTFCN_CODE	[none]

7.3.4 Data Source

The sources of the parameter values contained in the data files on the CD-ROM are:

Column Name	Date Source
SITE_NAME	Assigned by BORIS
SUB_SITE	Assigned by BORIS
DATE_OBS	Investigator
TIME_OBS	Investigator
CANISTER_NUM	Investigator
HT_AGL	Investigator
ISOPRENE_CONC	GC-FID
QA_CODE	Investigator
ETHANE_MIX_RATIO	GC-FID
PROPANE_MIX_RATIO	GC-FID
N-BUTANE_MIX_RATIO	GC-FID
ISOBUTANE_MIX_RATIO	GC-FID
N-PENTANE_MIX_RATIO	GC-FID
ISOPENTANE_MIX_RATIO	GC-FID
N-HEXANE_MIX_RATIO	GC-FID
2-METHYL-PENTANE_MIX_RATIO	GC-FID
3-METHYL-PENTANE_MIX_RATIO	GC-FID
N-HEPTANE_MIX_RATIO	GC-FID
METHYL-CYCLOHEXANE_MIX_RATIO	GC-FID
ACETYLENE_MIX_RATIO	GC-FID
ETHENE_MIX_RATIO	GC-FID
PROPENE_MIX_RATIO	GC-FID
1-BUTENE_MIX_RATIO	GC-FID
ISOBUTENE_MIX_RATIO	GC-FID
1-PENTENE_MIX_RATIO	GC-FID
1,3-BUTADIENE_MIX_RATIO	GC-FID
ISOPRENE_MIX_RATIO	GC-FID
ALPHA-PINENE_MIX_RATIO	GC-FID
BETA-PINENE_MIX_RATIO	GC-FID
CAMPHENE_MIX_RATIO	GC-FID
3-CARENE_MIX_RATIO	GC-FID
PARACYMENE_MIX_RATIO	GC-FID
D-LIMONENE_MIX_RATIO	GC-FID
BENZENE_MIX_RATIO	GC-FID
TOLUENE_MIX_RATIO	GC-FID
FILE_NUM	Investigator
REVISION_DATE	Assigned by BORIS
CRTFCN_CODE	Assigned by BORIS

7.3.5 Data Range

The following table gives information about the parameter values found in the data files on the CD-ROM.

Column Name	Minimum Data Value	Maximum Data Value	Missng Data Value	Unrel Data Value	Below Detect Limit	Data Not Clcltd
SITE_NAME	SSA-90A-FLXTR	SSA-OJP-FLXTR	None	None	None	None
SUB_SITE	TGB09-CON01	TGB09-MIX01	None	None	None	None
DATE_OBS	27-MAY-94	15-SEP-94	None	None	None	None
TIME_OBS	0	2305	None	None	None	None
CANISTER_NUM	-999	Y525	-999	None	None	Blank
HT_AGL	12	38	None	None	None	None
ISOPRENE_CONC	.001	9.72	-999	None	None	Blank
QA_CODE	1	4	None	None	None	Blank
ETHANE_MIX_RATIO	1.365	4.81	None	None	None	Blank
PROPANE_MIX_RATIO	.23	3.609	None	None	None	Blank
N-BUTANE_MIX_RATIO	.054	15.09	None	None	None	Blank
ISOBUTANE_MIX_RATIO	.022	9.654	None	None	None	Blank
N-PENTANE_MIX_RATIO	.021	2.898	None	None	None	Blank
ISOPENTANE_MIX_RATIO	.018	11.312	None	None	None	Blank
N-HEXANE_MIX_RATIO	.002	.586	None	None	None	Blank
2-METHYL-PENTANE_MIX_RATIO	.002	.911	None	None	None	Blank
3-METHYL-PENTANE_MIX_RATIO	.002	.527	None	None	None	Blank
N-HEPTANE_MIX_RATIO	.002	.149	None	None	None	Blank
METHYL-CYCLOHEXANE_MIX_RATIO	.002	.18	None	None	None	Blank
ACETYLENE_MIX_RATIO	.173	1.515	None	None	None	Blank
ETHENE_MIX_RATIO	.068	1.593	None	None	None	Blank
PROPENE_MIX_RATIO	.02	6.644	None	None	None	Blank
1-BUTENE_MIX_RATIO	.002	.199	None	None	None	Blank
ISOBUTENE_MIX_RATIO	.016	.254	None	None	None	Blank
1-PENTENE_MIX_RATIO	.002	.16	None	None	None	Blank
1,3-BUTADIENE_MIX_RATIO	.002	.041	None	None	None	Blank
ISOPRENE_MIX_RATIO	.079	1.304	None	None	None	Blank
ALPHA-PINENE_MIX_RATIO	.002	.494	None	None	None	Blank
BETA-PINENE_MIX_RATIO	.002	.165	None	None	None	Blank
CAMPHENE_MIX_RATIO	.002	.499	None	None	None	Blank
3-CARENE_MIX_RATIO	.002	.099	None	None	None	Blank
PARACYMENE_MIX_RATIO	.002	.044	None	None	None	Blank
D-LIMONENE_MIX_RATIO	.002	.123	None	None	None	Blank
BENZENE_MIX_RATIO	.044	.557	None	None	None	Blank
TOLUENE_MIX_RATIO	.022	1.456	None	None	None	Blank
FILE_NUM	-999	379	-999	None	None	Blank
REVISION_DATE	24-FEB-95	05-NOV-96	None	None	None	None

