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Cost share #: G-35-332  
Rev #: 7  
Active  
OCA file #: RES  
Work type :  

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Contract#: NAG-1-1438  
Prime #: /SUPP 5  

Center shr #: 10/22-1-F7454-0A0  
OCA file #:  

Subprojects #: Y  
Main project #:  

Project unit: E & A SCI  
Unit code: 02.010.140  

Project director(s):  
DAVIS D D  
E & A SCI  
(404)894-3895  

Sponsor/division names: NASA  
Sponsor/division codes: 105  

Sponsor/division names: NASA  
Sponsor/division codes: 105  

Award period: 920518 to 960917 (performance) 961217 (reports)  

Sponsor amount  
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Contract value 0.00 515,126.00  
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Title: DIAGNOSTIC MODELLING STUDIES OF THE HX OY - NX OY - 03 PHOTOCHEMICAL SYSTEM..  

PROJECT ADMINISTRATION DATA  

OCA contact: Anita D. Rowland 894-4820  

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(804)864-2720  

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Security class (U,C,S,TS) : U  
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Equipment title vests with: Sponsor  
GIT X  

NASA RESERVES THE RIGHT TO ITEMS=>$1,000; REF. GRANTS HANDBOOK, ENCLOSED  

Administrative comments -  
SUPPLEMENT 5 AWARDES A 6-MO NCE THRU 9.17.96
GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 02/20/97

Project No. G-35-642

Center No. 10/24-6-R7454-0A0_

Project Director DAVIS D D

School/Lab E & A SCI____

Sponsor NASA/LANGLEY RESEARCH CTR, VA

Contract/Grant No. NAG-1-1438

Contract Entity GTRC

Prime Contract No. 

Title DIAGNOSTIC MODELLING STUDIES OF THE HX OY - NX OY - 03 PHOTOCHEMICAL SYST

Effective Completion Date 960917 (Performance) 961217 (Reports)

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Comments

Subproject Under Main Project No. 

Continues Project No. 

Distribution Required:

- Project Director Y
- Administrative Network Representative Y
- GTRI Accounting/Grants and Contracts Y
- Procurement/Supply Services Y
- Research Property Management Y
- Research Security Services N
- Reports Coordinator (OCA) Y
- GTRC Y
- Project File Y
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NOTE: Final Patent Questionnaire sent to PDPI.
Six Month Report
May 1992 - November 1992
NASA Project # nag-1-1438

DIAGNOSTIC MODELING STUDIES
OF THE H₂O₂-N₂O₅-NO₃ PHOTOCHEMICAL
SYSTEM AND ITS COUPLING TO
SULFUR, CARBON, AND HALOGENS
BASED ON NASA GTE FIELD DATA

Submitted to:
Dr. Jack Fishman
Atmospheric Science Division
NASA/Langley Research Center
Mail Stop 401-A
Hampton, VA 23681

From:
Dr. Doug Davis
School of Earth and Atmospheric Sciences
Georgia Institute of Technology
Atlanta, GA 30332
During the first six month period of this project (May 1992-November 1992), my efforts have been focused on four areas of activity.

1. Participation in the first PEM-West(A) data workshop.
2. Data merging exercises.
3. Initial data runs on 9 of 18 data flights
4. Critical analysis of the PEM-West(A) UV data

Concerning activity (1), as co-mission scientist I, along with Dr. Shaw Liu (co-mission scientist) and Jim Hoell (project manager), organized the agenda for the workshop and served as co-discussion leader throughout the meeting. This five day workshop proved highly successful in that it presented to the science team a detailed overview of the PEM-West data set and also provided important guidelines for proceeding with interpretative analysis of the data.

Concerning activity (2), although there was an unofficial agreement that John Bradshaw and Scott Sandholm of Georgia Tech would provide a data merge disk for the entire PEM-West(A) data set, the time table for this product being available to the science team ranged from August 1992 to February 1993. Because of this potentially long delay and because we believed that an additional merged data set would add a quality control step to the master data merge, we opted to do our own data merge on the critical photochemical parameters required for our modelling exercises. This data merging activity was focused on a sub-set of the 18 data
flights, namely, flights 6, 7, 8, 9, 12, 13, 15, 16, and 17. The idea here was to get a cross-sectional look at the PEM-West data base.

