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Air Quality  
Research  
Branch

Annual Report

**1991-92**

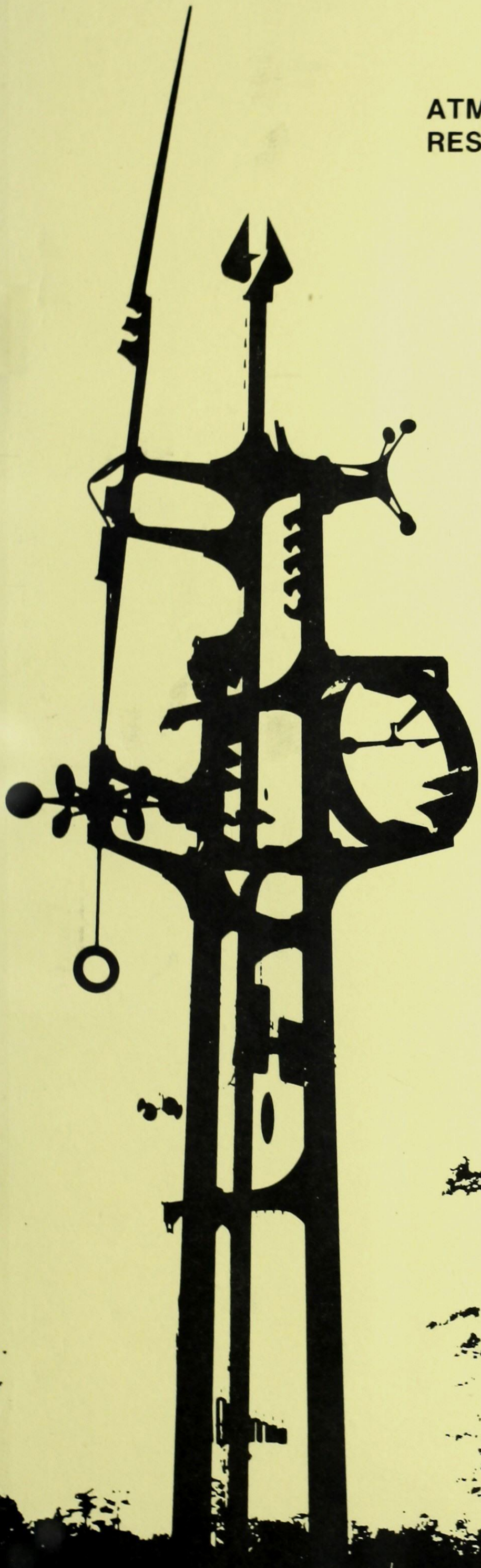


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AIR QUALITY RESEARCH BRANCH

ANNUAL REPORT

**AIR QUALITY RESEARCH BRANCH**

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Compiled by

Malcolm E. Still

November 1992

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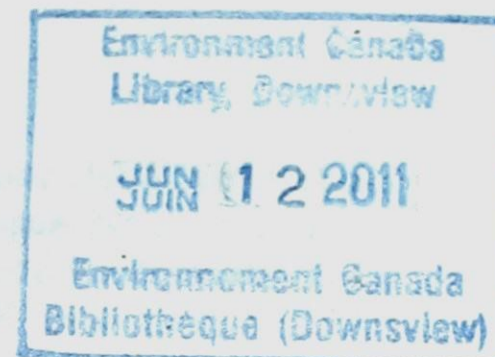


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## AIR QUALITY RESEARCH BRANCH

### ANNUAL REPORT

1991/92

#### 1.0 FOREWORD

Each year the Air Quality Research Branch recognizes AES employees that have contributed significantly to the achievement of the goals of this Branch. This "All Seasons Research Award" was initiated in 1988. A plaque indicating the past winners is on display in the AES library at 4905 Dufferin Street. The 1991 winners were:

Janusz Pudykiewicz for his significant contribution to our scientific understanding and to Canada's technical capabilities in large-scale atmospheric transport and dispersion.

Neil Trivett for his significant contribution to the development and fulfilment of Canada's role in Arctic air pollution through the establishment of the Alert BAPMoN Program.

