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

Forrest G. Hall and Sara K. Conrad, Editors

Volume 242

BOREAS TGB-10 Oxidant Flux Data over the SSA

H. Westberg, B. Hall, and A.V. Jackson

National Aeronautics and
Space Administration

Goddard Space Flight Center
Greenbelt, Maryland 20771

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BOREAS TGB-10 Oxidant Flux Data over the SSA

Hal Westberg, Brad Hall, Andrea V. Jackson

Summary

The BOREAS TGB-10 team collected several trace gas data sets in its efforts to determine the role of biogenic hydrocarbon emissions with respect to boreal forest carbon cycles. This oxidant data set contains measured peroxide (H_2O_2 and total organic peroxides (ROOH)) and ozone concentrations as well as H_2O_2 and ROOH deposition velocities. These data were obtained at the SSA-OJP site during the summer of 1994. Measurements were made from May to September 1994. The data are stored in tabular ASCII files.

Some important results were:

- Ozone concentrations were consistently low, 20-30 ppb, during the summer of 1994.
- Peroxide concentrations showed a seasonal variation with highest concentrations occurring in July (IFC-2).
- Midday H_2O_2 levels averaged around 1.4 ppb during IFC-2 and 0.4-0.5 ppb during IFC's 1 and 3.
- Midday organic peroxide concentrations were lower, averaging 0.8 ppb during IFC-2, and 0.4-0.5 ppb during IFC's 1 and 3.
- The rough pine forest canopy serves as a significant sink for H_2O_2.
- Midday H_2O_2 deposition velocities averaged 4-7 cm/s.
- Organic peroxide deposition velocities (measured as total ROOH) were approximately 40% as large as those of H_2O_2.

Table of Contents

1. Data Set Overview

1.1 Data Set Identification

BOREAS TGB-10 Oxidant Flux Data over the SSA

1.2 Data Set Introduction

The BOReal Ecosystem-Atmosphere Study (BOREAS) Trace Gas Biogeochemistry (TGB)-10 team collected oxidant flux data at the Southern Study Area (SSA) Old Jack Pine (OJP) site during the growing season of 1994. Ambient hydrogen peroxide and organic peroxides concentrations were determined by high performance liquid chromatography (HPLC) with fluorometric detection. Formaldehyde monitoring was performed based on the reaction of formaldehyde with dinitrophenylhydrazine (DNPH).

1.3 Objective/Purpose

Emission/deposition rates of biogenic hydrocarbons (or volatile organic carbon (VOC)) and oxidants (hydrogen peroxide and ozone) were measured along with ambient concentrations of biogenic hydrocarbons, hydrogen peroxide, and organic hydroperoxides. We will use these data to examine (a) the role of biogenic hydrocarbon emissions with respect to carbon cycles in the boreal forest, (b) the chemical fate of boreal biogenic emissions, (c) the hypothesis that biospheric VOC emissions contribute to peroxide formation, and (d) the deposition rates of hydrogen peroxide and organic peroxides.

1.4 Summary of Parameters

Investigations of tropospheric concentration gradients of hydrogen peroxide and organic hydroperoxides in a boreal forest.

1.5 Discussion

None given.

1.6 Related Data Sets

BOREAS TGB-08 Monoterpene Concentration Data over the SSA
BOREAS TGB-08 Photosynthesis Data over the SSA
BOREAS TGB-08 Starch Data over the SSA
BOREAS TGB-09 Above Canopy Non-Methane Hydrocarbon Data over the SSA
BOREAS TGB-10 Oxidant Concentration Data over the SSA
BOREAS TGB-10 Volatile Organic Carbon Data over the SSA

2. Investigator(s)

2.1 Investigator(s) Name and Title

Dr. Hal Westberg
Washington State University

Dr. Nick Hewitt
Lancaster University

2.2 Title of Investigation

Measurement of Biogenic Hydrocarbon Fluxes

2.3 Contact Information

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3. Theory of Measurements

The deposition velocity (Vd) of hydrogen peroxide is found from the eddy exchange coefficient and the normalized gradient.

$$Vd = K*(dC/dz)/C \text{ (m/s)}$$

where concentration is measured in ppbV.