CRTFCN_CODE	CPI	CPI	None	None	None	None

Minimum Data Value	--	The minimum value found in the column.				
Maximum Data Value	--	The maximum value found in the column.				
Missng Data Value	--	The value that indicates missing data. This is used to indicate that an attempt was made to determine the parameter value, but the attempt was unsuccessful.				
Unrel Data Value	--	The value that indicates unreliable data. This is used to indicate an attempt was made to determine the parameter value, but the value was deemed to be unreliable by the analysis personnel.				
Below Detect Limit	--	The value that indicates parameter values below the instruments detection limits. This is used to indicate that an attempt was made to determine the parameter value, but the analysis personnel determined that the parameter value was below the detection limit of the instrumentation.				
Data Not Cllctd	--	This value indicates that no attempt was made to determine the parameter value. This usually indicates that BORIS combined several similar but not identical data sets into the same data base table but this particular science team did not measure that parameter.				
Blank	--	Indicates that blank spaces are used to denote that type of value.				
N/A	--	Indicates that the value is not applicable to the respective column.				
None	--	Indicates that no values of that sort were found in the column.				

7.4 Sample Data Record

The following are wrapped versions of data record from a sample data file on the CD-ROM.

```

SITE_NAME,SUB_SITE,DATE_OBS,TIME_OBS,CANISTER_NUM,HT_AGL,ISOPRENE_CONC,QA_CODE,
ETHANE_MIX_RATIO,PROPANE_MIX_RATIO,N-BUTANE_MIX_RATIO,ISOBUTANE_MIX_RATIO,
N-PENTANE_MIX_RATIO,ISOPENTANE_MIX_RATIO,N-HEXANE_MIX_RATIO,
2-METHYL-PENTANE_MIX_RATIO,3-METHYL-PENTANE_MIX_RATIO,N-HEPTANE_MIX_RATIO,
METHYL-CYCLOHEXANE_MIX_RATIO,ACETYLENE_MIX_RATIO,ETHENE_MIX_RATIO,
PROPENE_MIX_RATIO,1-BUTENE_MIX_RATIO,ISOBUTENE_MIX_RATIO,1-PENTENE_MIX_RATIO,
1,3-BUTADIENE_MIX_RATIO,ISOPRENE_MIX_RATIO,ALPHA-PINENE_MIX_RATIO,
BETA-PINENE_MIX_RATIO,CAMPHENE_MIX_RATIO,3-CARENE_MIX_RATIO,
PARACYMENE_MIX_RATIO,D-LIMONENE_MIX_RATIO,BENZENE_MIX_RATIO,TOLUENE_MIX_RATIO,
FILE_NUM,REVISION_DATE,CRTFCN_CODE
'SSA-90A-FLXTR','TGB09-CON01',04-AUG-94,1003,'Y066',27.0,3.216,1,,,,,,,,,,,,,
,,,,,,,,,,'140',05-NOV-96,'CPI'
'SSA-90A-FLXTR','TGB09-CON01',04-AUG-94,1003,'Y042',38.0,2.644,1,,,,,,,,,,,,,
,,,,,,,,,,'139',05-NOV-96,'CPI'

```

8. Data Organization

8.1 Data Granularity

The smallest unit of data tracked by the BOREAS Information System (BORIS) was the data containing NMHC and isoprene concentrations measured on a particular date at a particular site.