Concerning activity (3), box model calculations were carried out on flights 6, 7, 8, 9, 12, 13, 15, 16, and 17 with the initial goal of assessing the level of photochemical activity in each of these quite different flights. Key species examined included: OH, HO₂, CH₃O₂, CH₃OOH, H₂O₂, and CH₂O. Two additional quantities evaluated were the ozone photochemical tendency, P(O₃), and the photochemical test ratio NO₂/NO. From these initial modelling runs, the single most surprising result that surfaced was the very large disparity between the experimentally observed NO₂/NO ratio and that predicted from photochemical box model calculations. The latter model had a complete set of H₂O₂-N₂O₅-O₃ reactions as well as a full oxidation scheme for CH₄. Non-methane hydrocarbon chemistry was treated using a "modified" Lurman condensed model where the modifications focused on: (1) allowing for all organic peroxide species to react with OH, and (2) the conversion of several stoichiometric NO reactions into elementary processes.

The very substantial disagreement between observations and predictions for the NO₂/NO ratio (e.g. factors of 3 to 6) led us initially to identifying one of the contributing factors as unrealistically high UV Eppley readings. The latter conclusion has resulted in a rather substantial amount of time being devoted to a critical analysis of PEM-West(A) UV data.
Activity (4)

The importance of the real-time UV aircraft readings lies in the fact that these data are used to correct our model generated photochemical J values for the effects of clouds. The cloud-correction factor (CCF) has been defined by us in the form of equation I:

\[(I) \quad (CCF) = \frac{(J_{\text{Expt}})_{NO_2}}{(J_{TS})_{NO_2}}\]

For all other J's, the values are adjusted for the effects of clouds using equation II, e.g.,

\[(II) \quad J_{\text{True}} = J_{TS} \times (CCF)\]

In equation I, \((J_{TS})_{NO_2}\) is the J value estimated for the photolysis of NO$_2$ based on a two-stream radiative-transfer model, and \((J_{\text{Expt}})_{NO_2}\) is the J value for NO$_2$ evaluated from an empirical equation (Madronich) that is based on Eppley UV sensor readings, e.g.,

\[(III) \quad J_{NO_2} = \frac{1.35E\mu}{(0.56 + 0.03z)\cos\theta + 0.21 - 0.015z} + 2(1.14)E_d\]

In the above equation E\(\mu\) and E\(_d\) are the upward and downward looking Eppley UV readings and z and \(\theta\) are the altitude and zenith angle, respectively.

Of considerable interest in the PEM data set was the fact that the average CCF value was 1.60. For all other previous GTE missions, the average value of CCF has ranged from 0.93 to 1.10. Based on the latter finding we made the decision to carry out a critical analysis of all GTE UV data using 10 sec time resolution data. The data bases examined included PEM, CITE-3, ABLE-3B, ABLE-
3A, and CITE-2. In an effort to make each data set directly comparable to PEM, the recorded upward and downward UV intensities were plotted as a function of solar zenith angle. Initial results based on these plots have shown that indeed the PEM aircraft data are substantially shifted from previous GTE missions for both UVZ and UVN. We expect to complete our analysis of the UV problem within the next month. Obviously, no meaningful interpretation of our modelling results can be completed until this UV sensor problem is fully understood, at least understood to the extent that an appropriate correction term can be defined.
Six Month Report  
November 1992 - May 1993  
NASA Project # nag-1-1438

DIAGNOSTIC MODELLING STUDIES  
OF THE $\text{H}_2\text{O} - \text{N}_2\text{O} - \text{O}_3$ PHOTOCHEMICAL SYSTEM AND ITS COUPLING TO SULFUR, CARBON, AND HALOGENS BASED ON NASA GTE FIELD DATA

Submitted to:  
Dr. Jack Fishman  
Atmospheric Science Division  
NASA/Langley Research Center  
Mail Stop 401-A  
Hampton, VA 23681

From:  
Dr. Doug Davis  
School of Earth and Atmospheric Sciences  
Georgia Institute of Technology  
Atlanta, GA 30332
During the second six month period of our NASA project (November, 1992-May, 1993) our efforts have been focused on three areas of activity:

(1) Photochemical analysis of the PEM-West(A) data.
(2) Presentations of photochemical box model results at the second PEM-West workshop.
(3) Reassessment of PEM-West(A) water vapor data.