Relaxed Eddy Accumulation (REA) Method Canopy-scale fluxes of biogenic hydrocarbons were determined by the REA method at the Old Black Spruce (OBS) site. These measurements were carried out in cooperation with Dr. Elizabeth Pattey (BOREAS Tower Flux (TF)-07 team). In this method, air is sampled at a constant rate and partitioned into one of two containers, contingent upon whether the vertical velocity component was positive (upward) or negative (downward). The flux is computed from the following expression:

$$F = b*sw*(C2 - C1) \ (gC/m^2/s)$$

where b (dimensionless) is a weak function of stability (determined by eddy correlation measurements of heat, water vapor, or CO_2 flux), sw (m/s) is the standard deviation of vertical wind speed, and C2 and C1 (g C/m^3) are the concentrations in the "upward" and "downward" containers, respectively. For a more complete description of the REA method, one should consult the TF-07 documentation.

Hydrogen Peroxide and Organic Peroxide Measurements Ambient hydrogen peroxide and organic peroxides concentrations were determined by HPLC with fluorometric detection. The detection method is similar to that described in the previous section.

Formaldehyde Monitoring The reaction of formaldehyde with DNPH was the basis for the measurement procedure used during this study.

4. Equipment

4.1 Sensor/Instrument Description

Hydrogen peroxide was measured by the dual-channel, enzyme-catalyzed, fluorometric method. The instrument was constructed at Washington State University (WSU), following the procedure outlined by K&K Instruments; Boulder, Colorado (Lazrus et al., 1986). Ozone was measured with a Dasibi 1003-AH ozone sensor.

4.1.1 Collection Environment

Tower-based measurements were conducted under ambient atmospheric conditions.

4.1.2 Source/Platform

All peroxide and ozone measurements were made from ground- and tower-mounted systems.

4.1.3 Source/Platform Mission Objectives

The objective of these experiments was to obtain canopy-scale fluxes of peroxides and branch-scale fluxes of biogenic VOCs in a boreal environment.

4.1.4 Key Variables

Emissions and/or ambient concentrations of the following trace gases were measured:

- isoprene
- alpha-pinene
- beta-pinene
- limonene
- monoterpenes
- hydrogen peroxide
- methylhydroperoxide
- hydroxymethlyhydroperoxide
- ozone

4.1.5 Principles of Operation

See Section 3.

4.1.6 Sensor/Instrument Measurement Geometry

Enclosure Sampling The instruments used for enclosure sampling were mounted on a battery-powered portable cart. The bag enclosure was mounted on a tripod base, allowing access to branches 1-3 meters from the ground.

Gradient Sampling Inlets were located on beams protruding 1 m off the west sides of the TF towers. With winds predominately from the south, west, or north, the samples usually contained unperturbed air. The inlet heights (above the forest floor) are summarized below.

```
OJP   16.5 m and 23.8 m Intensive Field Campaign (IFC)-1, IFC-2
OJP   17.2 m and 23.8 m IFC-3
```

The lower inlet at the OJP site was raised prior to IFC-3 to alleviate possible influences of the roughness sublayer.

4.1.7 Manufacturer of Sensor/Instrument

HP5890 gas chromatograph:
Hewlett Packard
15815 SE 37th St.
Bellevue, WA 98006

Dasibi 1003-AH ozone analyzer:
Dasibi Environmental
616 E. Colorado St.
Glendale, CA 91205

HP-3396A integrator:
Hewlett Packard
15815 SE 37th St.
Bellevue, WA 98006

The hydrogen peroxide system was custom-built at WSU:
WSU Technical Services
Washington State University
Pullman, WA 99164-2801

HPLC system:
Merck Ltd.
Merck House
Poole, Dorset
BH15 1TD, England

Data handling systems:
Labtech
400 Research Dr.
Wilmington, MA 01887

VG Data Systems
St. Georges Court
Hanover Business Park
Altrincham, Cheshire
WA14 5UG England

4.2 Calibration

Formaldehyde High-purity formaldehyde-hydrazone was prepared by conventional methods for use as a master standard. The master standard was diluted to concentrations of 0.2, 0.5, 1.0, 2.0, and 5.0 ppm to establish calibration curves.