8.2 Data Format(s)

The Compact Disk-Read-Only Memory (CD-ROM) files contain American Standard Code for Information Interchange (ASCII) numerical and character fields of varying length separated by commas. The character fields are enclosed with single apostrophe marks. There are no spaces between the fields.

Each data file on the CD-ROM has four header lines of Hyper-Text Markup Language (HTML) code at the top. When viewed with a Web browser, this code displays header information (data set title, location, date, acknowledgments, etc.) and a series of HTML links to associated data files and related data sets. Line 5 of each data file is a list of the column names, and line 6 and following lines contain the actual data.

9. Data Manipulations

9.1 Formulae

$$[\text{Sample}] = ((\text{sample pk area}) \times (\text{Response Factor}) / (\text{sample vol}))$$

where: [Sample] is the mixing ratio of the NMHC of interest in the sample.

(sample pk area) is the area in area counts of the chromatogram peak that corresponds to NMHC of interest in the sample.

Response Factor is the FID response in area counts per ppbv of the NMHC of interest per cc of sample.

(sample vol) is the volume of sample analyzed in cc.

9.1.1 Derivation Techniques and Algorithms

Calculations were performed by HP PC-ChemStation software.

9.2 Data Processing Sequence

9.2.1 Processing Steps

- HP PC-ChemStation integrates each peak in chromatogram.
- Operator verifies that software chose reasonable baseline and limits for peaks and manually sets baseline and limits if necessary.
- Peaks are identified by comparison to retention times found using standard mixtures.
- Operator transfers area count data to spreadsheet program for concentration calculations.

9.2.2 Processing Changes

None.

9.3 Calculations

Peak areas were converted to concentrations (mixing ratios) by formula in Section 9.1.

9.3.1 Special Corrections/Adjustments

Data Below Detection Limit: When the NMHC of interest is not detected by the GC-FID system, it is assigned a concentration of 0.002 ppbv, which is approximately the average between the detection limit of 0.005 ppbv and 0.000 ppbv.

Conversion to Greenwich Mean Time (GMT): Time at start of sampling was originally noted in local Saskatchewan time. This was converted to GMT by adding 6 hours.

9.3.2 Calculated Variables

None.

9.4 Graphs and Plots

None.

10. Errors

10.1 Sources of Error

The user is advised to check meteorological data carefully before using these data to calculate fluxes by the gradient method and to know the limitations of this method. Because compound identification is based on retention time, it is possible to misidentify a compound that is present in a real sample but not present in the calibration standard. The temperature programs have been adjusted to achieve good separation for the compounds in the calibration standards, but additional species present in real samples may co-elute. This is unlikely to cause problems for the C2-C6 data, because the calibration standard for light hydrocarbons is comprehensive, but there may be interferences in the C5-C10 data.

10.2 Quality Assessment

Laboratory analysis of the air samples was conducted, and the samples were examined for outliers. When an outlier was spotted, the original chromatogram was checked for correct integration and quantification.

10.2.1 Data Validation by Source

Time series plots for each hydrocarbon and hydrocarbon distribution plots were analyzed. Samples were collected in evacuated stainless steel canisters and shipped to the laboratory in Toronto, ON, for analysis by GC-FID. Concentrations in the pptv-ppbv range are reported for a variety of biogenic and anthropogenic NMCs. The measurements are sufficiently precise for use in calculating fluxes by the gradient method. They are also valuable as a record of the ambient trace gas concentrations present in the region.

10.2.2 Confidence Level/Accuracy Judgment

The investigators are quite confident in the C2-C10 data. Compound identification is made primarily by retention time only. This may lead to improper identifications, particularly for the larger hydrocarbons, such as C10. Users are cautioned that although the identifications are likely correct, they are not guaranteed.

10.2.3 Measurement Error for Parameters

Absolute concentrations are considered accurate within 20%, limited primarily by the uncertainty in the concentrations in the calibration standards. Uncertainty in gradients calculated from these concentrations is determined by the precision of the analysis, which is quoted in Section 4.2.1.1.

10.2.4 Additional Quality Assessments

As data from other investigators become available, these results will be compared with theirs and the data and documentation updated as necessary.

10.2.5 Data Verification by Data Center

Data were examined for general consistency and clarity.

11. Notes

11.1 Limitations of the Data

None given.