Concerning activities (1) and (2), our initial analysis of the PEM-West(A) data was focused on three sub-topical areas:

(a) The oxidizing capacity of the western Pacific.
(b) Test of photochemical theory using measured NO$_2$/NO ratios.
(c) DMS/SO$_2$ oxidation chemistry.

In assessing the oxidizing capacity of the western Pacific (e.g., items (a) and (b)), we have used photochemical box model results based on approximately one thousand independent observations. By filtering the observations according to a fixed zenith angle range (e.g. 30°-55°), meaningful latitudinal and altitudinal trends were assessed for model estimated levels of OH as well as values for the ozone tendency, P(O$_3$). These results showed that the highest levels of OH occurred at high latitudes (20°-40° N) and low altitudes (0-3 km). For these conditions the average value for OH was 7x10$^6$ molec/cm$^3$. By comparison, OH levels from 0°-20° N, for the same altitude range, were nearly a factor of 3 times lower. Also, at all latitudes for the highest altitudes sampled (10-12 km), the average OH level was nearly a factor of 3 lower than those in the 0-3 km range. The trends in OH tend to
reflect the distribution of the critical photochemical species \( \text{O}_3 \), \( \text{NO} \), and \( \text{H}_2\text{O} \).

A similar analysis of \( P(\text{O}_3) \) showed a somewhat similar trend to \( \text{OH} \) as related to latitude; but, with the exception of a small subset of data collected in the polluted marine boundary layer near the coast of Japan and China, the altitudinal trend in \( P(\text{O}_3) \) was found to be completely out of phase with that for \( \text{OH} \). For example, with the exception of the coastal data, \( P(\text{O}_3) \) was on average negative at all latitudes for altitudes less than 6 km with typical values ranging from -2 to \(-7 \times 10^5\) molec/cm\(^3\)/s. However, for the latitude range 20°-40° N and altitudes above 6 km, \( P(\text{O}_3) \) was nearly always positive with typical values ranging from 3 to \(7 \times 10^5\) molec/cm\(^3\)/s. Between 0-20° N and above 6 km, \( P(\text{O}_3) \) was found to be much lower in magnitude (e.g., \(2 \times 10^5\)) and to oscillate between negative and positive values. Overall, one of the most significant \( P(\text{O}_3) \) results was the observed trend that positive values of this calculated parameter increased with latitude and altitude. Correlations with other photochemical species/parameters revealed that the mixing ratio for NO was the single most important factor controlling the sign and magnitude of \( P(\text{O}_3) \).

In assessing the reliability of current photochemical models based on experimentally measured values of the test ratio \( \text{NO}_2/\text{NO} \) (e.g., item (b)), we have established that there are very large discrepancies between model predictions and the observations. This discrepancy is a strong function of altitude, being larger at high altitudes than at low altitudes. Several potential explanations for this behavior are currently being explored.
Concerning the oxidation of DMS as a source of SO2 (e.g., item (c)) , the principal data subset examined thus far have been the data from the three day/night flights, e.g. missions 8, 17, and 20. Although mission 17 provided the highest quality of the three missions, all three showed very similar trends. The two most important characteristics of these data were: (1) from pre-sunrise to post sunrise there was no significant decrease in the mixing ratio of DMS where the latest time sampled was approximately 3 hours after sunrise. In fact, it could be argued that there may have been a statistically significant small increase in DMS levels during the post sunrise period. (2) The levels of SO2 for each data set exceeded those of DMS by nearly a factor of two.