Sensors for the peripheral environmental measurements were calibrated at WSU prior to the field sampling program. Mass flow meters were tested against a precision wet-test meter at several flow rates. The thermocouples and amplifiers were calibrated against a National Institute for Standards and Technology (NIST) traceable mercury thermometer by measuring the response with all sensors immersed in a stirred ice-water bath slowly warmed to approximately 45 °C. The humidity sensor was compared to calculated values for air passed through a temperature-controlled water bath. All of the sensor calibrations were performed using the PC laptop data system employed in the field.

Hydrogen peroxide The continuous hydroperoxide system was calibrated twice daily with liquid standards of hydrogen peroxide in deionized water. The standards were prepared at the 10-8 M level by serial dilution of a 30% H_2O_2 reagent (Fisher). The concentration of the primary reagent was determined by titration against KMnO4, which was then titrated against a NIST-traceable sodium oxalate solution.

Line losses through the PFA Teflon tubing were measured before and after each IFC. A gas-phase H_2O_2 generation system was used to produce a sample stream with near-ambient levels of H_2O_2. Line losses were determined by sampling this stream with and without the tower sampling line. A critical aspect of the peroxide gradient system is the potential for bias introduced in the two separate inlet sections. Care was taken to ensure that bias introduced by the valve and 4-m inlet sections was well-known and correctable. Relative bias was determined every few days by placing both inlets at the same height and sampling ambient air for several hours. Subsequent gradients were corrected for bias, which ranged from -1 to 9%. When the bias surpassed 7%, samples were rejected and the valve and sample lines were cleaned with methanol, deionized water, and peroxide-free air. After cleaning, bias was reduced to a nondetectable level.

Hydroperoxides Peak identities were confirmed by comparison with retention times of authentic standards. Quantification was based on system response to hydrogen peroxide, as the same fluorescent dimer is formed for all hydroperoxides. Calibration was carried out twice daily and was found to be linear over the range $8x10^{-8}$ M to $5x10^{-6}$ M. The limit of detection has been determined to be less than 50 pptv.

Ozone The Dasibi ozone monitor was calibrated against a Dasibi ozone source/monitor model 1008-PC (serial #3226).

4.2.1 Specifications

Hydrogen Peroxide The H_2O_2 gradient measurements were occasionally subject to bias. It was extremely difficult to maintain clean sampling conditions at all times. Inlet filters cannot be used due to the potential for severe H_2O_2 loss on filter surfaces. Periods of unacceptable bias were encountered during the first IFC when the jack pine trees were pollinating, and occasionally during IFC-2 and IFC-3 when bugs would collect in the sample lines. The sample lines were sequentially flushed with methanol, water, and dry air periodically to remove dirt, pollen, and bugs.

Ozone The source instrument was recently compared to other instruments at the University of Idaho, and was found to agree within 1-2 ppb.

4.2.1.1 Tolerance

None given.

4.2.2 Frequency of Calibration

Calibrations were performed before and after each IFC. Bias checks for peroxide gradients were performed every few days during IFC-2 and IFC-3. No bias checks were performed during IFC-1.

4.2.3 Other Calibration Information

None given.

5. Data Acquisition Methods

Hydrogen Peroxide and Organic Peroxide Measurements Air was drawn at 4 L/min from the inlet (24 m height) on the TF tower through 1/4" TFE Teflon tubing to the tower base, where a gas-phase scrubber was used to scrub peroxides from the air stream. Samples were collected in 5 mL deionized water. HPLC analysis was performed immediately after sample collection.

HPLC separation was achieved on an Absorbosphere MF Plus C18 column (Altech) using an eluent of 0.001 M sulfuric acid and 0.0001 M EDTA delivered by a Merck-Hitachi L-6200 Intelligent HPLC pump at a flow rate of 0.6 mL/min. After separation, the peroxides were derivatized by addition of 0.026 M p-hydroxyphenylacetic acid with 10,000 units/L of horseradish peroxidase (type II Sigma Chemical) in 0.5 M potassium hydrogen phthalate buffer at pH 5.8. The reaction of the fluorescence reagent with the separated hydroperoxides takes place in a Teflon coil to ensure adequate mixing. The pH of the resulting solution is raised to above 10 to convert the dimer to its fluorescent anionic form using a membrane reactor constructed of Nafion (DuPont) tubing immersed in 30% ammonium hydroxide solution. Fluorescence measurements were made using a Merck-Hitachi spectrophotometer with excitation and emission wavelengths of 310 and 405 nm, respectively. The HPLC analytical system was located in the instrument hut.