Albert Wright for his considerable contribution to the efficient execution of research through his management of professional services to supply slides for presentations, prints for journal publications and typesetting/printing for special reports.

#### 2.0 BRANCH PROGRAM

##### 2.1 ACID DEPOSITION

###### 2.1.1 Program Management

- K.J. Puckett

A Ministerial announcement confirmed that the Federal Acid Rain Research Program would continue for a further 6 years. The Acid Rain submission, as part of the Green Plan, received approval and resources.

As part of the activities resulting from the recent signing of the Canada-U.S. Accord on Air Quality, sections were written on acid deposition modelling and monitoring for the first annual progress report.

Two new research projects were initiated: firstly, measurements of acid aerosols in co-operation with C&P and H&W; and, secondly, an assessment of visibility impairment and its linkage to changing air quality. The first initiative was in response to a Green Plan need and the second to a provision of the Canada-U.S. Accord on Air Quality.

###### 2.1.2 Lagrangian Model

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

The Sulphur/Nitrogen Lagrangian Oxidants Model (ALOM) was upgraded to a pseudo 2-layer model, dry deposition computations were revised, sensitivity tests were made, and inventories were revised. The Lagrangian and Eulerian models were again compared to measured data taken over 10 days during the Eulerian Model Evaluation Field Study (EMEFS). The results were sufficiently favourable that the investigations of the applications of a Lagrangian model to photo-oxidant simulations will be continued.

The sulphur model was used to recalculate the sulphur deposition in the Atlantic provinces using the latest Canadian and U.S. sulphur emissions control programs for 1994 and 2010, respectively.

Some preliminary investigations of the application of Fourier analysis to measured and modelled ozone data were very encouraging. Three distinct wave period regimes were observed in the measured data and the ADOM (Acid Deposition and Oxidants Model) results: diurnal/photo-chemical effects, 3-10 days meteorological episodic effects, and longer-term trend effects of several weeks-months.

### 2.1.3 Acid Deposition and Oxidants Model (ADOM) Evaluation

- K.J. Puckett, D. Davies, A.M. Macdonald, J. Padro and H.A. Wiebe

A 3-day workshop of the EMEFS Model Evaluation Team evaluated the model for two periods, July/August 1988 and September 1988. Although there was reasonable agreement between the surface measurements and the model calculations, the discovery of high ozone concentration zones aloft, which were subsequently linked to problems with the wind fields, cast doubt on the validity of the extent of agreement. The wind fields have since been corrected, problems with the natural VOC (volatile organic compounds) emissions have been resolved and the model code has been improved based on the evaluation of the dry deposition module.

In March, the External Review Panel met in Monterey, CA., to review the results of Phase 1 of the model evaluation effort.

### 2.1.4 Dry Deposition Modelling

- J. Padro

Evaluation of the dry deposition module in ADOM is ongoing. It was verified with ozone and sulphur dioxide data collected over the winter forest at Camp Borden, Ontario. The results have been published. A preliminary report is also available on the sensitivity of the ADOM ozone and sulphur dioxide concentrations to changes in the dry deposition module. A study has been completed on the use of flux-variance equations to estimate dry deposition velocities. This may serve as guidance in the AES efforts to set up a dry deposition network.

### 2.1.5 Dry Deposition Estimates for Sulphur and Nitrogen

- J.R. Brook

The project will centre on obtaining the capacity to estimate dry deposition both close to specific locations and over relatively large regions. Thus far, work has focused on a review of the past methods used by AES to estimate dry deposition and of the progress made by researchers in improving dry deposition estimation techniques. One product of this review has been a summary report outlining the options. To focus our efforts, further "in-house" discussions are planned, as well as external discussions with agencies such as the U.S. EPA, who are operating the National Dry Deposition Network in the U.S., and NOAA, where the largest amount of dry deposition research in North America has occurred over the past 10 years.