11.2 Known Problems with the Data

Three samples in this data set contain unusually high levels of anthropogenic hydrocarbons:

12.4 m 02-Jun-1994 13:25

12.4 m 02-Jun-1994 14:35

23.3 m 04-Jun-1994 12:00

This is not a problem with the GC analysis; values from the two GC-FID systems for C6 hydrocarbons agree well. The high concentrations of light hydrocarbons such as ethane and propane indicate that contamination of the canisters is not a factor; these species are removed very effectively by the cleaning procedure. In fact, 23.3 m 04-Jun-1994 12:00 was collected in a new canister purchased for this project. The investigators suggest referring to other measurements of trace gas concentrations at these times to determine whether a significant, transient, local anthropogenic source existed.

11.3 Usage Guidance

Not all species identified are included in this data set. Researchers interested in specific compounds should contact the investigators directly for further information about the data.

11.4 Other Relevant Information

None given.

12. Application of the Data Set

These data are intended for use in the study of atmosphere-biosphere interactions, and the atmospheric chemistry of biogenic and anthropogenic hydrocarbons. The data have been used in conjunction with other data collected at the sites by other researchers for the calculation of biogenic hydrocarbon emissions from the various sites.

13. Future Modifications and Plans

None given.

14. Software

14.1 Software Description

HP 5970 GC-MS Workstation v. 3.2 software HP PC-ChemStation v. 1.01 software

14.2 Software Access

Not applicable.

15. Data Access

The TGB-09 above-canopy NMHC data are available from the Earth Observing System Data and Information System (EOSDIS) Oak Ridge National Laboratory (ORNL) Distributed Active Archive Center (DAAC).

15.1 Contact Information

For BOREAS data and documentation please contact:

ORNL DAAC User Services
Oak Ridge National Laboratory
P.O. Box 2008 MS-6407
Oak Ridge, TN 37831-6407
Phone: (423) 241-3952
Fax: (423) 574-4665
E-mail: ornldaac@ornl.gov or ornl@eos.nasa.gov

15.2 Data Center Identification

Earth Observing System Data and Information System (EOSDIS) Oak Ridge National Laboratory (ORNL) Distributed Active Archive Center (DAAC) for Biogeochemical Dynamics
<http://www-eosdis.ornl.gov/>.

15.3 Procedures for Obtaining Data

Users may obtain data directly through the ORNL DAAC online search and order system [<http://www-eosdis.ornl.gov/>] and the anonymous FTP site [<ftp://www-eosdis.ornl.gov/data/>] or by contacting User Services by electronic mail, telephone, fax, letter, or personal visit using the contact information in Section 15.1.

15.4 Data Center Status/Plans

The ORNL DAAC is the primary source for BOREAS field measurement, image, GIS, and hardcopy data products. The BOREAS CD-ROM and data referenced or listed in inventories on the CD-ROM are available from the ORNL DAAC.

16. Output Products and Availability

16.1 Tape Products

None.

16.2 Film Products

None.

16.3 Other Products

These data are available on the BOREAS CD-ROM series.

17. References

17.1 Platform/Sensor/Instrument/Data Processing Documentation

Sample analysis is performed by standard chromatographic techniques. No knowledge specific to the GC-FIDs used is required in order to assess or interpret the data. Any analytical instrumentation text should give the user sufficient information about GC-FID.

17.2 Journal Articles and Study Reports

A comprehensive review of sample analysis and data analysis in the laboratory may be found in the Ph.D. dissertation of Byron Kieser and the Ph.D. dissertation of Bertram Thomas Jobson:

Kieser, B. 1997. Measurements of Biogenic Hydrocarbon Emissions from the Boreal Forest. Department of Chemistry, York University.

Jobson, B.T. 1994. Seasonal Trends of Non methane Hydrocarbons at a Remote Boreal and High Arctic Site in Canada Department of Chemistry York University.

Newcomer, J., D. Landis, S. Conrad, S. Curd, K. Huemmrich, D. Knapp, A. Morrell, J. Nickeson, A. Papagno, D. Rinker, R. Strub, T. Twine, F. Hall, and P. Sellers, eds. 2000. Collected Data of The Boreal Ecosystem-Atmosphere Study. NASA. CD-ROM.

Sellers, P. and F. Hall. 1994. Boreal Ecosystem-Atmosphere Study: Experiment Plan. Version 1994-3.0, NASA BOREAS Report (EXPLAN 94).

Sellers, P. and F. Hall. 1996. Boreal Ecosystem-Atmosphere Study: Experiment Plan. Version 1996-2.0, NASA BOREAS Report (EXPLAN 96).