Formaldehyde Monitoring The reaction of formaldehyde with DNPH was the basis for the measurement procedure used during this study. A DNPH/silica cartridge was connected to the inlet end of a 1/4" stainless steel tube extending to 3 m above the ground. The sample flow (1 L/min) was generated with a small pump and monitored with a Matheson flow meter. A calibrated Tylan digital totalizer was used to record the total volume sampled. The cartridges were exposed to the ambient air for nominal durations of 2, 4, or 6 hours. Cartridges were brought back to WSU for analysis.

Sample and blank cartridges were eluted with 3 mL acetonitrile. Hydrazone concentrations in the eluent were determined by reverse-phase HPLC. The HPLC analysis was performed using an LKB modular system consisting of two pumps (LKB #2150), a 190-600 nm ultraviolet/visible wavelength detector (LKB #2151) operated at 360 nm, and an LC gradient controller (LKB # 2152). A Brownlee-Rainin 10-cm OD-MPS column (or comparable) with a hydrophobic, nonpolar stationary phase (bonded on 5-micrometer spheres), preceded by a similar guard column was used for peak separation. A gradient elution, beginning with a 50:50 water:acetonitrile ratio was used, changing to a 30:70 water:acetonitrile ratio over a period of 21 minutes. The column flow rate was 0.5 mL/min, and the sample loop volume was 20 microliters.

Signals from the hydrogen peroxide and ozone instruments were stored as 1-minute averages via PC. Data acquisition software from Labtech was used to record signals (voltages). The gas chromatograph was interfaced to a pair of HP-3396A integrators for peak integration. Raw signals were also stored via PC for data reprocessing. The HPLC system for hydroperoxides was interfaced with a VG Data Systems Minichrom data acquisition system for chromatography. The connection of the HPLC to the data system was achieved using a chromatography server.

6. Observations

6.1 Data Notes

Hydrogen peroxide

Periods of unacceptable bias were encountered during the first IFC, when the jack pine trees were pollinating, and occasionally during IFC-2 and IFC-3 when bugs would collect in the sample lines.

Ozone

Some problems with the electronic zero were detected during IFC-1. An offset of -6 ppb relative to the data acquisition system was discovered. This offset was easily measured on a daily basis, and remained essentially unchanged throughout the experiment.

6.2 Field Notes

Peroxide data were deemed questionable (QC = 2) or unacceptable (QC = 3) during the following periods:

```
C *** QUALITY CONTROL (based local TIME and DAY)

25-May-1994          QC = 2          poor calibration
26-May-1994          QC = 2          poor calibration
27-May-1994          QC = 2          poor calibration
04-Jul-1994          QC = 3          extreme pollen event
05-Jul-1994          QC = 3          extreme pollen event
06-Jul-1994          QC = 2          moderate pollen event
09-Jul-1995          QC = 2          bias unknown
25-Jul-1994          QC = 2          poor calibration
31-Jul-1994          QC = 3          high noise level
04-Aug-1994          QC = 2          smoke
05-Aug-1994          QC = 2          smoke
06-Aug-1994          QC = 3          rain
01-Sep-1994          QC = 2          lost signal
02-Sep-1994          QC = 3          suspect line loss
```

7. Data Description

7.1 Spatial Characteristics

7.1.1 Spatial Coverage

Peroxide and ozone concentrations were measured at the OJP site only. The North American Datum of 1983 (NAD83) coordinates for the site are:

```
SSA-OJP   53.98717N, 105.11779W
```

7.1.2 Spatial Coverage Map

Not available.

7.1.3 Spatial Resolution

The data represent point source values at the locations given.

7.1.4 Projection

Not applicable.

7.1.5 Grid Description

Not applicable.

7.2 Temporal Characteristics

7.2.1 Temporal Coverage

Measurements were taken at SSA-OJP from 25-May-1994 to 09-Sep-1994.

7.2.2 Temporal Coverage Map

None given.

7.2.3 Temporal Resolution

Peroxide and ozone concentrations were measured continuously during daylight hours. In addition, many overnight sampling periods were obtained. No regular intervals of data collection were made at the site; however, data were collected on several days during the growing season of 1994.