Based on time dependent modelling calculations using these sulfur data, we have concluded the following: (a) the absence of any significant change in the DMS concentration following sunrise would seem to preclude there being a major marine source of Cl2 via the reaction of O3 with sea-salt aerosol. These observations, however, are consistent with OH being the principal mode of oxidation of DMS since at three hours past sunrise the rate of destruction of DMS by OH is just beginning to exceed the release rate of DMS. (b) DMS oxidation can not explain the high levels of SO2 even if it is assumed that 100% of the oxidized DMS is converted into SO2. In fact, the only way that such high levels of SO2 can be explained is either by the major entrainment of free tropospheric air (this air was approximately 1.5 times higher in SO2 than the marine boundary layer) or by there being present a reduced sulfur source other than DMS that was being oxidized to produce SO2 at a rate several times
greater than from DMS. More detailed analysis of these data is being planned.

Activity (3), a reassessment of the PEM-West(A) dew-point data, has involved assisting Langley Research Center in identifying which dew-point instrument was giving the most reliable value as a function of altitude. The primary difficulty here has been that under conditions where sampling was occurring in clouds the readings reported frequently exceeded the static air temperature. We have now been able to identify all data in this category and have suggested that the static air temperature be taken as the most reliable estimate of the true atmospheric dew-point for purposes of photochemical modelling.
Six Month Report
May 1993 - November 1993
NASA Project # NAG-1-1438

DIAGNOSTIC MODELLING STUDIES OF THE HxOy-NxOy-O3 PHOTOCHEMICAL SYSTEM AND ITS COUPLING TO SULFUR, CARBON, AND HALOGENS BASED ON NASA GTE FIELD DATA

Submitted to:
Dr. Jack Fishman
Atmospheric Science Division
NASA Langley Research Center
Mail Stop 401-A
Hampton, VA. 23665-5225

From:
Dr. Doug Davis
School of Earth and Atmospheric Science
Georgia Institute of Technology
Atlanta, GA. 30332
During the third six month period of our NASA project, our efforts have been focused in three areas:

(1) Preparation of a manuscript on the photochemical tendency of ozone, i.e. "AN ASSESSMENT OF THE PHOTOCHEMICAL O3 TENDENCY IN THE WESTERN NORTH PACIFIC AS INFERRED FROM GTE/PEM-WEST(A) OBSERVATIONS DURING THE FALL 1991".

(2) Preparation of a manuscript on the level of agreement between the observed and measured ratio of NO2/NO, i.e. "A PHOTOSTATIONARY STATE ANALYSIS OF THE NO2-NO SYSTEM BASED ON AIRBORNE OBSERVATIONS FROM THE WESTERN AND CENTRAL NORTH PACIFIC".

(3) Completion of our final revised zero-D photochemical modelling runs on approximately 3000 individual data runs and submitted these results to the NASA PEMWest(A) data archive. Included in these archived results were photostationary results for the species: OH, HO2, H2O2, CH3OO, CH3OOH, CH2O, NO2, NO3, N2O5, HNO3, HO2NO3 plus several of the more centrally important J values as related to the above species.

Results from the first draft of manuscripts (1) and (2) were presented at the 3rd PEMWest(A) workshop October 18-21, 1993. The final draft of each of the above two manuscripts is expected to be completed and submitted for publication in February 1994.

Future activity on this project will involve (a) a more detailed analysis of mid and high altitude NOx sources; (b) a
detailed analysis of marine sulfur sources (e.g. DMS) including an examination of the oxidation of DMS sulfur to SO2, MSA, and other sulfur products; and (c) a detailed photochemical analysis of marine boundary layer chlorine chemistry as related to ozone sea salt interactions.
Report
March 1994-March 1995
NASA Project # NAG-1-1438

DIAGNOSTIC MODELLING STUDIES OF THE HxOy-O3 PHOTOCHEMICAL SYSTEM AND ITS COUPLING TO SULFUR, CARBON, AND HALOGENS BASED ON NASA GTE FIELD DATA

Submitted to:
Mr. James Hoell, Jr.
Mail Stop 483
NASA Langley Research Center
Hampton, VA. 23665-5225

From:
Dr. Douglas D. Davis
School of Earth and Atmospheric Science
Georgia Institute of Technology
Atlanta, GA. 30332
For the time period of 3/17/94 to 3/17/95 the major emphasis of our research group has been on the completion and submission of manuscripts based on the results from NASA's PEM-West(A) field program. This effort has involved both contributions to papers in which this PI was a co-author (i.e., 9 papers) as well as those in which his group took the lead role in writing the paper (e.g. 3 papers). As of the end of March all manuscripts listed below had been submitted for publication to the special PEMWest(A) JGR issue. Some of these manuscripts, however, had not undergone final revision due to reviews not having been returned from JGR.

