

AIR QUALITY RESEARCH BRANCH

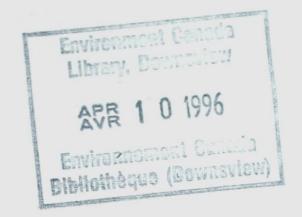
Annual Report 1994-95



Environment Canada

Atmospheric Environment Service Environnement Canada

Service de l'environnement atmosphérique



AIR QUALITY RESEARCH BRANCH

ANNUAL REPORT

1994/95

Compiled by

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AIR QUALITY RESEARCH BRANCH

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1.0 FOREWORD

1.1 <u>Awards</u>

- M. Still

The prestigious WMO Norbert Gerbier-Mumm international award for 1995 was won by Drs. Jim Kerr and Tom McElroy for their paper entitled "Evidence for Large Upward Trends in UV-B Radiation Linked to Ozone Depletion" published in the November 12, 1993, issue of Science. This annual award is presented through the WMO by the Mumm Foundation in recognition of the most prominent contribution in the field of meteorology. The paper demonstrates unequivocally the connection between the daily dose of UV radiation received at the earth's surface and the amount of ozone above. Tom McElroy accepted the award in a special ceremony held in Geneva on June 22, 1995.

In 1994, the Branch recognized three of its staff through the presentation of the All-Seasons Award.

Jan Bottenheim who did an excellent job in the planning and coordinating of the field study Pacific '93. The project produced a valuable data set for further scientific investigations into the NOx/VOC processes.

Marvin Olson who has produced a broad range of results from his trajectory model that have been applied successfully in areas such as the Long-Range Transport of Air Pollutants, airshed studies, health meteorology and ozone episode description. His trajectory model is used as a basic research tool in both national and international research centres.

Keith Puckett who, for many years, has provided strong scientific management and leadership for the Acid Deposition program. He managed the unmanageable, i.e., ADOM and EMEFS, ensuring that the maximum possible amount of science emerged.

1.2 Resource Report

- K. Ford and L. Grittani

In fiscal year 1994-95, the Air Quality Research Branch (AQRB) had a staff of 145 individuals. To ensure the availability of future research staff, AQRB hired post-doctoral fellows and students under various government initiatives. During the year, 11 post-doctoral fellows were working on scientific programs within the Branch and 30 students were employed each for four-month work terms.

Three employees departed during the year. Dr. Peter Summers, a long-time employee of AQRB who had worked for us part-time since his retirement three years earlier,

decided to retire permanently. Joe Markes, a senior electronics technician, retired in February 1995. Mark Underwood, who worked as a senior technician, left to join the Halton Police Force.

To fulfill international obligations and to maintain the Branch at the leading edge of research in air quality, staff attended numerous conferences and meetings during the year. In total, scientists attended 79 conferences: 24 internationally; 33 in the U.S.; and 22 in Canada. Staff also participated in 31 international workshop and business meetings.

The Branch began the year with a budget of \$17.7 million: salary (\$6.8 million); operating (\$6.8 million); and capital (\$4.1 million). This is an increase from last year's initial figure of \$14.5 million. The Green Plan component of our budget was virtually equivalent to our A-Base dollars (\$8.5 million vs. \$8.6 million, respectively); once again demonstrating our reliance on this important source of funding. During the year, allocations were confirmed for two other initiatives: \$0.7 million from EPS for the GLAP (Great Lakes Action Plan) and \$0.8 million for our Northern Contaminants program in partnership with DIAND.

Later in the year, the Branch received an extra \$1.5 million from a variety of sources. Most notably, the Northern Contaminants program received an additional \$0.4 million. A similar amount was received from elsewhere within CARD (Climate & Atmospheric Research Directorate) in support of global warming research. From outside the Directorate, but within the Atmospheric Environment Program, the Branch received about \$0.6 million for various programs with the balance (\$0.1 million) being received from other government departments and federal agencies.

Naturally, many of our programs operate nationwide and with the involvement of DOE's regional offices and other AES Directorates. This has resulted in budget transfers from the Branch of over \$1.5 million for the Regions to support our programs. The Smog, Stratospheric Ozone and Climate Change initiatives accounted for the bulk of the transfers.

2.0 **BRANCH PROGRAM**

2.1 **ACID DEPOSITION**

2.1.1 <u>Lagrangian Model</u>

- M.Olson, K.Oikawa and B.Pabla

The sulphur and nitrogen Lagrangian models were not run during this period because the next planned project required the 1990 emissions inventory which was not available. The trajectory model data archives were updated and the model code was converted and tested on the new Dorval computers.

The trajectory model was run for many users and a marketing strategy was begun for the PC-based plotting package developed at the University of Guelph.

The source-receptor matrices for sulphur and nitrogen were supplied to the Integrated Assessment Model (IAM) developers at CCIW and several model evaluation sessions were attended.

2.1.2 Visibility Measurements

- R. M. Hoff, Len Guise-Bagley, M. Moran and K. J. Puckett

Collaborators in this project are Iain Campbell (U. Guelph), K. MacDonald (DOE Region - WAES), S. Pryor (UBC), S. Sakayama (B.C. Environment) and R. Hughes (N.B. Environment).

Canada has been required to implement equivalent protection against visibility impairment as exists in the U.S. Clean Air Act. Part of Canada's response to this requirement has been an assessment of past and current atmospheric visibility across the nation, research into the sources and types of visibility reducing aerosols, and projections of future visibility impairment by modelling.

In order to understand Canada's historical visibility trends, a methodology has been developed to uncensor the synoptic station observer visibility. This method removes the 15-mile upper limit bias in the data and allows computation of realistic visibilities in western Canada where visibility is high. These results have been used to map average visibility across Canada and will be used in the 1996 Acid Rain Assessment to give historical semi-decadal trends.

In the north, Arctic haze decreases ambient visibility. An upcoming AMAP (Arctic Monitoring & Assessment Program) assessment document discusses the impacts of acidic aerosols on visibilities. Experimental work to determine the speciation of visibility-reducing aerosols took place at Egbert, Ontario, at Vancouver, British Columbia, in Waterton Lakes National Park, Alberta, and at St. Andrews, New Brunswick. This work has pointed out the importance of the variability of aerosol species and hygroscopicity to its light scattering properties.

Current models of acidic aerosols are expected to be able to predict the inputs to predictions of visibility reduction (primarily sulphates and humidity in the east, plus nitrates in the west). Model predictions of future visibility, using post-processors on the ADOM and ALOM models, are being examined for the 1996 Acid Rain Assessment.

2.1.3 <u>CAPMoN Operations</u>

- D. MacTavish, , R. Vet, W. Kobelka, A. Gaudenzi, M. Underwood and D. Ord

The Canadian Air and Precipitation Monitoring Network (CAPMoN) consists of 23 precipitation chemistry sites, 11

air filter pack measurement sites and 8 ozone monitoring sites. Operations were coordinated and supported from Downsview and managed by DOE regional inspection staff. On March 31, 1995, the Priceville, Ontario, precipitation chemistry monitoring site was closed and the field pH measurements network was discontinued.

In an effort to improve communications with DOE regional staff and reduce equipment down-time, a Bulletin Board system has been established and supplemented with an answering device, a cellular paging system and a cellular phone. Fax line managers and fax machines were installed at 7 monitoring sites to improve communications with the site.

A three-year program to assess and subsequently upgrade all precipitation sites to the MIC Model 300 precipitation collector will be completed with the installation of the last two sites in 1995. Four CAPMoN sites were upgraded to 5KVA UPS (Uninterruptible Power Supply) units in an effort to improve the quality of the available power.

CAPMoN staff continued to cooperate with the World Meteorological Organization's Global Atmospheric Watch program (WMO-GAW) by supplying technical expertise for on-site installation of equipment and training of personnel at Waliguan Mountain, China, and Firooz-Koh, Iran.

2.1.4 CAPMON National Laboratory

- D. MacTavish, N. Lance, R. Braga, N. Lance and K. So

The National Laboratory completed chemical analyses and—compiled laboratory data sets for the 1994 CAPMoN network samples. This included the analysis of over 15,000 filters and 7,500 precipitation samples, involving more than 154,000 chemical determinations.

Laboratory credibility was maintained by continued successful participation in international intercomparision studies, including Environment Canada's Long Range Transport of Air Pollutants Intercomparision, the WMO-GAW's Laboratory Intercomparision, the United States Geological Survey Intercomparision, and the Norwegian Institute for Air Research's European Measurement and Evaluation Program Laboratory Round Robin Study.

2.1.5 CAPMON Quality Assurance and Data Management - R. Vet, M. Shaw, S. Iqbal, S. Ahmed and W. Sukloff

The CAPMoN air, precipiation and ozone data underwent quality control/quality assurance and were finalized up to December 31, 1993. As scheduled, data from April to September 1994 were quality controlled by March 31, 1995, and the balance of 1994 data will be finalized by June 30, 1995. A new data base management and quality software system (RDMQ) was implemented for precipitation chemistry data to replace the now-defunct mainframe system (see Section 2.7.1). The system significantly reduced the

time and cost of data quality control. For the filter pack and ozone data, new systems were designed and partially implemented. Full implementation and testing will take place in the coming year. An audit/inspection system for the precipitation, air and ozone monitoring programs was implemented. The CAPMoN data were transferred to the National Atmospheric Chemistry (NatChem) database and the National Air Pollution Surveillance Network Database.

2.1.6 NAtChem Database

- R. Vet, C.U.Ro, D.Ord and W.Sukloff

The National Atmospheric Chemistry (NAtChem) database activity focused on several initiatives: updating the data base to 1992; preparing the "NAtChem 1992 Annual Report"; revising the report "Spatial Patterns of Acid Precipitation in Eastern North America from 1980-1991"; preparing the reports "12-Year (1980-1991) Long Term Trends of Acid Deposition in Eastern North America" and "Optimization of the APIOS Deposition Monitoring Networks"; and developing the NAtChem-Toxics database.

The NAtChem database has been successfully updated to 1992. It includes complete Canadian, US NADP/NTN (National Atmospheric Deposition Program/National Trends Network) and CASTNET (Clean Air Status and Trends NETwork) data. Drafts of the NAtChem 1992 Annual Report were distributed to provincial network coordinators for review. The NAtChem-Toxics database design and functional specification were completed, and the prototype database (sample and summary) was implemented using AES air organics and trace metal data. Eventually it will include all Canadian Integrated Atmospheric Deposition Network (IADN) data sets and standard analysis routines. It will be functioning as the IADN central database. The WMO Global Atmosphere Watch (GAW) World Data Centre Directors' meeting was held at AES and the NAtChem database system was thoroughly presented as a candidate to be used in the WMO World Precipitation Chemistry Data Centre.

NAtChem staff presented the 1992 Annual Report and data analysis results at the Nova Scotia Ministry of the Environment and helped ministry staff to make decisions to install one new station in Nova Scotia (near Cape Breton Highlands National Park) and to upgrade the existing site. NAtChem staff also responded to 72 other data and analysis requests.

2.1.7 <u>Assessment of Excess Sulphate Deposition</u> - D.M. Whelpdale

This project was undertaken in cooperation with B.L. Beattie and K.N. Keddy (AEB, Bedford). The objective of this project is to estimate the magnitude and distribution of wet sulphate deposition which is in excess of environmental objectives (target load and critical load) during the various stages of implementation of sulphur emission controls in North America.

Projected wet sulphur deposition fields for eastern Canada for the years 1994 to 2010 were derived from AES LRT model runs. These were used with (i) the current target load value of 20 kg ha-1 y-1, and (ii) the spatially variable critical load values derived for the 1990 assessment to determine the magnitude and distribution of excess wet sulphate deposition. Temporal changes in total area receiving excess sulphate deposition and in the total mass of this deposition were determined. The change is shown in Figure 1.

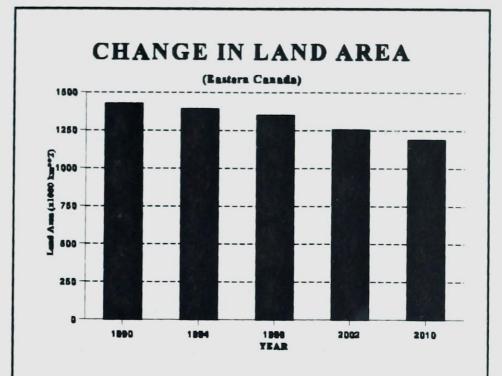


Figure 1: Change in land area in eastern Canada with excess sulphate deposition greater than critical loads

The current Canadian and American sulphur emission control programs will succeed in lowering wet sulphate deposition to less than the target load value of 20 kg ha-1 y-1 at almost all locations in eastern Canada by early in the next century. However, large areas of eastern Canada will continue to experience wet sulphate deposition that is in excess of the more stringent critical load values. Areas whose critical loads are greater than about 14 kg ha-1 y-1 should be protected, but others, whose critical load may be as low as 8 kg ha-1 y-1, will not be. Analysis of the uncertainties in the model projections, the meteorological and chemical data, and the methods used, suggests that the estimated excess sulphate deposition values may well have uncertainties of more than 50%. Work is underway to better quantify and reduce these uncertainties.