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
H2O2_CONC
ROOH_CONC
H2O2_CONC_GRAD
ROOH_CONC_GRAD
EDDY_DIFF
MEAN_H2O2_DEP_VELOC
SDEV_H2O2_DEP_VELOC
MEAN_ROOH_DEP_VELOC
SDEV_ROOH_DEP_VELOC
QUALITY_CODE
CRTFCN_CODE
REVISION_DATE

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-CCCCC, 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 CCCCC 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.
H2O2_CONC	The hydrogen peroxide concentration.
ROOH_CONC	The organic peroxide concentration.
H2O2_CONC_GRAD	Hydrogen peroxide concentration gradient.
ROOH_CONC_GRAD	The organic peroxide concentration gradient.
EDDY_DIFF	Eddy diffusivity for heat.

MEAN_H2O2_DEP_VELOC	The mean deposition velocity of hydrogen peroxide.
SDEV_H2O2_DEP_VELOC	The standard deviation of the deposition velocity of hydrogen peroxide.
MEAN_ROOH_DEP_VELOC	The mean deposition velocity of organic peroxides.
SDEV_ROOH_DEP_VELOC	The standard deviation of the deposition velocity of organic peroxides.
QUALITY_CODE	1:good data: normal operation, 2:good data: normal operation, but uncertainties are greater due to non-ideal sampling condition or equipment function, 3:data questionable or possible instrument malfunction
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).
REVISION_DATE	The most recent date when the information in the referenced data base table record was revised.

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]
H2O2_CONC	[parts per billion]
ROOH_CONC	[parts per billion]
H2O2_CONC_GRAD	[parts per billion][meter^-1]
ROOH_CONC_GRAD	[parts per billion][meter^-1]
EDDY_DIFF	[meters^2][second^-1]
MEAN_H2O2_DEP_VELOC	[millimeters][second^-1]
SDEV_H2O2_DEP_VELOC	[millimeters][second^-1]
MEAN_ROOH_DEP_VELOC	[millimeters][second^-1]
SDEV_ROOH_DEP_VELOC	[millimeters][second^-1]
QUALITY_CODE	[unitless]
CRTFCN_CODE	[none]
REVISION_DATE	[DD-MON-YY]

7.3.4 Data Source

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

Column Name	Data Source
SITE_NAME	Not applicable
SUB_SITE	Not applicable
DATE_OBS	Investigator
TIME_OBS	Investigator
H2O2_CONC	Gas chromatograph
ROOH_CONC	Gas chromatograph
H2O2_CONC_GRAD	Gas chromatograph
ROOH_CONC_GRAD	Gas chromatograph
EDDY_DIFF	PL Gas chromatograph

MEAN_H2O2_DEP_VELOC	Gas chromatograph]
SDEV_H2O2_DEP_VELOC	Gas chromatograph
MEAN_ROOH_DEP_VELOC	Gas chromatograph
SDEV_ROOH_DEP_VELOC	Gas chromatograph
QUALITY_CODE	Investigator
CRTFCN_CODE	Not applicable
REVISION_DATE	Not applicable