### 2.1.6 Eulerian Model Evaluation Field Study

- K.G. Anlauf, S.M. Li, A.M. Macdonald, A. Tham, M. Watt and H.A. Wiebe

All the 1990 Spring Intensive data (1-minute concentrations of NO, NO<sub>y</sub>, O<sub>3</sub>, SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and organic peroxides, solar radiation, 5-minute averages for NO<sub>2</sub>, 1-hour averages for HCHO, and 1.5- to 3.0-hour averages for filter pack measurements of particle SO<sub>4</sub>, NO<sub>3</sub>, gaseous HNO<sub>3</sub> and NH<sub>3</sub>) from the Lake Traverse and Egbert sites have been abstracted and quality controlled. Analysis of these data is now in progress and comparisons will be made to the 1988 Summer Intensive data; a preliminary analysis of the diurnal variation of most compounds has already been completed. Preliminary findings are that O<sub>3</sub> exhibits a much reduced diurnal variation in winter, as well as lower concentrations, and that NO persists much longer throughout the day. There was an unusually warm period at the end of April during the Spring Intensive, producing a typical summer-time episode in all compounds measured. This should be therefore a prime period for comparison with modelling efforts, especially the rapid changeover from typically winter to summer-like conditions.

### 2.1.7 Acid Aerosol Measurements

- J.R. Brook, H.A. Wiebe and S. Woodhouse

Measurement activities associated with aerosol acidity and the fraction of aerosol mass in the fine and coarse mode have expanded from 1 site to 3 sites. In addition to Egbert, Ontario, measurements are being made at Sutton, Quebec, and Windsor, Ontario. Future plans include the expansion to both rural and urban areas. Current discussions involve the identification of an additional rural site and the level of activity C&P are capable of undertaking in selected urban areas.

Other AES efforts associated with acid aerosols include collaboration with H&W and the Harvard School of Public Health to analyze the data collected during the 23-City Study. This study, which began in 1989, includes a number of Canadian cities and is currently continuing in Alliston, Ontario. Better information on the relationship between ambient acid levels and lung function in children is expected from the study. AES's involvement provides a better understanding of the spatial and temporal variability in ambient  $\text{SO}_4$  and  $\text{H}^+$  levels.

### 2.1.8 Visibility Research

- R.M. Hoff and M. Sheppard

As part of Canada's commitment to the Canada/U.S. Accord on Air Quality, the Prevention of Significant Deterioration provisions of the U.S. Clean Air Act may have impact on sources of pollution which cross the Canada/U.S. boundary. Canada has committed itself to evaluating the deterioration in visibility and having a plan in place by 1995 to protect pristine areas along the border.

To provide advice and guidance to agencies who will be responsible for monitoring visibility, AES has begun a research effort to scope out the measurement requirements for Canadian visibility regimes, to examine existing visibility data, and to contribute to a Canadian response to the Accord. A long-path transmissometer has been purchased for measurement of visibility in the range of 1-100 km visible range (the range which will be of use for air quality intercomparisons). This system is being set up at Egbert, Ontario, for the 1992 Air Toxics Particle Sizing Experiment. In the spring of 1992, delivery is expected of an open air nephelometer, which will give extinction measurements on unmodified aerosols. In addition, the lidar facility will provide aerosol scattering information and lower boundary layer profiling, the CAPMoN and Acid Mode programs will provide sulphate air concentrations, and the toxics program will provide TSP (total suspended particles) and TOC (total organic carbon) measurements. From this suite of measurement techniques, the various components affecting visibility in southern Ontario (particle concentration, particle size, particle speciation, relative humidity, particle extinction, scattering and absorption) can all be monitored and compared directly to the visibility measurements.

### 2.1.9 CAPMoN Operations

- S. McNair, W. Kobelka, A. Gaudenzi, S. Iqbal and M. Underwood

Improvements were made to the Field pH Program which collects precipitation pH data for inclusion in the weekly Acid Rain Report. The daily procedure now includes a quality control step which gives us high confidence that the pH readings are within  $\pm .1$  pH unit. A quarterly quality assurance procedure was also added. The QC and QA samples are prepared by NWRI in a manner similar to that used to produce LRTAP laboratory intercomparison samples.