2.1.8 Arctic Aerosol and Precipitation Chemistry

- L.A. Barrie, J. Kovalick and D.L. Toom

Routine measurements of 18 aerosol constituents that began in 1980 have continued at Alert. Important trace constituents, such as SO₄, Pb, V, Mn, Cu and Zn, as well as indicators of sea salt and soil dust, are measured. Health Canada used the Arctic filter archive generated from this effort to make Alert part of the National Monitoring Network for Radioactivity. In addition, in cooperation with the University of Calgary, samples are being analyzed for isotopes of sulphur to give a better insight into the components of Arctic haze anthropogenic sulphur.

In parallel with aerosol chemistry observations, this project has generated the first comprehensive observations of major ions in precipitation in the high Arctic. Four years of weekly samples collected between 1990 and 1994 have been analyzed and a paper is in preparation that compares the snowfall composition with that of aerosols. It also compares snowpack samples from the Arctic ocean with daily snowfall samples taken during Polar Sunrise Experiment 1992.

2.2 NOx/VOC MANAGEMENT PLAN

2.2.1 Program Management

- M. Lusis

This program furthers our understanding of the photochemical oxidants problem in Canada, and provides sound scientific information for Phase II NOx/VOC Management Plan emissions control measures.

The severity and extent of the oxidants problem in Canada was determined through the analysis of available datasets in impacted areas. The analysis assessed the frequency that the ozone objective was exceeded and the associated meteorological conditions, the long-term trends and the importance of transboundary transport. A quality assurance plan was developed for a national monitoring network established to determine the effectiveness of control strategies.

Another major area was the development of long-range transport models for oxidants and their precursors which can be used to guide control strategy development.

2.2.2 CAPMoN Ozone and NOx Measurements

D. MacTavish, R. Vet, W. Kobelka, A. Gaudenzi,
 M. Underwood, S. Iqbal and S. Ahmed

Continuous ozone measurements were maintained at eight of CAPMoN's air and precipitation monitoring sites.

Operations were coordinated and supported from Downsview and managed by DOE Regional Inspection Staff. The TECO model 165 ozone generator failed to meet expectations as a potential audit instrument and was replaced with the TECO model 49PS calibration instrument.

The year 1994 was the first year of a formal annual audit program designed to document and ensure the accuracy and quality of CAPMoN's ozone data. The 1993 ozone data set was finalized and submitted to the National Air Pollution Surveillance (NAPS) data base.

2.2.3 Ozone Data Analysis

- K.Anlauf, K. Hayden, J. Fuentes, J. Bottenheim, R. Hoff, F. Froude and A. Wiebe

Analyses were carried out of various data sets, in order to advance our understanding of the tropospheric ozone problem in Canada. Ozone data from Mount Sutton Ridge, Sutton Valley and Mt.Tremblant were fully abstracted and

corrected for 1986-1994. There was no observable trend in the annual average ozone levels at these sites. The analysis is ongoing.

A regional analysis of long-term ozone trends in Canada (including the Lower Fraser Valley, Edmonton and Calgary, the Windsor-Quebec City region and the Southern Atlantic region) was carried out. Hourly ozone concentrations were obtained and analysed using two approaches. First, statistical methods, using time series analysis principles, were employed to determine long-term ozone trends for individual monitoring sites. Then principal component analysis was used to identify groups of stations, representing regions within the above domain, whose ozone data sets exhibit similar statistical characteristics. Once regions were so delineated, ozone data for all stations within a given region were segregated to determine long-term trends using time series analysis.

By this technique, five regions in Canada were identified as having similar ozone regimes (see Table 1). Only the Lower Fraser Valley and Southern Atlantic region showed statistically significant declining ozone levels during the 1982-1993 period.

Region Name	Ozone Trend (% per year)
Lower Fraser Valley Calgary-Edmonton-Winnipeg SW Ontario SE Ontario and southern Quebec Southern Atlantic	-0.2 +1.5 +1.5 +1.8 -1.7

Table 1: Ozone trends in Canada

Extensive analyses were also carried out of data collected during the PACIFIC'93 field study. These were presented at a special session on PACIFIC'93 at the AGU Conference in San Francisco, December 1994.

2.2.4 Development of Measurement Methods

- K. Anlauf, J. Bottenheim, S.-M. Li, F. Hopper, P. Brickell, A. Gallant and A. Gaudenzi

Laboratory sensitivity tests of the TECO 42S NOx analyser to PAN and HNO₃ interference were carried out. The significance of PAN interferences under field conditions was assessed by operating the TECO 42S analyser concurrently with ambient PAN measurements at the CARE facility (Egbert, Ontario) and Kejimkujik in Nova Scotia. The results of these tests are being evaluated.

A cryogenic VOC preconcentration system was assembled and tested, and was subsequently interfaced with an HP Chemstation software package running on a PC for data acquisition and valve switching automation. The system underwent an initial evaluation during the Arctic Ocean

Expedition in the summer of 1994. Components were purchased for the continuous HNO, monitor, and are now being assembled. Improvements to continuous measurement of CO at background concentration levels were implemented by modifing commercially-available instruments.

2.2.5 Optical Properties of the Troposphere

- R. M. Hoff, K. B. Strawbridge, A. Sheppard and M. Harwood

This project has been the umbrella for AES lidar research for three years. This year, the prime experiment was the LITE (Lidar In-Space Technology Experiment) mission which flew on the Discovery space shuttle in September 1994. As part of the experiment, Dr. R. Hoff served at Houston Mission Control as one of the three shift Project Scientists. This allowed direction of the targets to be observed by the spaceborne lidar and first-hand observation of the real-time data returned from the shuttle. The experiment was a great success with over 50 observing hours of data taken around the globe. Highlights included the observation of two hurricanes (including the "eye" of Typhoon Melissa in the Pacific), large-scale tropospheric aerosol masses from desert dust and biomass burning sources, continual observation of the residual Pinatubo aerosol cloud, and surface reflectance measurements from land and ocean. Use of lidar from space now seems assured with the success of LITE. Future small satellite packages are on the drawing board.

The rest of the lidar team, along with D. McKay, A. MacDonald, S.-M. Li, R. Leaitch, W. Strapp, M. Wasey, C. Banic, K. Sung and the Convair Crew from IAR/NRCC in Ottawa, went to California to participate in the LITE Validation Experiment. The results of this underflight mission were very successful with the observation of anthropogenic plumes from Los Angeles, San Francisco and Bakersfield in California, and Phoenix in Arizona, while the space shuttle was gathering similar data. The results from the mission are being highlighted this spring in seminars at AES and at the Spring AGU Meeting. In addition, AES is preparing a video on the mission which it is hoped will get wide public distribution.

2.2.6 NOx/VOC Model Evaluation

- M.Olson, K.Oikawa and B.Pabla

The contract which was let through CIRAC (Canadian Institute for Research in Atmospheric Chemistry) to conduct a model evaluation project for the oxidant models participating in the Windsor-Quebec Corridor/Southern Atlantic Region (WQC/SAR) modelling project continued during this period. These models were: ROM 2.2, GESIMA/ADOM, ALOM (Lagrangian Oxidant Model with ADOM chemistry), and a new modelling system MC2/ADOM. The models were run on the first test period (August 1-6, 1988) and all, except MC2/ADOM which is in the test phase, were tested against EMEFS1 (Eulerian Model Evaluation Field Study Summer Intensive) and other network data, including the coarse mesh ADOM127 which had

already been run for EMEFS1. The model evaluation results have been published in a CIRAC data report and an Interim Modelling Working Group Phase 1 draft report is nearing completion.

2.2.7 NOx/VOC Model Enhancements

- J. Pudykiewicz and A. Kallaur

The main objective of this project is to couple the MC2 model with the chemical tracer model (CTM) featuring an accurate advection algorithm, and comprehensive oxidants chemistry and deposition modules. The emissions inventory for the Eulerian Model Evaluation Field Study Summer Intensive (EMEFS1) period, including point sources, biogenic sources and mobile sources, was installed on a computer system and verified. The MC2 model was run for a period of ten days during August 1988 to generate the meteorological fields for ozone episode simulation. These fields were then used in a simulation of the regional scale NOx/VOC chemistry (ADOM 1989 version) on a 40 km grid with twenty-one vertical levels centred over the Windsor-Quebec Corridor. The model simulated correctly the shape of the observed surface ozone distribution, and reproduced relatively well the observed maximum ozone concentrations. Results are currently being evaluated in detail (see 2.2.6).

2.2.8 ADOM Chemistry Module

- P. Makar, S-M Li and J. Bottenheim

Two main studies are in progress to examine the extent to which the problems in ADOM (Acid Deposition & Oxidant Model) with predicting ozone maxima are due to the chemistry module.

The first of these was a comparison between the gas-phase chemistry algorithm used in ADOM and a more accurate solver based on the work of Gear in 1971. ADOM's module uses a slightly altered version of the algorithm of Young and Boris published in1976. The two algorithms were used to perform 1195 half-hour chemistry integrations for a multi-day diurnal run located at Toronto for July 1-6, 1994. Most of the advected species showed relatively little change between ADOM and Gear numerics; all of the ozone results showed less than a 1% difference between solution methods. However, for some of the species (usually at low concentrations, NO being an example) the errors were high. The higher NO errors have since been corrected by making minor changes to the ADOM solver.

To determine whether the ADOM solver resulted in errors which increased over time, a five-day simulation was performed with each method. The Gear code produced 4 ppbv more ozone than the ADOM numerics over 5 days. This trend shows that the ADOM chemistry solver is biased towards lower ozone concentrations, but the bias is small and unlikely to affect the results of ADOM for ozone episodes. In conclusion, the gas-phase chemistry numerics used in ADOM have a slight tendency to underpredict ozone, but

this effect is not sufficiently pronounced to be the cause of the large underpredictions resulting from the entire model.

The second study examined the input to the chemistry module; the ADOM reaction mechanism itself. In the Eurotrac Mechanism Intercomparison, tropospheric chemistry mechanisms were compared by researchers in several countries (Germany, Norway, United States, Canada, Netherlands, United Kingdom and France). Each participant was given the same sets of initial conditions. From these, multi-day simulations of tropospheric chemistry were made. The results were compared for several key species, e.g., O_3 , NO, NO₂, HNO₃, HNO₄, H₂O₂, ROOH and HCHO.

The main results showed that all of the mechanisms had similar results for O₃ in the "plume" cases, with concentrations in excess of 100 ppbv by the sixth day of simulation. When photolysis rates supplied by Eurotrac were used, the ADOM mechanism O₃ results were midway between all mechanisms tested. When the photolysis rates from ADOM's rate routine were used, the ADOM results on the sixth day have the lowest ozone. All of the other mechanisms are more recent than MC2/ADOM, implying that the photolysis rates currently in use in the regional ADOM model will have a tendency to underpredict ozone. After six days of simulation, this may result in an ozone deficit of 19 ppbv, in comparison to other mechanisms.

The variation in results was much greater for some species, e.g., H_2O_2 and ozone. Maxima for H_2O_2 varied up to a factor of 2 between different mechanisms, while the O_3 variation was in the tens of percent range. Therefore, most current mechanism formulations are more likely to produce similar ozone concentrations than similar results for other species.

The update of the ADOM mechanism is concurrently taking place. An examination of the techniques used to combine or "lump" hydrocarbon reactions in the ADOM and RADM reactions has resulted in an improved technique. These changes will have a significant effect on the production rates of aldehydes, e.g., HCHO, from the previous version, but initial tests indicate little change in ozone concentrations.

2.2.9 <u>ADOM Dry Deposition Module</u>J. Padro, L. Zhang and W. Gong

The modelling of dry deposition of NO, NO₂ and O₃ was studied, including the possibility for chemical reactions. The results showed that it is important to include chemical reactions in computing the dry deposition of NO and NO₂, but they do not appear to be essential for O₃. These reactions are currently being incorporated in the dry deposition module for MC2/ADOM.

2.2.10 <u>Dry Deposition</u> - J. Padro

A paper was written that provided computations which included the chemical reactions of NO-NO₂-O₃ when

computing the dry deposition of these species. The chemistry can make a difference to the dry deposition in some cases.

Another paper determined whether or not dry deposition of ozone and sulphur dioxide can be computed more accurately in air quality models using a multiple-layer dry deposition module or the more simple one-layer bulk models. Some computations were made using measured and ADOM modelled sulphur concentrations, and ADOM modelled dry deposition velocities to estimate area averages of dry deposition in Eastern North America. These were done for the 1988 EMEFS measurements.

A summary paper on dry deposition modelling in AES is presently been prepared.

2.2.11 <u>Mesoscale Flow in the Southern Atlantic Region</u> - W. Gong

A numerical study was carried out to define the characteristics of the mesoscale flow and marine/coastal boundary layer in order to assess their impact on the oxidants in the Canadian Southern Atlantic Region (SAR).

Numerical simulation of the flow over SAR during the NARE93 summer intensive campaign was conducted. The simulation period, August 27 - 29, 1993, coincided with a ground-level ozone episode in the region. A series of self-nested MC2 model runs were performed for the simulation with horizontal resolutions cascading from 100-km to 5 km with an intermediated grid resolution of 25 km. The initial coarse grid runs were driven by CMC global objective analysis. Preliminary model results, especially from the fine resolution runs, have revealed some interesting features of the flow at lower levels in that region which offers some explanation to the behaviour of the ground-level ozone.

2.2.12 MC2/ADOM Modelling of SAR Oxidants - W. Gong

The ADOM meterological driver was replaced with the newly-developed mesoscale, compressible, community model -- MC2. The new MC2/ADOM modelling system will have self-nesting capability to allow higher resolution modelling focused on the area of interest. This modelling system is expected to be applied to the SAR, in time to assist with the 1996 NOx/VOC Management Plan Assessment.