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 Cllctd
SITE_NAME	SSA-OJP-FLXTR	SSA-OJP-FLXTR	None	None	None	None
SUB_SITE	TGB10-FLX01	TGB10-FLX01	None	None	None	None
DATE_OBS	25-MAY-94	09-SEP-94	None	None	None	None
TIME_OBS	0	2358	None	None	None	None
H2O2_CONC	-.01	3.55	None	None	None	None
ROOH_CONC	-.03	1.55	None	None	None	None
H2O2_CONC_GRAD	-.1088	.1799	None	None	None	None
ROOH_CONC_GRAD	-.0199	.0618	None	None	None	None
EDDY_DIFF	-1	10.64	None	None	None	None
MEAN_H2O2_DEP_VELOC	-195.6	278.4	-999	None	None	None
SDEV_H2O2_DEP_VELOC	0	34.1	-999	None	None	None
MEAN_ROOH_DEP_VELOC	-139.6	286.5	-999	None	None	None
SDEV_ROOH_DEP_VELOC	0	20.3	-999	None	None	None
QUALITY_CODE	1	3	None	None	None	None
CRTFCN_CODE	CPI	CPI	None	None	None	None
REVISION_DATE	24-OCT-96	24-OCT-96	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,H2O2_CONC,ROOH_CONC,H2O2_CONC_GRAD,
ROOH_CONC_GRAD,EDDY_DIFF,MEAN_H2O2_DEP_VELOC,SDEV_H2O2_DEP_VELOC,
MEAN_ROOH_DEP_VELOC,SDEV_ROOH_DEP_VELOC,QUALITY_CODE,CRTFCN_CODE,REVISION_DATE
'SSA-OJP-FLXTR','TGB10-FLX01',25-MAY-94,609,.59,.42,.0145,0.0,-1.0,-999.0,-999,
-999.0,-999.0,2,'CPI',24-OCT-96
'SSA-OJP-FLXTR','TGB10-FLX01',25-MAY-94,650,.56,.42,.0153,-.0006,-1.0,-999.0,
-999.0,-999.0,-999.0,2,'CPI',24-OCT-96
'SSA-OJP-FLXTR','TGB10-FLX01',25-MAY-94,730,.49,.4,.0074,.0022,-1.0,-999.0,
-999.0,-999.0,-999.0,2,'CPI',24-OCT-96
'SSA-OJP-FLXTR','TGB10-FLX01',25-MAY-94,803,.44,.37,.0229,.0193,-1.0,-999.0,
-999.0,-999.0,-999.0,2,'CPI',24-OCT-96
```

8. Data Organization

8.1 Data Granularity

The smallest unit of data tracked by the BOREAS Information System (BORIS) was oxidant concentrations measured on a particular day 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

The peroxide gradient was computed from three successive measurements of peroxide concentration at two levels (10-18 minutes at each level).

$$\text{Peroxide\_gradient} = (C2 - 0.5*(C1+C3))/\text{delta\_Z}$$

where: C1 = concentration measured at lower level (period t)
C2 = concentration measured at upper level (period t+1)
C3 = concentration measured at lower level (period t+2)

Special note: If the standard error associated with C1,C2,or C3 was greater than 0.05%,the peroxide gradient was deemed unacceptable. This procedure was performed in order to screen periods of highly variable concentration, which might suggest unsteady-state conditions (gusts or large eddies) which are not conducive to K-theory. This data screening procedure helps eliminate many unrealistic deposition velocities, but does not affect the overall conclusions.

Peroxide_deposition_velocity = (peroxide_gradient)/(C_avg)*(eddy_diffusivity)

where: C_avg = average peroxide concentration (over both levels)

9.1.1 Derivation Techniques and Algorithms

None given.

9.2 Data Processing Sequence

9.2.1 Processing Steps

None given.

9.2.2 Processing Changes

None given.

9.3 Calculations

Emission rate:

E = C*Q/B

where: C is the concentration of a specific VOC
Q is the flow rate of air through the chamber
B is the dry leaf (needle) biomass of the enclosed branch

Deposition velocity (Vd):

Vd = K*(dC/dz)/C

9.3.1 Special Corrections/Adjustments

Peroxide Bias adjustment: C1 = C1*fb C3 = C1*fb

where: fb = bias relative to upper sampling level
(range 0.99 to 1.07 for H_2O_2, 0.99 to 1.02 for ROOH)

9.3.2 Calculated Variables

None given.

9.4 Graphs and Plots

None.

10. Errors

10.1 Sources of Error

Hydroperoxides:

- Fluctuations in air flow rate.
- Error in preparing sample volume.
- Fluctuations in sample collection efficiency with temperature.
- Possible condensation in sample lines.
- Interference due to smoke particles.
- Error associated with the serial dilution of H_2O_2 standards.

10.2 Quality Assessment

10.2.1 Data Validation by Source

None given.

10.2.2 Confidence Level/Accuracy Judgment

Hydrogen peroxide concentrations are good to approximately 30%. Total organic peroxide concentrations have not been corrected for collection efficiency. Reported total organic peroxide concentration may be underestimated by as much as 60%. Individual deposition velocity measurements are subject to 50-80% uncertainty due to uncertainties in the measured gradient, the measured eddy diffusivity, and the natural variability of a turbulent atmosphere. Ozone concentrations are good to +/- 5 ppb for IFC-1, and +/- 3 ppb for IFC-2 and IFC-3.

10.2.3 Measurement Error for Parameters

None given.

10.2.4 Additional Quality Assessments

None.

10.2.5 Data Verification by Data Center

BORIS processed the data by:

- Reviewing the initial data files and loading them online for BOREAS team access.
- Designing relational data base tables to inventory and store the data.
- Loading the data into the relational data base tables.
- Performing the conversions on measurements into System International (SI) units.
- Extracting the standardized data into logical files.

11. Notes

11.1 Limitations of the Data

Peroxide deposition velocities at OJP are subject to some uncertainty (factor of 2) simply because we do not know for certain that the application of Kh is appropriate for peroxide transport. The eddy diffusivity for water vapor over OJP was lower than that of heat. Therefore, average peroxide deposition velocities should probably be taken as an upper limit.

11.2 Known Problems with the Data

None given.

11.3 Usage Guidance

Peroxide deposition rates are extremely difficult to measure in the field. Individual measurements of peroxide deposition velocity hold little significance due to the uncertainties mentioned in Section 10.2. However, because of the large amount of data collected, these deposition rates are a valuable component of the peroxide budget. Vd data should be used to assess average deposition rates to a rough, boreal pine forest.

11.4 Other Relevant Information

None given.

12. Application of the Data Set

The data can be used to examine (a) the role of biogenic hydrocarbon emissions with respect to carbon cycles in the boreal forest, (b) the chemical fate of boreal biogenic emissions, (c) the hypothesis that biospheric VOC emissions contribute to peroxide formation, and (d) the deposition rates of hydrogen peroxide and organic peroxides.

13. Future Modifications and Plans

None.

14. Software

14.1 Software Description

All software programs used to gather data were standard scientific packages.

14.2 Software Access

None given.

15. Data Access

The TGB-10 oxidant flux 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

None given.

17.2 Journal Articles and Study Reports

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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

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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
DNPH    - dinitrophenylhydrazine
EOS     - Earth Observing System
EOSDIS  - EOS Data and Information System
GIS     - Geographic Information System
GMT     - Greenwich Mean Time
GSFC    - Goddard Space Flight Center
HPLC    - High Performance Liquid Chromatography
HTML    - Hyper-Text Markup Language
IFC     - Intensive Field Campaign
NAD83   - North American Datum of 1983
NASA    - National Aeronautics and Space Administration
NIST    - National Institute for Standards and Technology
NMHC    - Non-Methane Hydrocarbon
NSA     - Northern Study Area
OA      - Old Aspen
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OBS       Old Black Spruce
OJP     - Old Jack Pine
ORNL    - Oak Ridge National Laboratory
PANP    - Prince Albert National Park
REA     - Relaxed Eddy Accumulation
SI      - System International
SSA     - Southern Study Area
TF      - Tower Flux
TGB     - Trace Gas Biogeochemistry
URL     - Uniform Resource Locator
VOC     - Volatile Organic Compound (or Carbon)
WSU     - Washington State University
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13. ABSTRACT *(Maximum 200 words)*

The BOREAS TGB-10 team collected several trace gas data sets in its efforts to determine the role of biogenic hydrocarbon emissions with respect to boreal forest carbon cycles. This oxidant data set contains measured peroxide (H_2O_2 and total organic peroxides (ROOH)) and ozone concentrations as well as H_2O_2 and ROOH deposition velocities. These data were obtained at the SSA-OJP site during the summer of 1994. Measurements were made from May to September 1994. The data are stored in tabular ASCII files. Some important results were:

- Ozone concentrations were consistently low, 20-30 ppb, during the summer of 1994.
- Peroxide concentrations showed a seasonal variation with highest concentrations occurring in July (IFC-2).
- Midday H_2O_2 levels averaged around 1.4 ppb during IFC-2 and 0.4-0.5 ppb during IFC's 1 and 3.
- Midday organic peroxide concentrations were lower, averaging 0.8 ppb during IFC-2, and 0.4-0.5 ppb during IFC's 1 and 3.
- The rough pine forest canopy serves as a significant sink for H_2O_2.
- Midday H_2O_2 deposition velocities averaged 4-7 cm/s.
- Organic peroxide deposition velocities (measured as total ROOH) were approximately 40% as large as those of H_2O_2.

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