There are 25 precipitation collectors operating at 23 sites in the CAPMoN network. There was little change in the program although the collectors used in this program and the Field pH program are being upgraded to one common specification. This will simplify maintenance and sparing. Turnaround time for analysis of precipitation samples at Burlington was reduced to less than one week. The CAPMoN network also has 11 filter pack sites measuring air chemistry. The value of design improvements to the filter pack sampling heads was evident as data completeness statistics show well over 95% of samples are valid 24 hour samples. Responsibility for maintenance and calibration of the field equipment was passed to Atlantic, Quebec and Pacific regions. This transfer will continue to other Regions next year. New data logger software was written to significantly enhance our ability to do near real-time quality control on the system. In 92/93 telemetered site data will be reviewed by technicians on a daily basis.

#### 2.1.10 CAPMoN Analytical Chemistry Laboratory

- S. McNair, D. MacTavish, T. Knott, S. Ahmed, R. Braga and R. Kessler

The lab has been successful in maintaining a turnaround time for analytical data of 90 days from date of sampling. The backlog of samples left to be analyzed decreased by 75% from September 1991 to May 1992. This has been largely due to the use of term employees rather than students. The reduction in backlog has enabled the laboratory to improve the quality of analysis, to undertake special projects, and to prepare for the merging of precipitation and air analysis laboratories. The laboratory has maintained an excellent standing in LRTAP laboratory intercomparisons.

Analytical methods were developed for doing  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  analyses on CAPMoN teflon and dichot filters from the site at Esther, Alberta. This is in support of a project to provide some information on the suitability of using open face filter packs in a dusty environment. The operation of CAPMoN filter packs at Esther will also provide the first non-urban  $\text{SO}_2$  data in the province.

Considerable effort went into method development for a filter pack method of measuring  $\text{NO}_2$ . Filters were prepared and analyzed for the Egbert and Frankfurt intercomparisons. A paper has been drafted on the Egbert results and initial results from Frankfurt will be presented at an EMEP workshop focusing on measurement of nitrogen oxides.

#### 2.1.11 CAPMoN Quality Assurance and Data Management

- R.J. Vet

CAPMoN precipitation data were quality controlled and made available to the end of 1991; air filter pack data were quality controlled to the end of 1991 but require blank correction before general distribution. CAPMoN ozone data were quality controlled to the end of 1991 but require final quality assurance before release.

A quality control program was added to the pH Report Program. As of May 1991, site operators measure the pH of a quality control check solution before each daily precipitation pH measurement. This assures that the quality of the pH values disseminated through the media is  $\pm 0.1$  pH unit. Intermittent multi-point quality assurance checks of the pH meters were also carried out to assure the accuracy of the measurements over the complete range of sample pHs. A project began for developing speciality software for transferring CAPMoN precipitation data on floppy disk and allowing the user to view the data. It will likely be extended to filter pack and ozone measurement data.

#### 2.1.12 CAPMoN Data Analysis

- A. Sirois

A paper has been written on the trend of the concentration of sulphate and nitrate in precipitation at 24 sites across eastern North America. The calculation for the estimation of the precision of the precipitation samples collected by CAPMoN has been completed. The calculation for comparison of the CAPMoN and U.S. NADP/NTN datasets has been completed.



#### 2.1.13 National Atmospheric Chemistry Data Base (NAtChem)

- R.J. Vet

NAtChem activity was focused on establishing the precipitation chemistry data bases and producing system documentation. Data conversion programs for provincial and federal networks were developed and test data sets were created to examine unusual data of each network. A seasonal and annual statistical summary program was developed. The program was verified by comparing its results with those produced by the networks. Print tables were developed for presenting NAtChem statistics and the software was completed so the data statistics can be generated and published automatically.

The NAtChem System, composed of the Network Information System (NIS), Site Information System (SIS) and Chemistry Information System (CIS), was documented in the form of "NAtChem System Documentation" which describes NIS, SIS and CIS and the "NAtChem Operators' Manual" which provides guidance for system operations and maintenance.

The NIS contains data from the following networks: CAPMoN, APIOSC, APIOSD, NB, NS, NFLD, ALTA, MAN, BC, Quebec and GLPN. The SIS database contains roughly 200 sites from the above networks. The CIS holds data from 270 sites in 12 provincial and federal networks from 1978 to 1989. The annual summaries of the US Acid Deposition System Database are also included in the CIS from 1980 to 1988. An agreement was struck with the U.S. National Atmospheric Deposition Program/National Trends Network for exchange of their data.