The development of the MC2/ADOM modelling system involves establishing an interface between MC2 and ADOM, and modifying of the ADOM boundary conditions (concentration) so that they will be temporally variable. Most of the meteorological fields required by ADOM can be extracted readily from MC2; others can be derived from the model results.

For the SAR application, a base simulation of the EMEFS1 intensive period (August 1988) will be carried out. This

base simulation will be compared with the EMEFS field data, and intercomparisons with other models involved in the CIRAC model evaluation program will also be performed. Model evaluation will be further achieved through sensitivity tests, and the emission scenario runs will follow only after the modelling system being reasonably evaluated. The simulation will be conducted on two grids: a coarse grid with a horizontal resolution of 127 km; and a nested fine grid with a resolution of 21 km focusing on the SAR.

The interface between MC2 and ADOM has been developed. ADOM has been run successfully with the meteorological fields generated from MC2 on the 127 km grid. Test runs are being conducted for the fine resolution grid to establish the nesting mechanism for ADOM.

2.2.13 <u>Investigation of Ozone Formation</u> - M.Olson

The AES Lagrangian Oxidants Model (ALOM) was used to test various modelling assumptions and carry out sensitivity runs, and was run for the EMEFS1 period. The model was also used in a number of preliminary emission scenario evaluation runs.

ALOM was run to test the importance of a nocturnal boundary layer, morning entrainment of ozone trapped aloft and their effects on maximum ozone concentrations. A nocturnal boundary layer was found to be very important in simulating minimum overnight ozone concentrations, and in trapping ozone aloft during the night. The height of this nocturnal layer was not critical in simulating the afternoon ozone maximum, but the value of the concentration trapped overnight and entrained during the morning was crucial. This effect allowed the model to produce the high afternoon concentrations observed during EMEFS1.

Several sensitivity runs were also made to examine ALOM's reaction to changes in emissions, initial conditions and mixing heights. The results were very informative and are reported in Windsor-Quebec City Corridor -Southern Atlantic Region NOx/VOC Modelling Working Group Phase 1 Model Evaluation Interim Report.

The results of the EMEFS1 model evaluation showed that ALOM was capable of simulating well the diurnal ozone variations, high afternoon peaks, as well as overnight values, and produced correlations comparable to the more complex Eulerian models, as well as acceptable geographic ozone distributions and system movement.

2.3 AIR TOXICS

2.3.1 <u>Integrated Atmospheric Deposition Network</u>
 R. M. Hoff, F. A. Froude, F. Maclean, B. Martin,
 J. Woods, K. A. Brice, K. Su, L. Liao,
 N. P. Alexandrou, B. Sukloff and S. Cussion

The Integrated Atmospheric Deposition Network (IADN) is

a binational program to assess the input of toxic chemicals to the Great Lakes and their basin. Currently, Point Petre, Burnt Island and Egbert are the AES stations in the network.

In June 1994, a workshop was held at Windsor, Ontario, to synthesize the air, water and precipitation information from the Great Lakes research community and to produce 1994 estimates of the loadings of toxics to the lakes. A journal article is being prepared of the results.

By mid-1995, it is expected that the IADN data for trace elements, total suspended particulates and total organic carbon will be published complete through to 1994. The intent is to have similar completeness for the organics data for Point Petre through to 1992 with analysis completed for the Point Petre station PAHs through to 1993.

2.3.2 Organics Analysis Laboratory

 K.A. Brice, N. Alexandrou, K. Su, L. Liao and M. Shoeib

The Organics Analysis Laboratory (OAL) provides an inhouse service for the determination of trace organic chemicals in air samples, meeting responsibilities within the binational Integrated Atmospheric Deposition Network (IADN) mandated by Annex 15 of the Great Lakes Water Quality Agreement. The target organic species selected for "semi-routine" determination include polychlorinated biphenyl congeners (PCBs), organo-chlorine pesticides (OCs) and polycyclic aromatic hydrocarbons (PAHs). Samples are regularly collected at three Canadian IADN sites: Point Petre (PTP), Burnt Island (BI) and Egbert (EGB). Ambient samples for trace organics are collected using the PS-1 sampler, which employs a glass-fibre filter (GFF) for particle retention, followed by a polyurethanefoam (PUF) cartridge as a vapour-phase adsorbent. The two sample components are analysed separately to provide "operationally-defined" information on phase distributions.

The backlog of unanalyzed samples from the network continues to be a major issue. In an effort to reduce this backlog, a decision in April 1994 changed sampling to a 1 day-in-12 frequency, reducing the number of samples collected annually at each site by a factor of 2. Furthermore, to provide the fastest possible route to obtaining a reasonable degree of data coverage for all three sites, it was decided in October 1994 to adopt a similar 1 day-in-12 analytical frequency for PTP from 1993 onwards and potentially for EGB and BI retroactively to 1990 and 1993, respectively. Data obtained in this basis would still provide good overlap with the sampling/analysis schedules utilised at the US sites. Over the past twelve months, excellent progress has been made with the analysis of samples for PAHs, but it has proved difficult to significantly accelerate the task of PCBs/OCs determination because of its inherent complexity. and need for experienced manual interpretation and confirmation. However, the decisions on sampling and analytical frequency have already produced some notable improvements in the temporal coverage.

For PTP PUF samples, data are now available for PCBs/OCs (January 1990 to December 1993) and for PAHs (January 1990 to June 1992. For PTP GFF samples, data are available for PAHs (January 1990 to January 1994): for PCBs/OCs, the ambient levels are close to instrument detection limits so that little useful data can be obtained. Limited data are available for the BI and EGB sites.

OAL has been active in developing and ultimately implementing new or improved analytical methods and procedures for organic contaminants. Three special projects were undertaken this year.

- 1) Application of multi-dimensional gas chromatography (GC-EC) to measurements of co-planar PCBs: Archived extract fractions from ambient air samples (vapour phase and particle-bound) taken at Point Petre during 1990 have been re-analysed, with 12 typical sampling periods being selected, to generate a "snapshot" of seasonal trends and partitioning behaviour. A report on the data analysis is in preparation.
- Development of analytical procedures for determination of toxaphene in air samples using electron capture negative ion mass spectrometry (ECNI-MS): The performance of the MS-Engine mass spectrometer in ECNI mode for toxaphene has been optimised for source temperature, methane CI gas pressure and ion selection for SIM acquisition. Attention has been given to the establishment of a valid calibration approach for this complex, multi-component species to comparisons with earlier data obtained by GC-EC techniques where "congener clusters" were typically reported. The issue of possible co-elution of important toxaphene components with PCBs and other OCs has been fully addressed. Preliminary measurements of toxaphene have been made in a number of archived extract fractions from PTP PUF air samples taken during 1992.
- Evaluation and implementation of supercritical fluid extraction (SFE) techniques for extraction of exposed glass fibre air sample filters (GFF) and subsequent determination of PAHs, PCBs and OCs. A series of matrix spike runs and Soxhlet/SFE comparisons using actual exposed air sample filters were intended. However, difficulties arose in reproducing the system performance achieved in the earlier tests: investigations showed that a dominant reason for poor recoveries was the poor collection efficiency achieved by the solvent collection vial downstream of the outlet restrictor. Substantial carry-over into additional traps included in series was observed. Possible reasons as to the non-observation of this mechanism during earlier work are unclear at present.

2.3.3 <u>GLWQA Quality Assurance</u> - S. Cussion

The Quality Assurance Program Plan (QAPP) for the Great

Lakes Water Quality Agreement (GLWQA) Integrated Atmospheric Deposition Network (IADN) received final approval by all agencies and was signed by the Canadian and U.S. Representatives to the International Joint Commission (IJC) in May 1994. Printing and distribution of the document to all agencies was completed by September 1994.

The results from Phase 2 of the IADN Interlaboratory Study Project were collected from the participating laboratories and subjected to evaluation and analysis. Reports were prepared and submitted for peer review, followed by printing and distribution: the report for the Study 93-4 (PAHs) was still outstanding as of March 1995.

In August 1994, a workshop was organised to develop a design for Phase 3 (Matrix Spikes) of the IADN Interlaboratory Study. Studies were proposed as follows:

- Spiking of target trace metals on filters (ambient air) and in precipitation;
- o Spiking of target organics (PCBs, OCs and PAHs) on filters and adsorbents (ambient air);
- Spiking of target organics (PCBs, OCs and PAHs) into precipitation, followed by passing through collection columns and distribution;
- Collection of a bulk air sample for organics, followed by extraction and splitting for distribution.

2.3.4 <u>Atmospheric Sources of Pesticides (Great Lakes)</u> - T. Bidleman

During the 60s and 70s large quantities of organochlorine (OC) pesticides were used in the U.S. "cotton belt". Trajectory analysis of sampling events at Egbert, Ontario, provides strong evidence that air currents arriving from the southern U.S. carry elevated levels of OC pesticides. In August 1994, a pilot project measured the atmospheric concentrations of OCs in the southern states and examined agricultural soils for OCs. From August 1994 to January 1995, air samples were collected in Columbia, South Carolina. Mean levels of chlordane and toxaphene from this sampling period were 5-10 times higher than those at Egbert in 1989. Three soil samples from Alabama cotton fields contained 40-200 ng/g toxaphene and 10-450 ng/g DDT residues, indicating that substantial quantities of OCs remain and are available for volatilization.

A record of chlordane concentrations in Columbia air is available which goes back to 1979. The main use for chlordane since the early 1970s was for termite control. A large number of homes in the southern U.S. have been treated with chlordane and/or heptachlor. The pesticide was banned in 1988 and replaced with the organophosphate chlorpyrifos. Air collections are continuing to determine whether levels of chlordane in air are declining. Samples collected within a few years of the ban (1989-92) do not

appear to be lower in chlordane, but the 1994 results suggest a slight drop compared to pre-1988 levels. The remaining air samples need to be analyzed and the results statistically evaluated before making conclusions.

2.3.5 <u>Canadian Global Emissions Inventory Centre</u> - Y.-F. Li

The need for accurate and complete emissions data is recognized internationally. The compilation of global data on emissions of a wide range of pollutants to the atmosphere is a first step in designing and implementing pollution control strategies, and is also essential in assessing specific regulatory programs once they are in place. To serve both the national and international scientific and policy-making communities, Environment Canada, in conjunction with ORTECH Corporation, has recently established the Canadian Global Emissions Inventory Centre (CGEIC).

CGEIC is a comprehensive emissions inventory service, available to the scientific, industrial and policy-making communities. The primary purpose is to provide data for mathematical models, and to evaluate strategies to minimize the impact of atmospheric pollutants. Establishing the sources of pollutants is a first step towards reducing their levels in the environment. The analysis of emission trends is also important in developing ways to manage such chemicals more effectively.

The objectives of CGEIC are:

- o to play an important role in facilitating the exchange of emissions data between Canada and other countries;
- o to compile emissions data on chemical species of concern;
- to provide up-to-date, quality-assured emissions data in customized form;
- to implement and apply sophisicated emission models;
- to assemble global meteorological, climatological and geophysical data for input to models; and
- to develop and apply advanced methods for data management.

2.3.6 <u>Emissions Inventories</u>

- E. Voldner and Y. -F. Li

It is important to establish reliable emission inventories in order to understand the atmospheric pathway, to interpret measurements, to assess the importance of bioaccumulation and to assess control options. Models require inventories to estimate net deposition and to establish source/receptor relationships.

The Canadian Global Emissions Inventory Centre (CGEIC) is participating in a number of international activities, such as the International Geosphere-Biosphere Program and the various UN ECE Working Groups. The primary purpose of CGEIC is to provide emissions inventory input for a variety of environmental modelling activities, such as:

- O CGEIC has produced global gridded emissions inventories at 1x1 degree latitude/longitude resolution under the Global Emissions Inventory Activity (GEIA), a component of the International Global Atmospheric Chemistry Project (IGAC). Global gridded SOx, NOx, lead and VOC (volatile organic compounds) inventories have been produced.
- o Population is frequently used as a surrogate for the distribution of emissions when actual emissions or usage data are not available. A population data base on a 1° x 1° latitude/longitude grid is being developed for the year 1985. The development of a 1990 population data base is a further planned project for CGEIC.
- O CGEIC started a project with the Environmental Protection Agency of Shanxi Province, China. This project includes creating a database to store population statistics, data on emission sources, and ambient air and water monitoring data. A processing system is being developed to produce gridded data sets for the province on 1/6° x 1/4° latitude/longitude grid for pesticide usage rates, and emissions of SOx, NOx and lead.

2.3.7 <u>Sorption of PCBs to Urban Aerosols</u>

- T. Bidleman, R. Falconer and T. Harner

This project, supported by the U.S. Environmental Protection Agency, emphazises "coplanar" polychlorinated biphenyls (PCBs) -- congeners which have four or more total chlorines and none or only one ortho-substituted chlorine. The goals are to determine concentrations of coplanar PCBs in ambient air and test the hypothesis that ortho-chlorine substitution patterns affect partitioning of PCBs to urban aerosols. Preferential sorption of coplanar PCBs may enhance their wet and dry deposition inputs to the Great Lakes. The coplanars contribute substantially to dioxin-type toxicity in fish, marine mammals and aquatic birds.