Sellers, P., F. Hall, and K.F. Huemmrich. 1996. Boreal Ecosystem-Atmosphere Study: 1994 Operations. NASA BOREAS Report (OPS DOC 94).

Sellers, P., F. Hall, and K.F. Huemmrich. 1997. Boreal Ecosystem-Atmosphere Study: 1996 Operations. NASA BOREAS Report (OPS DOC 96).

Sellers, P., F. Hall, H. Margolis, B. Kelly, D. Baldocchi, G. den Hartog, J. Cihlar, M.G. Ryan, B. Goodison, P. Crill, K.J. Ranson, D. Lettenmaier, and D.E. Wickland. 1995. The boreal ecosystem-atmosphere study (BOREAS): an overview and early results from the 1994 field year. Bulletin of the American Meteorological Society. 76(9):1549-1577.

Sellers, P.J., F.G. Hall, R.D. Kelly, A. Black, D. Baldocchi, J. Berry, M. Ryan, K.J. Ranson, P.M. Crill, D.P. Lettenmaier, H. Margolis, J. Cihlar, J. Newcomer, D. Fitzjarrald, P.G. Jarvis, S.T. Gower, D. Halliwell, D. Williams, B. Goodison, D.E. Wickland, and F.E. Guertin. 1997. BOREAS in 1997: Experiment Overview, Scientific Results and Future Directions. Journal of Geophysical Research 102(D24): 28,731-28,770.

17.3 Archive/DBMS Usage Documentation

None.

18. Glossary of Terms

None.

19. List of Acronyms

ASCII	- American Standard Code for Information Interchange
BOREAS	- BOReal Ecosystem-Atmosphere Study
BORIS	- BOREAS Information System
CD-ROM	- Compact Disk-Read-Only Memory
DAAC	- Distributed Active Archive Center
EOS	- Earth Observing System
EOSDIS	- EOS Data and Information System
FID	- Flame Ionization Detector
GC	- Gas Chromatograph(y)
GIS	- Geographic Information System
GMT	- Greenwich Mean Time
GSFC	- Goddard Space Flight Center
HP	- Hewlett Packard
HTML	- HyperText Markup Language
IFC	- Intensive Field Campaign
MSD	- Mass Selective Detector
NAD83	- North American Datum of 1983
NASA	- National Aeronautics and Space Administration
NMHC	- Nonmethane Hydrocarbons
NSA	- Northern Study Area
OA	- Old Aspen
OBS	- Old Black Spruce
OJP	- Old Jack Pine
ORNL	- Oak Ridge National Laboratory
PANP	- Prince Albert National Park
ppbv	- Parts Per Billion by Volume
pptv	- Parts Per Trillion by Volume
psi	- Pounds Per Square Inch
SSA	- Southern Study Area
TGB	- Trace Gas Biogeochemistry
URL	- Uniform Resource Locator

20. Document Information

20.1 Document Revision Date

Written: 22-Nov-1994

Last updated: 30-Jul-1999

20.2 Document Review Date(s)

BORIS Review: 02-Jul-1998

Science Review:

20.3 Document ID

20.4 Citation

When using these data, please contact Byron Kieser (see Section 2.3) and cite any relevant papers in Section 17.2.

If using data from the BOREAS CD-ROM series, also reference the data as:

Niki, H., "Ambient Measurements of Nonmethane Hydrocarbons." In Collected Data of The Boreal Ecosystem-Atmosphere Study. Eds. J. Newcomer, D. Landis, S. Conrad, S. Curd, K. Huemmrich, D. Knapp, A. Morrell, J. Nickeson, A. Papagno, D. Rinker, R. Strub, T. Twine, F. Hall, and P. Sellers. CD-ROM. NASA, 2000.

Also, cite the BOREAS CD-ROM set as:

Newcomer, J., D. Landis, S. Conrad, S. Curd, K. Huemmrich, D. Knapp, A. Morrell, J. Nickeson, A. Papagno, D. Rinker, R. Strub, T. Twine, F. Hall, and P. Sellers, eds. Collected Data of The Boreal Ecosystem-Atmosphere Study. NASA. CD-ROM. NASA, 2000.

20.5 Document Curator

20.6 Document URL

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6. AUTHOR(S) B.N. Keiser, V.L. Young, and H. Niki Forrest G. Hall and Sara K. Conrad, Editors				
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