The 1988 precipitation chemistry data for Eastern North America have been analyzed. The annual wet deposition patterns of excess sulphate and nitrate and their wet deposition maps have been produced.

#### 2.1.14 North Atlantic Regional Study

- D.M. Whelpdale

The objective of this project is to quantify large-scale sulphur (S) and nitrogen (N) atmospheric fluxes into and out of the North Atlantic Ocean atmosphere. Based on model results and reported measurements, sulphur fluxes (Tg S/y) are 4.3-7.2 in via atmospheric transport from continental sources, 0.6-3.6 in from marine emissions, 1.1-1.9 out via the atmosphere and 9-13 out via deposition. Nitrogen fluxes (Tg N/y) are 1.4-3.2 in via the atmosphere, 0.6-0.8 out via the atmosphere, and 3-4 out via deposition. Future work will focus on reducing the discrepancies between inputs and outputs.

#### 2.1.15 Is CAPMoN Satisfying Its LRTAP Client?

- D.M. Whelpdale, A. Sirois and J. Brook

The goal is to examine the role of the CAPMoN in the context of AES Acid Deposition program needs to evaluate the adequacy of sulphur emission controls. Predicted future concentration and deposition fields, created from runs of the AES Long Range Transport model and the U.S. RADM, which in turn were based on sulphur emission reduction scenarios for Canada and the U.S., served as the basis for a number of statistical analyses. Preliminary results indicate that CAPMoN station density and configuration are adequate (within the current region where deposition is greater than 20 kg/ha/y) to detect deposition changes within about 3 years, and to quantify these changes within an additional 6-7 years. However, the current CAPMoN configuration and station density do not appear to be adequate to track changes in the area or the structure of the region where wet deposition is greater than 20 kg/ha/y.

## 2.2 NOx/VOC MANAGEMENT PLAN

### 2.2.1 Ozone Measurements

- K.G. Anlauf and R.S. Schemenauer

The Fraserdale 1990 ozone data have been abstracted and analyzed, and will be incorporated with the CHEF (Chemistry of High Elevation Fog) data for future publication. Also, the data abstraction for this site has been automated so as to greatly reduce the time taken to produce final concentrations. The CHEF ozone data for 1986-1990 have also been assimilated and analysis is in progress.

### 2.2.2 Operational Ozone Measurements

- S. McNair, W. Kobelka, S. Iqbal, A. Gaudenzi and S. Ahmed

CAPMoN continued to operate an interim network of 7 sites. The network will continue to operate at this level until the NOx/VOC Ambient Air Monitoring Working Group recommends on changes to current programs in order to better coordinate activities at a national level. The need for real-time data to support Smog Advisories is being addressed by having on-site spares. Data logger software has been re-written to provide enough on-site data processing and remote quality control to enable us to provide the data directly to Regional Chemists on a real-time basis to support the Smog Advisories program. The transfer of responsibility for maintenance and calibration is proceeding in parallel with that for the air system.

### 2.2.3 Nitrogen Dioxide Intercomparison Field Study

- K.G. Anlauf, A. Tham, M. Watt and H.A. Wiebe

The study compared TDLAS, chemiluminescence and filter pack measurements of nitrogen dioxide (NO<sub>2</sub>) and other nitrogen oxides (NO<sub>x</sub>) type compounds. Acquired data have been abstracted and analyzed. The study found unusually large discrepancies in the NO<sub>2</sub> measurements; however, it could not be determined whether these were calibration errors or true measurement differences. The methods differed by as much as 25%.

### 2.2.4 Nitrogen Dioxide Measurements

- S. McNair, W. Kobelka, D. MacTavish, T. Knott et al.

TEA (Tri-ethanol-amine) filter data from Egbert intercomparison were analyzed and showed that the method had both promise and problems. Most of the problems were related to analytical methods and understanding interferences. Changes were made and we participated in an EMEP intercomparison in Germany. Results of that field study will be presented in June 92.

The TEA filter pack method for measuring nitrogen dioxide (NO<sub>2</sub>) was also operated during an EMEP NO<sub>2</sub> intercomparison which took place in Germany in April and May 1991. The filters have been analyzed and the data provided to study organizers. The results from the study will guide further development work on both the filter preparation and analytical methods.