Three approaches were used to gauge the ability of PCBs to associate with urban aerosols: a) predictions based on vapor pressure, using the Junge-Pankow adsorption model, b) field measurements of particle/gas distribution in Chicago, and c) laboratory experiments in which filters loaded with Chicago particulate matter were exposed to gaseous PCBs in a laboratory equilibration chamber at constant temperature and humidity. The conclusion, from all three methods, was that particulate percentages of coplanar PCBs were higher than for PCBs having multiple ortho-chlorines.

This study was a major part of Renee Falconer's dissertation research for a Ph.D. in chemistry (University of South Carolina, August 1994). Tom Harner, a Ph.D. student at the University of Toronto, is continuing this project by determining particle/gas partition coefficients for different classes of aromatic compounds and carrying out laboratory experiments to distinguish between adsorption and absorption mechanisms. Air samples were collected in Chicago during March 1995 to measure PCBs, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated naphthalenes (PCNs), and to compare the particle/gas distributions for these three classes of aromatics. A laboratory system has been set up to measure octanol/air partition coefficients (Koa) for PCBs. The intent is to use Koa as a surrogate for PCB partitioning (absorption) into organic liquid films on aerosols and vegetation. Values of Koa have been measured at -10 to +30°C for a series of tetrachlorobiphenyls having three (PCB-53), two (PCB-49), one (PCB-66) and zero (PCB-77) ortho-chlorines. The octanol/air partition coefficients increased with decreasing number of ortho-chlorines. K_{oa} for PCB-77 was nearly 40 times higher than for PCB-53. An absorption model based on vapor partitioning into a liquid film also predicts that coplanar PCBs will be enriched on aerosols.

2.3.8 <u>Toxaphene and Hexachlorocyclohexanes (Arctic)</u> - T. Bidleman and L. Jantunen

This work is supported by DIAND. Goals are to: a) determine concentrations and compare the gas exchange rates of toxaphene and hexachlorocyclo-hexanes (HCHs) in arctic waters; b) determine the physicochemical properties of toxaphene that affect its atmospheric transport and deposition; and c) characterize the changes in the toxaphene complex mixture that accompany its transfer from air to water to the lower food chain. Three field trips have been made to collect air and water samples from arctic and subarctic regions: Resolute Bay (August-September 1992); the Bering and Chukchi seas (BERPAC-93, August-September 1993); and the Arctic Ocean Sections cruise (AOS-94, July-September 1994). Conclusions from the Resolute Bay and Bering-Chukchi studies were published.

Approximately 20 air and 45 water samples were taken along the AOS-94 cruise track across the North Pole from Nome to Halifax. Preliminary results from the air samples show low values for α -HCH (66 pg/m³), in line with the downward trend seen for post-1990 measurements at Resolute Bay and the Bering-Chukchi seas. The mean for γ -HCH (16 pg/m³) is also typical of recent values from other arctic locations.

2.3.9 <u>Pesticides as Tracers of Biogeochemical Processes</u> T. Bidleman

This project is supported under the Great Lakes Water Quality Program, and has the overall goal of developing techniques to distinguish "old" and "new" sources of atmospheric pesticides. Certain chiral pesticides exist as right- and left-handed enantiomers, which are in a 1:1 ratio (racemic) as manufactured. Because enzymes are also chiral molecules, soil microbial activity may lead to preferential degradation of one enantiomer. The result would be an enantiomeric ratio (ER) which differs from racemic. The ER signature may thus serve to differentiate soil-volatilized from newly-applied pesticides. Objectives for the first year were to develop methods of analysis for chiral OC pesticides, to apply the technique to pesticide residues in soils, and to investigate the ERs of chiral pesticides in arctic air and water.

There has been good success separating the enantiomers of α -HCH, the chlordanes and o,p'-DDT using a combination of cyclodextrin columns from different manufacturers. Work has begun with Alexander McNeish, University of Liverpool, to determine the enantiomeric composition of methylhexachlorocyclohexanes (MHCHs) in the Mersey River Estuary. Biota in the estuary are contaminated with MHCHs, which are industrial by-products of the photochlorination of toluene. The MHCH enantiomers have been separated on the same columns used for HCHs. The compound, α -MHCH, appears to be enantio-selectively degraded in three fish species and mussels.

This work with chiral pesticides has established AES as a North American leader in this field. Nearly all enantiomeric work on pollutants has been done in Europe. Two recent papers are the first publications of this type from Canada. To stimulate interest, a symposium has been organized on "The Analytical and Environmental Chemistry of Chiral Pollutants" to be held at the SETAC World Conference, Vancouver, in November 1995. Co-organizers are Renee Falconer (Youngstown State University, formerly at AES), Laura McConnell (U.S. Dept. of Agriculture), Hans-Rudolph Buser (Swiss Federal Research Station) and Terry Bidleman.

2.3.10 <u>Photochemical Reactions of Naphthalene</u> - D.A. Lane

The project objective is to determine the products of the reactions of polycyclic aromatic hydrocarbons (PAHs) under simulated atmospheric conditions. The research being carried out at York University is a collaborative effort between Dr. Don Hastie (York University), Dr. Paul Shepson (Purdue University) and Dr. Nigel Bunce (University of Guelph). Several graduate students from York and Guelph Universities are currently using the chamber for their thesis research.

The work carried out during the fiscal year addressed, specifically, the reaction of naphthalene with the OH radical in the 10 m³ smog chamber at York University. The irradiation source was designed to optimize the production of the OH radical and not to simulate atmospheric sunlight. A stream of pure air passed through a heated (50°C) glass tube containing naphthalene crystals carrying naphthalene vapour into the chamber. When the concentration of naphthalene reached the desired initial concentration, as determined by an

on-line gas chromatograph, isopropyl nitrite and gaseous NO in nitrogen were added to the chamber. A fan in the chamber ensured that effective mixing of the reactants occurred. The lights were turned on for a specified period of time, ranging from a few seconds to a few minutes, after which the lights were turned off and a gaseous sample was withdrawn from the chamber and passed through a liquid nitrogen cooled impinger. The collected sample was taken up in dichloromethane and then analysed.

The reaction was pseudo first order with respect to naphthalene. Products detected to-date include, besides unreacted naphthalene, 1,2-benzenedicarboxaldehyde, phthalic anhydride, 1(3H)-isobenzofuranone, 1,4-naphthalenedione, 4-methyl-2H-1-benzopyran-2-one, 1-naphthol, 2-naphthol, 2-formylcinnamidehyde, 1-nitronaphthalene, 2-formylcinnamic acid, 2-nitronaphthalene, 4-nitro-1-naphthol, 2 nitro-1-naphthol, 1,4-naphthoquinone-2,3-epoxide, 2,4-dinitro-1-naphthol, phthalic acid, 3-nitrophthalic anhydride, and several other cinnamaldehyde derivatives. It should be noted that the hydroxynitro- and dinitro- derivatives are suspected of being extremely potent, direct acting mutagens. At present, less than half of the products have been identified.

Recently, the quantum chemical modeling programs, developed by Scott Fielder and Stanley Townsend of York University, have been applied to the naphthalene reactions being investigated. Very promising results have indicated that it should be possible both to predict products of the reactions and to assess the veracity of mechanistic pathways determined from a classical chemical approach.

2.3.11 <u>Gas and Particle Measurements of PAH</u> - D.A. Lane

The objective has been to improve gas/particle partition measurement instrumentation and techniques for semivolatile organic compounds (SVOCs), in general, and for polycyclic aromatic hydrocarbons (PAHs), in particular.

Between 1983 and 1988, AES and ORTECH developed an instrument (the GAP sampler) for collecting atmospheric samples to determine the gas/particle partition ratio of SVOCs. The sampler comprises two sampling trains: one to collect the total air sample; the other, after trapping the gas phase components on a multi-annular diffusion denuder, to collect the particle phase. The vapour phase is determined by measuring the difference between the results from the two sampling trains. Over the past 3 years, scientists at the Lawrence Berkeley Laboratory (LBL) have developed the Integrated Organic Vapour and Particle Sampler (IOVPS) which is, also, an annular diffusion denuder sampler. The IOVPS denuder coating can be efficiently solvent extracted to yield a direct measurement of the gas phase components of interest. Although the GAP sampler is large and expensive, and requires a difference determination to obtain the vapour phase, it has a high capacity for SVOCs and can be used for long sampling times (24-48 h). The IOVPS, on the other

hand, is small and inexpensive, and allows direct vapour phase determinations, but it has low capacity and can be used only for a maximum of 3 hours.

A collaborative development program was proposed and initiated with LBL to combine the two technologies to produce a single sampler capable of carrying out high capacity, 24-hour sampling, yet permitting direct analysis of the vapour phase component of the SVOCs. Two GAP samplers and 6 GAP multi-annular denuders were shipped to LBL, and two of the denuders were modified and coated according to the LBL method. To accomplish this, the LBL coating procedure had to be modified significantly in order to accommodate the much larger GAP denuders. In March 1995, air samples were collected with the modified GAP sampler and the IOVPS samplers at LBL. The samples are currently awaiting analysis.

LBL was successful in its application for a Cooperative Research and Development Agreement (CRADA) to transfer the denuder technology to a company in the private sector, and to assist this company in producing commercial samplers for measuring the gas/particle partition ratios of SVOCs in ambient air. A commercial sampler will be available within one year. The development and testing of the sampler will focus on the analysis of PAH.

2.3.12 <u>Aerial Application of Pesticides</u> - R.E. Mickle

Spray efficacy trials in Pinery Provincial Park were carried out to evaluate two treatments made with a gypsy moth virus. Meteorological data using tethered balloons and towers were taken to document the conditions during which the sprays took place. On board the Cessna 188 spray aircraft, positional information from a Differential Global Positioning Guidance system was logged each second intervals along with aircraft height, ground speed, flow rates and AU4000 atomizer rotational speed. These data were used as inputs to the AgDisp model to predict spray deposit for the spray block. Comparisons with measured deposits on oak leaves, artificial foliage and ground cards gave a linear correlation between predicted and measured deposit. The modelled deposits were then compared with pupal counts from burlap traps at a number of sampling sub-plots within the treated block. This comparison showed a strong correlation between predicted deposit and pupal counts. Using this technique, the fate of the sprayed pesticide can be predicted both on and off the block so that potential environmental impacts from operational spraying could be assessed.

2.3.13 <u>Establishing Buffer Zones in Canada</u> - R.E. Mickle

In 1989, the Canadian Interdepartmental Task Force on Pesticide Drift was formed to develop new regulatory guidelines in the registration of pesticides by assessing the potential for drift associated with a given use strategy. The outcome of this process would be an assessment of the expected environmental concentrations which, in association with the toxicology data already provided by the applicant, could be used to determine the environmental significance of the predicted drift and, if necessary, to estimate buffer zones as a mitigative measure. These predictions would rely heavily on scientific results from field trials that were compiled into a database or on scientifically-based models that had been validated against the database.

Early this year, Triclopyr, a silvicultural herbicide, received temporary registration in Canada for aerial application. As part of the agreement, DowElanco will provide to the provinces a copy of the FSCBG(AgDisp) computer model for estimating drift and establishing appropriate buffer zones. In response to this temporary registration, a 2-day course was developed to train attendees on the running of this model and to carry out case studies using the model to establish buffer zones for Triclopyr. To date, courses have been given in Toronto, Edmonton and Quebec City to 70 attendees from across Canada including federal and provincial regulators, forest pest managers, environmental inspectors and industry representatives. The course involved an intensive hands-on introduction to FSCBG given by Continuum Dynamics with emphasis put on the use of the Near Wake code with continuous deposition to the ground which is available in the advanced version of the model. Participants were able to explore the model utilizing an operational scenario relevant to forestry herbicide spraying and to investigate the impacts of various operational spray scenarios on buffer zones utilizing the Buffer Zone graphics package.

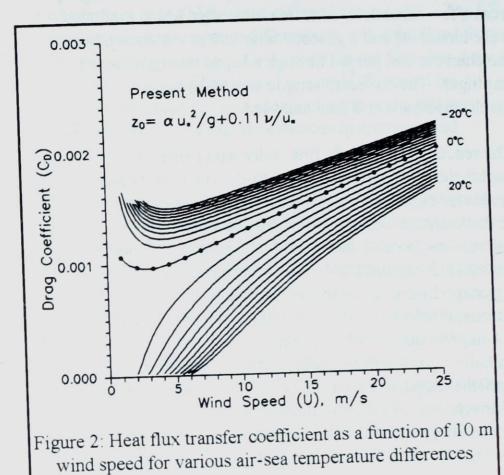
For each scenario, a range of operational sprays was evaluated to assess their impact on the size of buffer zones using specific biological endpoints from the Decision Document on Triclopyr. The impact of block size, aircraft/atomizer combination, aircraft height and meteorology were all explored in terms of their relevance to buffer zone size. The model provided the user an opportunity to observe the impact of operational parameters on deposit uniformity and drift fate.

This same model has also been used in Quebec and Ontario for aerial applicators to quantify the fate of pesticides for their particular use strategies. By tailoring the model to the specific aircraft setup, the output has been used to track the transport of the different emitted droplet sizes and investigate the influence of meteorology and aircraft height. Modification of nozzle location and nozzle type were investigated as alternatives to reducing pesticide drift.