Co-authored Papers

(1) Large-scaled Air Mass Characteristics Observed Over the Western Pacific during the Summertime. E. Browell-lead author.


(6) Low Ozone in the Marine Boundary Layer of the tropical Pacific Ocean: Photochemical Loss, Chlorine Atoms, and Entrainment. H. Singh-lead Author

(7) Reactive Nitrogen and Ozone Over the Western Pacific: Distribution, Partitioning and Sources. H. Singh-lead author.

(8) Tropospheric Western Pacific Air Mass Classification Schemes for the PEM-West (A) Experiment. S. Smyth-lead author.

(9) Sulfur Dioxide as a Source of CN in the Upper Troposphere of the Pacific Ocean. D. Thornton-lead author.

D. Davis (or group members) listed as lead author:

(A) A Photostationary State Analysis of the NO₂-NO Systems Based on Airborne Observations from the Western and Central North Pacific.
(B) An Assessment of Ozone Photochemistry in the western North Pacific as Inferred from PEM-West (A): Observations during Fall 1991.

(C) Potential Impact of Iodine on Tropospheric Levels of Ozone and other Critical Oxidizing Species.
Final Report
NASA Project # NAG-1-1438

DIAGNOSTIC MODELLING STUDIES OF THE HxOy-O3 PHOTOCHEMICAL SYSTEM AND ITS COUPLING TO SULFUR, CARBON, AND HALOGENS BASED ON NASA GTE FIELD DATA

Submitted to:
Mr. James Hoell, Jr.
Mail Stop 483
NASA Langley Research Center
Hampton, VA. 23665-5225

From:
Dr. Douglas D. Davis
School of Earth and Atmospheric Science
Georgia Institute of Technology
Atlanta, GA. 30332
For the time period of this grant 3/17/92 to 3/17/95 a total of 14 manuscripts based on the results from NASA’s PEM-West(A) field program. This effort has involved both contributions to papers in which this PI was a co-author (i.e., 10 papers) as well as those in which his group took the lead role in writing the paper (e.g. 4 papers). As of the end of December 1996 all manuscripts listed below had been accepted for publication or had appeared in print as related to the special PEMWest(A) and PEM-B JGR special issues. Six additional manuscripts have either been submitted for publication or are now in preparation.

Co-authored Papers

(1) Large-scaled Air Mass Characteristics Observed Over the Western Pacific during the Summertime. E. Browell-lead author.

(2) Hydrogen Peroxide and Methylhydroperoxide Distributions Related to Ozone and Odd-Hydrogen Over the North Pacific in the Fall of 1991. B. Heikes-lead author.


(6) Low Ozone in the Marine Boundary Layer of the tropical Pacific Ocean: Photochemical Loss, Chlorine Atoms, and Entrainment. H. Singh-lead Author

(7) Reactive Nitrogen and Ozone Over the Western Pacific: Distribution, Partitioning and Sources. H. Singh-lead author.

(8) Tropospheric Western Pacific Air Mass Classification Schemes for the PEM-West (A) Experiment. S. Smyth-lead author.

(9) Sulfur Dioxide as a Source of CN in the Upper Troposphere of the Pacific Ocean. D. Thornton-lead author.

(10) Evidence of heterogeneous chemistry on sulfate aerosols in stratospheric air masses measured in PEM-West B. Kotamarthi lead author.

D. Davis (or group members) as lead author:

(A) A Photostationary State Analysis of the NO₂-NO Systems Based on Airborne Observations from the Western and Central North Pacific.

(B) An Assessment of Ozone Photochemistry in the western North Pacific as Inferred from PEM-West (A) Observations during the Fall 1991.

(C) Potential Impact of Iodine on Tropospheric Levels of Ozone and other Critical Oxidants.

(D) Implications of Large Scale Shifts in Tropospheric NOx Levels in the Remote Tropical Pacific.