It was decided to put some effort into evaluating the TECO 42S as a potential network instrument with a sufficiently low detection limit and reliable performance.

### 2.2.5 Measurement of Nitrogen Oxides at Kejimikujik

- J. Bottenheim, A. Gallant and F. Hopper

PAN monitoring continued until the fall of 1991. Analysis of the data indicated major deterioration of the equipment, and monitoring was terminated at that time. During the summer a new commercial instrument (LPA-4 from Scintrex Corp.) for PAN and NO<sub>2</sub> monitoring was tested with limited success. However, sufficient potential was established to merit further study.

At the request of NOAA, a modified CO monitor was installed and operated from mid-July to mid-September, to collect CO data. These and CAPMoN's concurrent O<sub>3</sub> data were compared with similar data collected by NOAA at other locations in the Maritimes in preparation for the NARE-1993 study.

#### 2.2.6 VOC Measurements

- M. Shepherd, J. Bottenheim and A. Gallant

Whole air samples were collected at 2-3 day intervals at four CAPMoN sites (Kejimikujik, Nov. 90 - Jan. 92; Montmorency, Dec. 90 - Jan. 92; Egbert, Jan. 91-Jan. 92; Saturna, June 91 - Jan. 92). The samples were analyzed for C<sub>2</sub>-C<sub>6</sub> hydrocarbons with the purpose to obtain seasonal information on their occurrence in rural Canada. This was a prototype network operation that may become part of the routine monitoring program to support the NO<sub>x</sub>/VOC management plan of the CCME. Results of the one year operation have been analyzed and are summarized in a branch report. Part of the work involved special studies to investigate the suitability of the methodology, effect of sampling frequency, and upgrade of the analytical equipment.

#### 2.2.7 Differential Optical Absorption Spectrometer (DOAS)

- R.M. Hoff and M. Sheppard

In order to measure some of the nitrogen species in the atmosphere, including HONO and NO<sub>3</sub>, a DOAS is being constructed at CARE. This system will measure the concentration of the absorbing gas species in the air by examining the differences in absorption with wavelength over a long path in the atmosphere. During the first half of 1991, a diode array detector package was purchased to evaluate its stability and suitability for the DOAS. In addition, two optical chopping techniques are being investigated for use with the more traditional wavelength modulation detection used in DOAS.

#### 2.2.8 Differential Absorption Lidar

- R.M. Hoff and M. Sheppard

The Differential Absorption Lidar (DIAL), operated during the 1988 EMEFS Summer Intensive through the use of the dye laser capability of the system, was found to have insufficient laser power to probe higher than 2-3 km. In order to improve the DIAL's range resolution, a new Nd-YAG laser is being purchased which will become the on-line channel for the O<sub>3</sub> DIAL system. The new channel, coupled with the Raman shifting techniques in hydrogen deuteride and deuterium to generate the ultraviolet wavelengths, should increase the laser output power by a factor of 30 to 50. This increase in signal alone will result in a 5-7 fold increase in the height that can be reached in profiling ozone. In addition, photon counting was added to the system in 1991 and the combination of the two techniques should make it possible to regularly reach the tropopause with this system. The DIAL system, in combination with the stratospheric ozone lidar at York University, will make Toronto one of a very few areas where ozone is profiled from the surface to 40 km using remote sensing.

#### 2.2.9 San Joaquin Valley Air Quality Study (SJVAQS)

- G. den Hartog, R.E. Mickle, H.H. Neumann, J. Deary and J. Arnold

This was a collaborative study with the California Air Resources Board with the aim of measuring and parameterizing the dry deposition velocity of ozone for a variety of surface types in the San Joaquin Valley in California. It included surface-based ozone flux measuring teams from AES, from NCAR, and from the University of California, as well as the Twin Otter Aircraft from NRC. The purpose of the experiment from the California perspective was to obtain input parameterizations for an air quality model for the San Joaquin Valley. Also, AES was seeking to gather further test data from a variety of surfaces that could be used to investigate the performance of the dry deposition module in ADOM and to further investigate the comparability of surface-based and airborne measurements of ozone deposition.