2.3.14 Transfer Coefficients at an Air-Water Interface - A. K. Lo

An explicit method for evaluating transfer coefficients at an air-water interface was developed. In contrast to conventional bulk transfer methods using empirical formulae which tend to bias one's own data, the present method is based solely on boundary layer theory using air-water temperatures and a single level of wind speed as input data.

This method eliminates the need of site-specific empirical formula and thus can provide more efficient calculation and more accurate results on transfer coefficients. The transfer coefficients are shown in figure 2.



2.3.15 Northern Contaminants Monitoring - L.A. Barrie and D.L. Toom

Since 1992 routine aerosol and gas phase observations have been made in the high Arctic of Canada and Russia for potentially toxic substances. These include polycyclic aromatic hydrocarbons (PAHs) and industrial synthetic chemicals, such as polychlorinated biphenyls (PCBs), as well as agriculture persistent compounds, e.g., herbicides and pesticides. Currently, three years of weekly observations are available for Alert, N.W.T., and two years for Tagish, Yukon. In addition, two years of observations have been made at Dunay Island, Russia, at the mouth of the Lena River. Results of the data analyses have been published.

2.3.16 <u>Arctic Ocean Sections Expedition 1994</u> - L.A. Barrie

As part of a scientific expedition to study pollution, global warming and biology in the Arctic, Branch staff conducted research measurements aboard the ice-breaker Louis St. Laurent. The expedition took place in August 1994. The participants and the projects are listed in Table 2.

A workshop was held in December 1994 to discuss the preliminary data analyses. Along the transect, cloud condensation nuclei concentrations appear to be linked with the concentrations of dimethylsulphide in the Arctic ocean and atmosphere. Thus, it is likely that cloud optical properties such as solar reflectivity are affected at least in part by biogenic sulphur emissions. These data will be compared with satellite observations of cloud reflectivity and

possibly observations of clouds from the ship.

Measurements of organohalogens will help estimate the contribution of northern oceans to the chlorine, bromine and iodine available for ozone destruction in the atmosphere.

Carbon dioxide measurements in air, coupled with surface water measurements, will be used to estimate the exchange of this important greenhouse gas between the atmosphere and the ocean. Finally, observations in air and surface water of persistent organic compounds (herbicides and pesticides), that are potentially toxic to Arctic marine species and the humans that harvest them for food, will be useful in understanding the impact of global agricultural practices on the polar biosphere.

RESEARCH GROUP	AREA OF STUDY
S. Sharma/F. Hopper (AES)	Biogenic sulphur in air and water
M. Gosselin (U. Quebec/ Rimouski)	Marine sulphur production
M. Levasseur (DFO)	Marine sulphur production
J. Grovenstein/V. Saxena (U. North Carolina)	Physical properties of aerosols
R. Leaitch (AES)	Cloud chemistry and physics
F. Hopper (AES)	CO, O ₃ , black C, aerosols in air
D. Worthy/N. Trivett (AES)	CO ₂ , CH ₄ in air
L. Barrie/ D. Toom (AES)	Aerosol chemistry
R.Moore/C. Geen (Dalhousie U.)	Organohalogens in ocean water
T. Bidleman/L. Jantunen (AES)	Persistent organic compounds
Y. Yokouchi (NEIS/Japan)	Organohalogens in air
R. Krouse/Barrie (U. Calgary)	Aerosol sulphur isotopes
P. Brickell/J. Bottenheim (AES)	Non-methane hydrocarbons in air

Table 2: Participants and projects in the 1994 expedition

2.4 CLIMATE CHANGE

2.4.1 Program Management

- M. Lusis

The main thrust of this program is to monitor and research the effect of greenhouse gases on the climate. This is achieved by operating the Canadian Greenhouse Gas Monitoring Program at Alert, Sable Island, Estevan and Fraserdale and submitting the resultant data to the WMO World Data Centre. In order to understand behaviour/effects of air pollutants in the arctic, measurements of aerosol and snow chemistry, and of PAN, CO and O₃ were taken at Alert. Another major study was the Arctic transect icebreaker expedition in July and August 1994.

To understand the source/sinks of CO2 and CH4 and their

role in climate change, work was completed on the 2-D carbon cycle model in which the sensitivity of Alert CO₂ measurements to spatial source/sink distribution in the Arctic was evaluated.

2.4.2 Global Carbon Cycle/Climate Modelling

- K. Higuchi

Using the 2-dimensional global carbon cycle/climate model developed under a previous PERD (Panel on Energy Research and Development) project, the significance of some of the interactive processes between the global carbon cycle and the physical aspect of the climate system has been investigated in this present PERD project.

The project addresses those environmental scientific issues related to production of carbon dioxide and its impact on the climate and on global change. The results have impact on resource management in regards to fossil fuel consumption for energy generation, and to deforestation and reforestation in the forestry industry.

A 2-dimensional multi-level energy balance climate model coupled interactively to the second version of the land biosphere carbon cycle model has been produced. The oceanic component at the present time is a static 50 m mixed layer model. The original 2-dimensional ocean model (specified advection and diffusion) is now being replaced by a much more realistic 2-dimensional model with calculated advection in which the density field is a dynamically predicted parameter. The original simple inorganic marine carbon cycle model has been deleted. In its place, a modified version of the Fasham marine carbon cycle has been incorporated.

The model will predict with greater confidence the future evolution of the global carbon cycle, particularly with respect to the rate of rise in the atmospheric carbon dioxide due to anthropogenic perturbation. The global carbon cycle/climate model will thus be a useful tool for assessing the integral effects of CO₂ emission strategies on the global carbon cycle and climate warming.

2.4.3 <u>Carbon Sources and Sinks in the Arctic</u>

- K. Higuchi

Using an existing 3-dimensional atmospheric regional dynamical model, the atmospheric CO₂ measurements taken at Alert were interpreted in terms of regional distribution of carbon sources and sinks in the Arctic.

After obtaining the model from Dr. Han-Ru Cho of the University of Toronto, it was modified to sit over the North Pole, with the outer boundary of the model extending to around 40°N. A number of improvements were made in the model to reflect the physical processes in the high latitude regions and to better simulate the Arctic atmospheric circulation. The model also has an atmospheric chemistry package which can be used to study various interactions

between the chemistry and the physical circulation in the Arctic. In addition, because of the importance of the polar regions in the overall global change, employment of the regional Arctic model developed has been proposed as part of the scientific strategy in various climate programs.

Results of the study will provide a better understanding of the way the anthropogenic carbon emissions in and around the Arctic is affecting the atmospheric CO₂ level in the atmosphere. This will allow better monitoring of any future industrial activities of Arctic nations through proper interpretation of CO₂ measurements taken at Alert.

2.4.4 <u>Canadian Baseline Program</u>

- N. Trivett

The six hourly averaged atmospheric mixing ratios of carbon dioxide and methane at Alert, N.W.T. from January, 1988 to December 1994, are plotted in Figures 3 and 4, respectively, along with the seasonal cycle and long term trend. The data show significant seasonal variations mostly due to the seasonal variations in the biological activity and, in the case of methane, to the changes in the photochemical sink.

The decrease in carbon dioxide is primarily due to the uptake of carbon by vegetation, whereas the decrease in methane is primarily due to the chemical destruction by the reaction of methane with the hydroxyl (OH) radical. Air mass 5-day back trajectories indicate that most of the defined wintertime episodes are related to synoptic meteorology and rapid air mass transport directly across the polar basin, suggesting northern Asia and Europe as the major source regions.

The accumulated growth curves for methane and carbon dioxide are plotted in Figure 5. The accumulated growth curve is calculated as the difference between the monthly average of one year and the monthly average from the previous year, i.e., January 1994 - January 1993, and then accumulating all the differences.

Figure 5 shows that initially the methane mixing ratios were increasing and then stabilized around June 1992. Of note is the large decrease in methane observed from September 1992 to September 1993. The methane growth rate returned to more normal levels in September 1993. It should be noted that Alert showed the largest drop in mixing ratio relative to any other sites in the GAW program and the decrease appears to be only a northern hemispheric phenomena. There has also been considerable speculation as to the cause of the methane decrease, such as the decrease in industrial activity in Russia, but this cannot account for the general decrease evident in all the northern hemispheric data and is not supported by the methane stable carbon isotope data. It should also be noted that this decrease in the methane mixing ratio at Alert was not observed at Fraserdale.

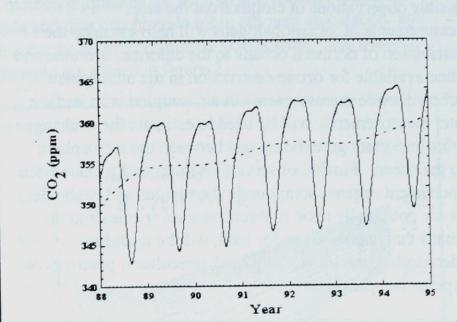


Figure 3: Infrared (NDIR) measurements of carbon dioxide from Alert averaged over 6 hours with the long term trend and seasonal cycle.

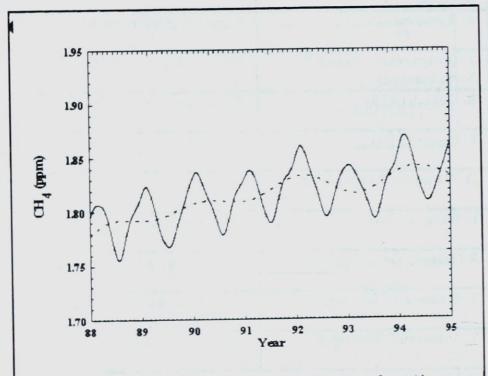


Figure 4: Gas chromatographic measurements of methane from Alert averaged over 6 hours along with the long term trend and seasonal cycle.

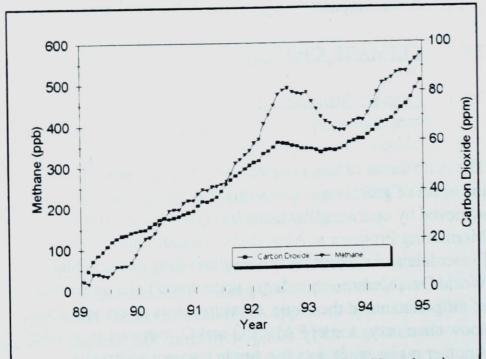


Figure 5: Accumulated growth curves for carbon dioxide and methane from Alert, N.W.T.

The growth rate in the carbon dioxide mixing ratios showed a similar trend, in that the growth rate was curtailed between September 1992 to September 1993 before returning to more normal levels. It should be noted that what was observed for the growth patterns for carbon dioxide and methane was also observed for many other trace gases such as carbon monoxide and nitrous oxide supporting a wider explanation for the decrease, such as a climatological effect.

2.4.5 Carbon Dioxide Program

- D. Ernst, L. Leeder and N. Trivett.

The central calibration database for CO2-in-air standards is now in use in the Canadian Baseline Monitoring Program but further development is improving its efficiency and speed.

At a meeting in Boulder the calibration values assigned to the Canadian National Standards by the Central Calibration Laboratory at the Scripps Institute of Oceanography (SIO) and the National Oceanic and Atmospheric Climate Diagnostics and Monitoring Laboratory (NOAA/CMDL) were reported. SIO calibrated the suite of nine Canadian National standards in 1986 and 1991, while NOAA/CMDL calibrated the same tanks in 1989, 1993 and 1995. In 1995, Canada purchased 18 new tanks from SIO to form a new set of National Standards. These tanks were used to check the concentrations of the original nine National standards. There is a serious discrepancy between the SIO and NOAA/CMDL calibration values, despite the fact that SIO calibrated the NOAA/CMDL tanks, and creates a serious problem in determining the correct scale for the original Canadian National Standards. Both SIO and NOAA/CMDL are to investigate this problem. It should be noted that the amount of intercalibration between these institutions is unprecedented in the carbon dioxide community, and this discrepancy raises the concern for all the international programs, because many of them have their scales determined relative to only one calibration (usually done at SIO). It also further emphasizes the importance of regular interlaboratory calibrations.

Gas Chromatographic Program 2.4.6

- D. Worthy and M. Ernst

A new Hewlett Packard 6890 gas chromatographic (GC) system, along with the automated HP Chem Station has been purchased. The system will be developed to analyze carbon dioxide, methane and nitrous oxide from both flasks and calibration tanks, and will replace the old HP 5890 GC system. The system will be automated to allow for the flasks and calibration tanks to run overnight, and have the results processed and stored in the data base immediately after completion of the run. This system will replace the current NDIR system for carbon dioxide flask analysis. The GC requires more time to analyze each flask and is not as precise as the NDIR, but it can analyse more trace species from each flask. The Trace Analytical GC system developed last year will be augmented with the HP 6890 to permit the analysis of carbon monoxide on the same flasks and calibration tanks.

The GC system for F-11, F-12 and F-113 continues to operate at Alert. A preliminary comparison of the in situ data with the NOAA halocarbon flask data has been carried out. A new instrument for measuring N2O has been developed at NOAA/CMDL and will be installed at Alert this summer. This will be a cooperative effort with NOAA with NOAA supplying the gas standards and performing the data analysis, and AES maintaining the system.

Carbon Dioxide Flask Sampling Program 2.4.7

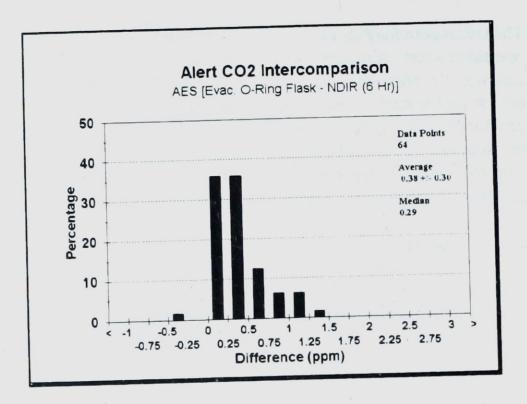
- V. Hudec and N. Trivett

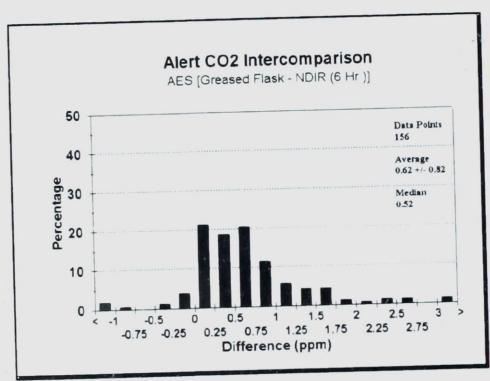
The AES carbon dioxide (CO₂) flask program collects samples at Alert, Sable Island and Estevan Point using three different flask types. All three flask types are currently used at Alert. The historical flask data set, from 1975 to present, consists of data from flask samples taken using two-litre evacuated, thick-wall borosilicate glass flasks, fitted with 6mm bore high vacuum stopcocks (greased with Apiezon-N).

In August 1992, a two-litre evacuated, thick-wall borosilicate glass flask, fitted with a glass barreled high vacuum stopcock with double Viton o-ring seals was added to the program as a possible replacement flask for the greased stopcock flask. In June 1993, AES implemented a pressurized flask sampling program at Alert and added a two-litre, thick-wall borosilicate glass flask, fitted with double glass barreled high vacuum stopcocks with double Buna-N o-ring seals. AES plans on phasing out the old greased stopcock flasks and replacing them with the new flask designs. An intercomparison of the three AES flask programs relative to the AES in-situ nondispersive infrared (NDIR) program (at Alert) started in March 1995. The evaluation results for the three AES programs relative to the AES in-situ program are shown in Figure 6.

It is evident that the greased stopcock flask results deviate the most relative to the NDIR results. The greased stopcock data set is also subject to the most sampling problems as is evident from the large number of positive outliers. The pressurized Buna-N flasks produce results closest to the NDIR. Student t-tests on the flask data sets relative to the NDIR have shown the greased stopcock flask data to be significantly different from both new flask data sets. Further laboratory and field tests will be necessary before the old greased stopcock data set can be merged with the new flask data sets. This same problem is evident in the NOAA Alert flask data set which is comprised of data taken from two different flask types.

The AES CO2 flask and in-situ programs were also evaluated relative to the two independent Alert CO2 flask programs of the National Oceanic and Atmospheric Administration (NOAA) and the Scripps Institute of Oceanography (SIO). The results from the AES and NOAA flask evaluations illustrate the problems that can be encountered when trying to merge data sets from different flask types.





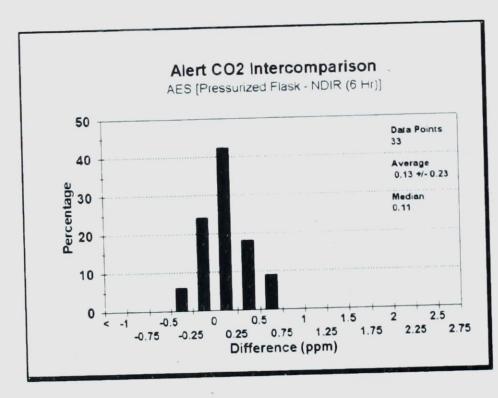


Figure 6: Intercomparison of AES Alert CO2 Flask and In-situ Programs.

There are a number of co-operating agencies collecting samples globally. If the data sets are to be merged into a global data set, then there is a great need for studies relating the measurements from the various independent programs. AES presented a proposal for an extensive inter-flask and inter-laboratory comparison at the CO₂ experts meeting in

Boulder, Colorado. The details of the proposal have yet to be finalized, but AES will take the lead role in the study.

2.4.8 <u>Data Analysis and System Capability</u> S. Racki, N. Trivett and D. Worthy

The Novell Netware facilities have been augmented with an NT server. The main field data resides on the network server and the user files reside on the NT server. Total network on line storage has increased from 11 to almost 18 giga bytes to allow the isotope laboratory to come on line as well. The increase in users and system capabilities has caused an increase in maintenance and support for the system. A stable version of Flagger (our primary QC program) is now in use but development continues to improve speed and additional user requested features.

2.4.9 Station Operations

Alert:

N. Trivett, D. Worthy, D. Ernst, C. Webster,
 V. Hudec, M. Ernst, S. Racki, L. Leeder,
 E. Wallgren, J.F. Hopper and K. Anlauf

The Gossen PAH analyzer installed at Alert has replaced the CN counters as a local contamination indicator. The CN counters continued to be troublesome and were removed from the program. Due to government-wide cuts in funding the Department on National Defense has requested that Alert office facilities adjacent to the weather station be closed and moved into the main complex. The move will take place some time in the next year. In addition, operations will be combined with Prairie and Northern Region to reduce costs.

Sable Island:

- N. Trivett, D. Ernst and L. Leeder

Due to other priorities, the pilot study to evaluate Sable Island as a possible future background air chemistry monitoring site terminated in the spring of 1993. The Sable Island program remains in serious trouble with the possible closure of the Aerology Station by the Atlantic Region.

Fraserdale:

- N. Trivett, D. Ernst, D. Worthy, M. Ernst, L. Leeder, V. Hudec, J. Kovalick and J.F. Hopper

The monthly means of the methane mixing ratios for the years 1988 to 1995 were compared to the NOAA flask data at Cape Meares and Cold Bay (which are at similar latitudes to Fraserdale) to determine the representative background of that area. The Fraserdale data set is approximately 30 percent higher than the coastal sites, due to both anthropogenic and natural sources. The diurnal cycles of methane and carbon dioxide are very similar during the summer period due to the inversion layers close to the ground. An important difference is that carbon dioxide reaches its maximum 1 to 2 hours before methane due to the carbon dioxide sink of the boreal forest around Fraserdale.

It was also noticed that the interannual variation of the methane is large from year to year especially during the wetland active season. The carbon dioxide seasonal amplitudes were compared to the methane seasonal amplitues and large differences were observed between different years. The differences are believed to be due to interannual variations of the source strength of the wetlands.

Under the Canada/Germany MOU and with the University of Heidelberg, radon flux density measurements were taken in an area around Fraserdale. The results of the campaign produced an estimate of 0.5 g CH₄/km²s. Assuming an equally active season (wetland methane emission season) of 130 days and an area of 320,000 km², this translates into a methane source strength of 1.8 Tg/yr for the Hudson Bay Lowlands. Comparing this to the results of NOWES/ABLE 3B it is more then three times higher. It should be noted that these are preliminary values. Another experiment will be carried out this summer with a more precise radon detector.

2.4.10 Canadian-Chinese Bilateral Agreement

N. Trivett, D. Worthy, M. Ernst, E. Wallgren,
 W. Kobelka, K. Anlauf and S-M Li

Under the bilateral agreement between Canada and China, gas chromatographs for CO₂/CH₄ and CO, built in our laboratory by two visiting Chinese scientists, were installed in July 1994 at the GAW Baseline Observatory on Waliguan Mountain in China. In addition, AES installed troposheric ozone, black carbon, precipitation and aerosol chemistry, as well as meteorological measurements on the 86 m tall tower. Three groups helped in the installation, provided expert advice, and trained the local staff on instrument operation and quality control procedures.

The next step under the agreement is to develop the proposal for the major computer analysis systems for data storage and for quality controlling the station data, and to develop the Chinese version of the trajectory program. It is also expected that a Chinese expert will spend some time in Canada to learn the quality control procedures utilized in the program and to become more familiar with the intricacies of the equipment installed at Mount Waliguan.

2.4.11 Boreal Forest Study (BOREAS)

- N. Trivett and D. Ernst.

An CO₂/H₂O profile system measuring at 8 different levels performed well during the Boreal Forest Study and provided one of the most complete data sets of its kind. The analysis of the data is being done by Drs. den Hartog and Neumann.

2.5 STRATOPHERIC STUDIES

2.5.1 Arctic Stratospheric Observatory

H. Fast, K. Nassim, A. Ullberg, J.J. Bellefleur,
 F. Karpenic and R.H. Hoogerbrug

Another winter campaign, starting in early September 1994

and ending in mid-April 1995, was conducted at the observatory in Eureka.

Atmospheric absorption spectra of trace gases were recorded with the Bomem DA8 interferometer system when the sun was visible above the horizon. The University of Denver installed an interferometer to obtain atmospheric emission spectra for measuring trace gases even during polar night. Two Raman channels were added to the ozone Differential Absorption LIDAR (DIAL) system enabling ozone profiles to be measured from low altitudes without interference from aerosol scattering. The PSC/Haze LIDAR system detected Polar Stratospheric Clouds (PSCs) for the first time at Eureka. Under the auspices of the Canadian Network for Space Research (CNSR) two Bomem atmospheric emission interferometers were operated to monitor the temperature and winds in the atmosphere above 80 km. An experimental "red" Brewer and, for the first time, a stellar Brewer were also deployed by CNSR.

2.5.2 <u>Infrared Measurements Development</u>

- H. Fast, K. Nassim, W.J. Clark, A. Ullberg and R.H. Hoogerbrug

The capability of retrieving trace gas column densities from their infrared absorption spectra was validated by participation in an international intercomparison involving six different algorithms and 17 institutions. SFIT, the spectral fitting software developed by the NASA Langley Research Centre, was used for the retrieval of gas columns from interferometer spectra recorded at Eureka and at CARE (Egbert, Ontario). Atmospheric infrared absorption spectra were recorded once a week at CARE with the 0.01 cm-1 resolution interferometer for monitoring of trace gases. Spectra were also obtained from CO for correlative measurements during overpasses of the MAPS instrument on board the space shuttle in April and October 1995.

2.5.3 <u>Aircraft and Space Experiments</u>

- C.T.McElroy, C. Midwinter, R.B. Hall and D.V. Barton

The Composition and Photodissociative Flux Measurement (CPFM) experiment was flown as part of the NASA ER-2 Airborne Southern Hemisphere Ozone Experiment/ Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) between February and November of 1994. The SunPhotoSpectrometer used for the ER-2 flights was originally developed by the AES for use on the 1992 US Space Shuttle. It was included in the ER-2 chemistry research payload during the Stratospheric Photochemistry, Aerosol and Dynamics Expedition (SPADE) which took place in May 1993, and provided information about the radiation environment of the aircraft during flight. The instrument provides data which allows the calculation of photochemical reaction rates and the direct measurement of the albedo of the earth-atmosphere system below the aircraft, as well as the column amount of ozone above the flight level. These flights are aimed at developing

a more comprehensive understanding of mid-latitude stratospheric chemistry so that the impact of the operation of proposed, advanced supersonic transports can be accurately assessed.

Participation in the ER-2 chemistry program has allowed AES scientists and the Canadian co-investigators on the project to have unique access to all of the data collected by the whole ER-2 science team. The comprehensive instrument package flown on the ER-2 collects information on more than a dozen chemical species which are crucial to the chemistry of ozone in the stratosphere. Several investigations of research issues important to the understanding of the chemistry of the stratosphere are now underway using the data from the CPFM experiment and from the larger chemistry data set. Co-investigators on the project include scientists from the Johns Hopkins Aplied Physics Laboratory, the University of Califonia at Irvine and York University.

2.5.4 World Ozone and Ultraviolet Radiation Data Centre - E.W. Hare, D.I. Wardle and J.B. Kerr

The World Ozone Data Centre (WODC) was created in the early 1960s under the direction of AES scientist Carl Mateer and for many years was managed by Larry Morrison. AES operates this data centre for the WMO. The WODC, which began as a card reading, flat file archive using a mainframe computing environment, has transformed into a semi-automated data reporting centre which now uses a Novell Netware file server in a PC environment with an Oracle relational database engine. Output data from the WODC database are currently posted on the AES ftp server. In June 1992, AES agreed to a request from WMO to add ultraviolet radiation data to the WODC. The new centre has now been named the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) with two component parts: WODC and the World Ultraviolet Radiation Data Centre (WUDC).

The WODC processes, archives and publishes world ozone data reported by over 300 stations. These data are published bi-monthly in a publication entitled "Ozone Data for the World" along with an annual catalogue which details all the data received each year. Data output from several data collection and measurement techniques comprise the database input which includes: total column ozone, surface ozone, vertical profile data derived from lidar, ozonesonde and Umkehr techniques. Total ozone measurements are made using several different instruments, most notably the Dobson and Brewer spectrophotometers. ARQX (where the Brewer was designed) operates and manages the national Brewer data centre which is sent to the WODC for publishing.

The Brewer also collects high resolution ultraviolet (UV) spectral data and, since the establishment of the WUDC, Japan and Canada now regularly submit yearly UV data to be posted on the ftp server for worldwide use. The WUDC now has about 25 station-years of spectral UV data measured by

the Brewer spectrophotometer. These data are from four stations in Japan and five in Canada.

2.6 CORE RESEARCH

2.6.1 <u>Mixing Height Models</u> - C.S. Matthias

The daily maximum mixing height is an important variable in the calculation of hourly to daily pollutant concentrations. It is usually calculated using a scheme developed by G. Holzworth. His approach uses the morning upper air temperature profile and the daily maximum surface temperature. The accuracy of Holzworth's scheme under ideal and non-ideal meteorological conditions is being investigated. A second model uses the afternoon upper air profile, and a third model searches for the first significant temperature gradient (kink method). An alternate model is being examined which uses only surface observations and does not require an upper air temperature profile. It models the solar input and the surface energy budget.

2.6.2 <u>Boundary Layer Flux Parameters</u> - A.K. Lo

The role of humidity effects in the determination of atmospheric stratification and flux parameters in a marine surface layer is evaluated. The present results demonstrate that conventional approaches ignoring the humidity effect can introduce significant errors, especially for flow of low air humidity over a warm water surface. For relative humidity of air at 70% and water surface temperature of 20°C, errors can be as high as 30% in near-neutral stratification. Since the virtual temperature is a measure of humidity content in an air parcel, an approximation as a function of virtual and potential air and water surface temperatures for evaluating errors in stratification is derived. The accuracy of this approximate formula is well within 10% of the exact solution and is extremely simple to calculate. This approximate formula can thus be very useful for in-situ use during marine boundary layer field studies. This is shown in Figure 7.

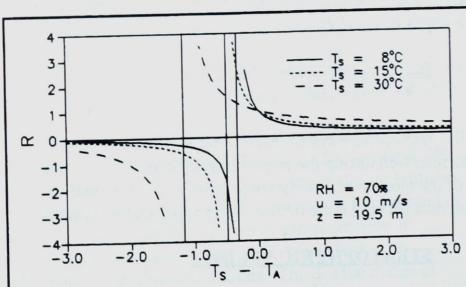
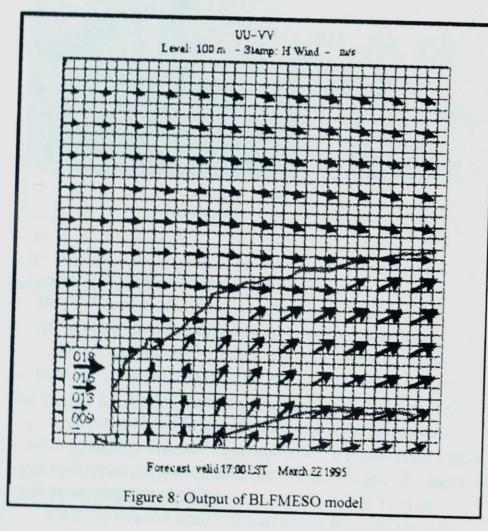


Figure 7: Ratio, R, of stability contribution to total static stability due to humidity effect at different sea surface temperatures, T_s

2.6.3 <u>Mesoscale Boundary Layer Forecast Model</u> S.M. Daggupaty and P. Cheung

A paper describing all the physical processes and numerical formulations of the three-dimensional mesoscale boundary layer forecast model (BLFMESO) along with preliminary results was published. Interest was expressed for collaboration by using this model with chemistry packages from private companies, universities, and government agencies from the U.S. and from Europe. Two agencies will collaborate with AES for joint studies using two chemistry models (Urban Airshed Model and CALGRID).

The mesoscale model code has been modified for operation on an HP workstation for any user-opted window region of the North American continent. Coupled with the Regional Finite Element (RFE) model using the 50 km grid interval forecast data for initialization and for realtime prediction, it should be applicable for short term (< 24 hr) predictions, specifically for accidental spills. An example of the output is shown in Figure 8.



This feature has been used in the recent Ontario Nuclear Exercise for Pickering NGS accident response. Periodic updating of the mesomodel data with objectively analyzed data will aid in the long term simulation studies. The model with an air pollution module will be of use to study impacts of air pollution on regions like Hamilton Harbour, Sarnia and others near the Great Lakes. Combining the boundary layer mesoscale model with air pollution dispersion and chemistry modules will enhance the BLFMESO's potential air quality applications. Collaborative studies will aid in the development of a System of Atmospheric Mesoscale Modelling for Air Quality Prediction (SAM MAP).

2.6.4 Flow Over Complex Terrain - J.L. Walmsley

In collaboration with Prof. S.R. Karpik, University of Toronto, improvements were made in the MSFD model. The formulation of the top boundary condition was improved, and all model equations and code were thoroughly checked with the MAPLE symbolic algebra software.

Progress is being made incorporating pollutant concentration and flux equations in the MSFD model. This work, being done jointly with Dr. J. Padro, will incorporate a new version of Wesely's dry deposition scheme, as modified by Walmsley & Wesely. Coding of the main program was delayed while the MSFD-PC software was being revised, but is now complete. The remaining coding relates to post-processing modules, which will be completed early in 1995.

Last year it was reported that the MS-Micro/3 model had been applied to Roundtop Mountain, near Sutton, Quebec, to produce wind fields to be used in estimating acid deposition from fog. This project is being undertaken in collaboration with Prof. H.A. Bridgman, University of Newcastle, Australia, and Dr. R.S. Schemenauer (ARMP). Work continued on fog deposition calculations, but progress has been slow due to other commitments. Beginning in January 1994, software sales were handled by Zephyr North of Burlington, Ontario, first through an interim agreement and later through a more formal Licence Agreement. The latter includes a provision to enter into a sub-licence agreement with Building Research Establishment, U.K., for producing and selling an integrated package called MS-MicroGB. Revenue generation continued at about the same rate as last year (\$2,600).

2.6.5 <u>Wind Energy</u> - J.L. Walmsley

Progress on a contract titled "Testing the Accuracy and Methods of Applying the Wind Correlation Model" was slower than expected. Nevertheless, the first step, preparation of a PC-based version of the STAR stability analysis program, has been completed. It is planned to award another contract which should result in a tested, user-friendly capability to relate short-term measurements at a candidate wind-turbine site to long-term wind climatology at a nearby weather or climatological station. The method, however, should have wider application to the general case of two-site correlation of winds.

2.6.6 <u>Modulating Effects of Mesoscale Processes</u> Y. Qi and J.L. Walmsley

There is no doubt that impacts of mesoscale meteorological processes induced by complex terrain, such as gravity waves and slope wind systems, on atmospheric pollution are very important, particularly in local areas. However, those meteorological-modulating effects are still not clear and are often ignored in regional air pollutant transport models. One

of the main reasons is lack of the knowledge of the mesoscale meteorological processes. Recently, using the mesoscale numerical model with second-order turbulent closure, the mesoscale processes over topography were investigated. A general theory on the interactions among the patterns in a mesoscale terrain flow with the evolving atmospheric boundary layer has been proposed from a unified view of wave, vortex and boundary-layer dynamics.

To continue studies on the modulating effects of mesoscale meteorological processes in a realistic geographical region, the Canadian Mesoscale Compressible Community Model (MC2) has been chosen as a second tool. Since MC2 is a new model, the first step in using the model was to evaluate its performance. It was found that the current nesting scheme of MC2 causes reflection waves near lateral boundaries. A new module for an improved nesting scheme has been developed and is now available. In addition, the error growth of MC2 has been assessed and some preliminary results have been obtained.

Meanwhile, MC2 has been used to simulate the EMEFS1 period. Orographically-forced flow patterns have been separated from the model results of a 5 km resolution cascade run using a powerful new tool-wavelet analysis. Further results and the modulating effects of the mesoscale flow patterns in air pollution will be obtained in the near future.

2.7 AIR QUALITY SERVICES

2.7.1 <u>RDMQ System</u> - W. Sukloff

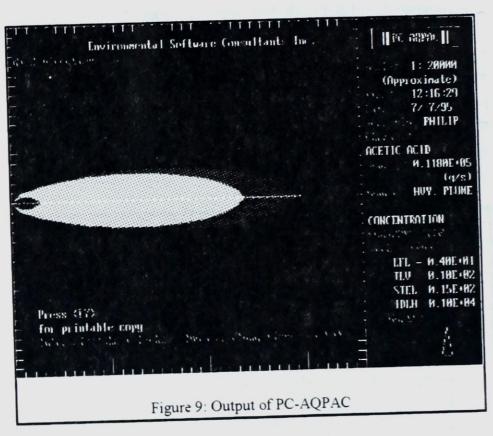
The Research Data Management and Quality Control (RDMQ) system for the Great Lakes Integrated Atmospheric Deposition Network (IADN) was refined and applied to all available IADN-AES toxics data. The system accepts laboratory and field data, allows quality control and validity flagging, carries out blank corrections, and produces standard statistical summaries and graphical outputs. An RDMQ user manual was published and distributed.

Work continued under a grant from the U.S. Environmetal Protection Agency to adapt the RDMQ system to the U.S. IADN program. The use of RDMQ by both countries enhances data compatibility and eases data merging.

2.7.2 <u>Modelling for Air Pollution Emergency Response</u> - S.M. Daggupaty and P. Cheung

In a neutral gas plume model validation exercise using data from a tracer dispersion study (1979-1983) over a forested region at Whiteshell Laboratories, the PC-version of the Air Quality Package for Environmental Emergency Response (PC-AQPAC) was run for several case studies of field experimental data. In the validation study, the participants are not supplied with the tracer concentration data but are given only available meteorological tower data, and source

quantity and release conditions. The models are run to give concentrations at specific receptors in three dimensional space. The results are analysed and statistical analysis is done by an independent group. PC-AQPAC's plume model results are fairly represented with the observed centerline and lateral spread of the gas plume concentrations. However, vertical distribution of modelled gas concentration is not good enough. Overall PC-AQPAC is considered as the second best of the models compared. A second evaluation study is being finalised with further set of experimental trials. The validation exercise is initiated by COG (Candu Operators Group) and is managed by AECL, Chalk River. A typical output is shown in Figure 9.



PC-AQPAC has been exhibited at "Innovations 1994", an Environment Canada workshop and at "Decision 2001", an international conference. An agreement, first of its kind in AES, was completed with a company to sell PC-AQPAC. Franklin county, Ohio, U.S.A. is using PC-AQPAC as their response modelling package for chemical spills. Environment Canada regional offices, DND command centers and other Canadian agencies are also using this AES package. Though AQPAC has been in use for more than six years, the package is continuously refined and updated as the our understanding of chemicals and their behaviour in the atmosphere improves.

2.7.3 <u>Air Quality Services</u> - M.E. Still

Building on a previous retreat in 1993, the Branch's management committee held another retreat to review the impact of the 1994 government-wide program review. As a result of this review, resources are expected to decrease by 25-30% from present levels. The first two sessions of this retreat discussed the issues and activities of the Branch to give a background for the third session. In this third session, the following key questions were examined. For each of these questions, action items were detailed which will be tracked on a regular basis.

- o What are the most important issues for our Branch in the next four years?
- o What are the most important functions of the Branch?
- o What is our relationship to other groups in the federal government, in provincial agencies and in international agencies?
- o Are there any new issues expected in the next five years?
- o Can the Branch's structure be improved to increase efficiency and effectiveness?

In 1972, Holzworth published a mixing height climatology of the U.S. to be used to assess the potential for urban air pollution. Ron Portelli (then with AES) completed a similar study for Canada in 1977. Even though Portelli's analyses produce climatology data that are used in most provinces of Canada for Environmental Impact Assessments, the results of his analyses differed from Holzworth's at the Canada-U.S. border.

A contract let in 1994 to Senes Consultants Ltd analyzed these differences. The contract was co-funded by the Atmospheric Environment Service (AES), the Ontario Ministry of the Environment and Energy (MOEE), Alberta Environment and the contractor. The report completed in June 1994 summarized the findings and recommended the method for finalizing the climatology for Canada and the U.S. A follow-up contract will be let to finalize the mixing height climatology for North America.

2.7.4 <u>Centre for Atmospheric Research Experiments</u> - F. Froude

The Centre for Atmospheric Research Experiments (CARE) is an atmospheric research facility operated by the Air Quality Research Branch. Located in Essa Township 15 km south of Barrie, CARE collects data in support of various air quality and climate programs.

Since purchase of the property in 1986, concerns have been expressed regarding the impact of future uncontrolled residential development surrounding the site. A report submitted to Essa Township in 1990 outlined these concerns and requested protection of the monitoring programs through land use regulations. Township council did not share our concern. In 1993 the matter was referred to the Ontario Municipal Board (OMB) for a hearing. As a result of the hearing in 1994, an agreement was negotiated with thetownship that was accepted by the OMB as a fair and reasonable settlement. This agreement provides protection for the research programs from the cumulative impacts of surrounding development. The Township Official Plan has been amended to restrict the development of residential subdivisions within 4 km of CARE but has little effect on any

severance associated with standard farming activities.

Experiments are carried out by research groups of Environment Canada and others including universities and private organizations in cooperation with on-site staff. Projects are initiated by proponents contacting the CARE manager with a project request. A summary of current projects and their 1994 status is listed in Table 3. A more detailed description of each project is available in the annual CARE report or elsewhere in this report under the appropriate program activity.

2.8 BRANCH PUBLICATIONS

2.8.1 <u>Journal Publications (1994/95)</u>

- Anlauf, K.G., R.E. Mickle and N.B.A. Trivett 1994: "Measurements of ozone during Polar Sunrise Experiment 1992", J. Geophys. Res., 99(D12), p.25,345-25,353.
- **Barrie, L.A.**, **S.-M. Li, D.L. Toom**, **S. Landsberger** and W.T. Sturges 1994: "Lower troposphere measurements of halogens, nitrates, and sulphur oxides during Polar Sunrise Experiment 1992", J. Geophys. Res., <u>99(D12)</u>, p.25,453-25,467.
- Barrie, L.A., R.M. Staebler, D.L. Toom, B. Georgi, G. den Hartog, S. Landsberger and D. Wu 1994: "Arctic aerosol size-segregated chemical observations in relation to ozone depletion during Polar Sunrise Experiment 1992", J. Geophys. Res., 99(D12), p.25,439-25,451.
- Bidleman, T.F., R.L. Falconer and M.D. Walla 1995: "Toxaphene and other organochlorine compounds in air and water at Resolute Bay, N.W.T.", Sci. Total Environ., 160/161, p.55-63.
- Bidleman, T.F., L.M. Jantunen, R.L. Falconer, L.A. Barrie and P. Fellin 1995: "Decline of hexachlorocyclohexane in the arctic atmosphere and reversal of air-sea gas exchange", Geophys. Res. Lett., 22, p.219-222.
- Bridgman, H.A., **J.L. Walmsley** and R.S. Schemenauer 1994: "Modelling the spatial variations of wind speed and direction on Roundtop Mountain, Quebec", Atmos.-Ocean, <u>32</u>, p.605-619.
- Burrows, W.R., M. Vallée, **D.I. Wardle**, **J.B. Kerr**, L.J. Wilson and **D.W. Tarasick** 1994: "The Canadian operational procedure for forecasting total ozone and UV radiation", Met. Apps, 1(3), p.247-265.

NETWORKS

NAME	TYPE OF MEASUREMENT	SPONSOR	
Atmospheric Mercury - Pt. Petre, Burnt Island	Network of 10 sites in Great Lakes region One 24-hour sample every 6 days	U. Michigan	
Aldehyde Sampling	* Daily 24-hour sample in August * One 24-hour sample every 6 days fall & winter	EC - EPS	
nterferometer Testing	* No change	AES - ARQX	
NOx/VOC PAN Study	* Study of PAN concentrations during periods of Arctic air mass intrusions into southern Ontario	AES - ARQM	
CAPMoN - precipitation	* Duplicate system installed for precision study * pH measurements from November 1994 to March 1995	AES - ARQM	
CAPMoN - VOC measurements	VOC samples collected daily July & August Schedule changed to 1 day in 6 in September	EC - EPS	
CAPMoN - MOEE ozone	* CAPMoN ozone measurements included in MOEE network	MOEE	
NDDN (National Dry Deposition Network)	* Upgraded to CASNET specifications in July * Meteorological data * Leaf wetness	U.S. EPA	
Acid Aerosols & Health Effects	* No change	AES - ARQP EC - EPS Health Canada	
Tropospheric Gases	* No change	AES - ARQP	
Integrated Atmospheric Deposition Network - Egbert, Point Petre & Burnt Island	* Sampling frequency reduced by half to 1 sample every 12 days	AES - ARQP AES - CARE	
Integrated Atmospheric Deposition Network - Organics	* No change	EC - IWD	
Climate Reference Station	* ONTAP added - manual telephone call-up reporting procedure of current observations	AES - Ont. Reg.	
Visibility Monitoring - IMPROVE	* No change	U.S. National Parks U. Guelph	
Light Scattering	* No change	AES - ARQP	

Table 3: Projects at CARE

INTENSIVE FIELD STUDIES

NAME	TYPE OF MEASUREMENT	SPONSOR
Carbon Aerosol Survey	* Study of carbonaceous aerosols * TOC/TSP, IMPROVE, aethelometer, filter packs * LIPM (Laser Integrating Plate Method) * PESA (Proton Elastic Scattering Analysis)	AES - ARQP AES - ARQM AES - CARE AES - Ont. Reg.
Microwave Emissions from Snow Cover	 Microwave radiometer measurements at 19, 37 and 85 GHz to measure snow depth, grain size, water equivalent, stratigraphy and wetness 	AES - CCRP
POSS Validation	POSS sensor validation for measurement of frozen precipitation accumulation	AES - CCRP AES - AWPT/M
MAPS	* Radiosonde support for space shuttle mission monitoring atmospheric CO	AES - ARQX AES - CARE
Interferometer	* Atmospheric solar absorption spectra	AES - ARQX
Fog Water Contaminants - Pt. Petre	* Fog water samples collected for analyses at external laboratory	AES - CARE AES - ARQP
Tropospheric Gases	* No change	AES - ARQP
Sunshine Recorder Intercomparison	Comparison of AES electronic sunshine recorder and Campbell- Stokes completed	AES - CCID
Radio Spectrum Monitoring	Upgraded to provide more control & flexibility	DOC
National Precipitation Evaluation Station	* No change	AES - CCRP
Climate Processes Monitoring	* Reporting stations reduced from 5 to 3	AES - CCRP
Autostation Comparison	* No change	AES - CCRP

INSTRUMENTATION TESTING

NAME	TYPE OF MEASUREMENT	SPONSOR	
Wedding PM 10 Test	Evaluation of high-volume sampler using a critical orifice device for flow control	AES - CARE	
Soil Thermistor	* No change	AES - AWPT	
Temperature Shield and Humidity	* No change	AES - AWPT	
CO Measurements using MOPITT	Ground-based CO measurements to compare with space shuttle MAPS	U. Toronto	
FTS Tipping Bucket Intercomparison	* Completed	AES - CCAD/D	
National Emergency Response	* Transmittal test of upper air data from mobile source	AES - CARE AES - CMC	

Table 3 (continued): Projects at CARE

- Chan, D., K. Higuchi and C.A. Lin 1995: "The sensitivity of the simulated normal and enhanced CO₂ climates to different heat transport parameterizations in a two-dimensional multilevel energy balance model", J. Climate, 8, p.844-852.
- Claussen, M., and **J.L. Walmsley** 1994: "Modification of blending procedure in a proposed new PBL resistance law", Boundary-Layer Meteorol., <u>68</u>, p.201-205.
- Crabbe, R.S., M. McCooeye and **R.E. Mickle** 1994: "The influence of atmospheric stability on wind drift from ultralow volume aerial spray applications", J. Appl. Meteorol., 33(4), p.500-507.
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- Eck, T.F., P.K. Bhartia and **J.B. Kerr** 1995: "Satellite estimation of spectral UV-B irradiance using TOMS derived total ozone and UV reflectivity", Geophys. Res. Lett., <u>22(5)</u>, p.611-614.
- **Falconer, R.L., T.F. Bidleman** and D.J. Gregor 1995: "Airwater gas exchange and evidence for metabolism of hexachlorocyclohexanes in Resolute Bay, N.W.T.", Sci. Total Environ., 160/161, p.65-74.
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- Hillery, B., **R.M. Hoff** and R. Hites 1995: "Atmospheric deposition of organic contaminants and trace elements to the Great Lakes" In: <u>Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters</u> (ed.: J.E. Baker), Soc. of Environ. Toxicol. and Chem., Washington, DC.
- Hoff, R.M., and J.E. Baker 1995: "Contaminant transport through the airshed", In: Great Lakes Fisheries Policy and Management: A Binational Perspective (ed.: W.W. Taylor), Michigan State University Press, Lansing, MI.

- **Hopper, J.F.**, and **W. Hart** 1994: "Meteorological aspects of the 1992 Polar Sunrise Experiment", J. Geophys. Res., 99(D12), p.25,315-25,328.
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 hydrocarbons during the Polar Sunrise Experiment:
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 Res., 99(D12), p.25,355-25,368.
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- **Kerr, J.B.**, and **C.T. McElroy** 1994: "Response to analysing ultraviolet-B radiation: Is there a trend?", Science, <u>264</u>, p.1,342-1,343.
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- Li, S.-M., Y. Yokouchi, L.A. Barrie, K. Muthuramu, P.B. Shepson, J.W. Bottenheim, W.T. Sturges and S. Landsberger 1994: "Organic and inorganic bromine compounds and their composition in the Arctic troposphere during polar sunrise", J. Geophys. Res., 99(D12), p.25,415-25,428.
- McConnell, J.J., and **T.F. Bidleman** 1995: "A review of field experiments to determine air-water gas exchange of persistent organic pollutants", Sci. Total Environ., <u>159</u>, p.101-117.
- Mickle, R.E., 1994: "Utilizing vortex behaviour to minimize drift", Environ. Sci. Health, <u>B29(4)</u>, p.621-645.
- Muthuramu, K., P.B. Shepson, J.W. Bottenheim, B.T. Jobson, H. Niki and K.G. Anlauf 1994: "Relationships between organic nitrates and surface ozone destruction during Polar Sunrise Experiment 1992", J. Geophys. Res., 99(D12), p.25,369-25,378.
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- Reinsel, G.C., G.C. Tiao, D.J. Wuebbles, **J.B. Kerr**, A.J. Miller, R.M. Nagatani, L. Bishop and L.H. Ying 1994: "Seasonal trend analysis of published ground-based and TOMS total ozone data through 1991", J. Geophys. Res., 99(D3), p.5,449-5,464.
- Sirois, A., M.P. Olson and B. Pabla 1995: "The use of spectral analysis to examine model and observed data", Atmos. Environ., 29(3), p.411-422.
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2.8.2 Other Publications (1994/95)

- Bailey, R., **L.A. Barrie**, D. Dougherty, P. Fellin, B. Grift, D. Muir and **D. Toom** 1994: "Preliminary measurements of PCCs in air at Tagish, Yukon", In: <u>Proc. Yukon</u>

 <u>Contaminants Committee Workshop</u>, February 1994, Whitehorse, Yukon.
- Daggupaty, S.M., R.S. Tangirala and H. Sahota 1994: "A mesoscale boundary layer meteorological model for inhomogeneous terrain", In: Proc. 20th Int. Tech. Mtg. on Air Pollution Modelling and its Application, Valencia, Spain, November 29-December 3, 1993, II, p.209-214.
- **Falconer, R.L.**, 1994: "Physicochemical properties and partitioning of organochlorine compounds in air and water", Ph.D. dissertation, Dept. of Chemistry and Biochemistry, University of South Carolina, 173pp.
- Fellin, P., L.A. Barrie, D. Dougherty, D. Muir, N. Grift, L. Lockhart and B. Billeck, 1993: "Air monitoring at Alert: Results for 1992 for organochlorines and PAHs", In: Proc. Symp. Ecological Effects of Arctic Airborne Contaminants (eds.: Christie and Martin), October 4-8, Reykjavik, Iceland,, USA CRREL Rep. 93-23.

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AIR QUALITY RESEARCH BRANCH

ANNUAL REPORT

1994/95

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AIR QUALITY RESEARCH BRANCH

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	ULLBERG, A.	4706	4S422
	WU, E.	4256	Rooftop (wue@aestor.am.doe.ca)

AIR QUALITY RESEARCH BRANCH

SCIENTIFIC EXPERTISE

Anlauf, K.G. Atmospheric chemistry; pollution measurement instruments and methods

Barrie, L.A. Atmospheric chemistry; Arctic haze; atmospheric removal processes - wet and dry

Bottenheim, J.W. Atmospheric chemistry; measurements; modelling; nitrogen chemistry

Daggupaty, S.M. Air quality modelling; transport and dispersion in boundary layer; mesoscale meteorology

den Hartog, G. Dry deposition; eddy fluxes; micrometeorology

Higuchi, K. Global biochemical cycles and climate research

Hoff, R.M. Lidar and DIAL; remote sensing; toxic chemicals; Arctic haze

Hopper, F. Naturally emitted compounds & their impact on climate

Kerman, B.R. Boundary layer turbulence; acoustic sounding; underwater sound; air-sea interactions; gas/particle

exchanges

Kerr, J.B. Ozone depletion; ozone trends; UV radiation

Lane, D.A. Photochemistry of PAH; chemical and physical properties of PAC; mass spectrometry; instrument and

methods development

Lo, A.K. Meteorological parameters and flux profile relations in transport and deposition of air pollutants

Matthias, C.S. Short range dispersion modelling

McArthur, L.J.B. Solar radiation; UV radiation; measurement techniques

McElroy, C.T. Remote sensing of atmospheric constituents and pollutants; UV radiation

Mickle, R.E. Detailed measurements of planetary layer using tethersondes; drift and deposition of pesticides from

aerial application

Neumann, H.H. Dry deposition measurement; micrometeorology; air pollution

Padro, J. Boundary layer; dry deposition; climate

Schroeder, W.H. Atmospheric chemistry; toxic chemicals

Trivett, N.B.A. Microclimatology; energy balance; RAGS monitoring

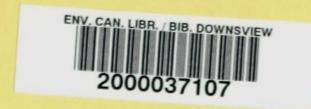
Walmsley, J.L. Computer modelling of wind flow in complex terrain

Wardle, D.I. Ozone science; UV radiation

Whelpdale, D.M. Acid rain; chemical meteorology; atmospheric chemistry

Wiebe, H.A. Atmospheric chemistry; environmental chemical measurements; acid precipitation in eastern Canada

network operations



Environment Canada - Environnement Canada

Annual Report (CANADA. Atmospheric Environment Service. Air Quality Research Branch)

DATE: 1994/1995

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OTM ANNUAL REPORT

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