The field program lasted about six weeks from the beginning of July. The AES contingent consisted of a tower ozone flux team and of a tethered sonde team measuring surface layer ozone profiles. Measurements by AES were made over a vineyard near Ripperdan, CA. The other flux teams measured ozone fluxes over a cotton field and over unirrigated rangeland. The aircraft routinely flew comparative flights near each of the surface sites and measured ozone fluxes over a variety of other surfaces in the valley and surrounding foothills. Conditions in the valley were nearly ideal for this type of study. Inclement weather was never a problem, and large fields and flat terrain provided excellent fetches in micrometeorological terms for both tower and aircraft flux measurements. AES measured flux and profiles continuously from July 11th through August 4th, with interruptions only for periodic calibrations and data removal. The aircraft program was just as successful, with one or more flights every day for this period except for scheduled off-days on Sundays. Initial comparisons of data in the field showed excellent comparability of aircraft and tower fluxes. A data and experiment report was prepared for and submitted to the California Air Resources Board at the end of February 1992.

#### 2.2.10 Lower Fraser Valley

- J.L. Walmsley and J.W. Bottenheim

This work has been undertaken mainly by AES Pacific Region in collaboration with the Province of British Columbia, the Greater Vancouver Regional District and Prof. D. G. Steyn, UBC. Advice and consultation have been provided by Drs. J. W. Bottenheim and J. L. Walmsley. There are plans to implement the Urban Airshed Model and to adapt the CSU-RAMS model for use in the Lower Fraser Valley. Progress has been made in updating the emissions inventory, upgrading the monitoring system and planning for a modest field experiment in summer 1992 with a more extensive experiment projected for summer 1993.

#### 2.2.11 European Monitoring and Evaluation Program (EMEP) Workshop

- D.M. Whelpdale

A successful international workshop was held in Halifax, September 1991. Forty-four participants, 15 of them European, from 10 countries, attended. The theme of the meeting was the combined application of model results and of measurements to various issues, with the purpose of having these two types of scientist come together. Special emphasis was placed on the issue of  $\text{NO}_x$ /VOCs/oxidants, since it is important both in North America and in Europe.

### 2.3 GREAT LAKES WATER QUALITY/AIR TOXICS

#### 2.3.1 IADN/Master Station Operations

- R.M. Hoff, F. Froude, P. Heck, J. Woods and J.B. Martin

Work continued to complete Phase I of the implementation of Integrated Atmospheric Deposition Network (IADN) which is part of AES's contribution to the Great Lakes Water Quality Agreement (GLWQA). This network is designed to measure toxic deposition to the Great Lakes from the air. AES has been operating the Point Petre, Ontario, IADN Master Station since November 1988. Samples of organics in air, trace metals in air, total suspended particulates and total combustible carbon have been taken for 24 hours every sixth day.

The second Master Station on Lake Huron is on Burnt Island (western Manitoulin Island) and was operational by January 1992. In addition to these sites, sampling has been conducted at CARE, at ELA (Kenora, Ontario), at Boulder, Colorado, and at Hampton, Virginia.

### 2.3.2 Organics Analysis (Air Toxics) Laboratory

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

The primary role of the Organics Analysis Laboratory has continued to be the provision of an in-house service for the determination of trace organic chemicals in air samples collected as part of AES activities under Annex 15 of the GLWQA, with emphasis on a set of target species (PCB congeners, OC pesticides and PAHs) identified for "semi-routine" determination.

Actual measurement of the targeted trace organics in the network air samples has continued steadily accompanied by some significant refinements and improvements to the sample extraction, clean-up and analytical procedures. Overall progress with these determinations was substantially slower than anticipated at the beginning of the year. However, measurements on the samples have been proceeding satisfactorily since February 1992. Sample processing capacity has been increased by the setup and validation of an identical sample extraction/drying/volume reduction facility at Concord Environmental Corporation.

To resolve differences between data reported by the two agencies, AES and OME have been co-operating in an informal comparison of analytical standards for PCBs and OCs. AES has also been involved in the design of a formal interlaboratory study for IADN participants, which is scheduled to take place during May-July 1992.

### 2.3.3 Mercury in the Atmosphere

- W. Schroeder and J. Markes

This research project is being conducted in support of a major thrust in Annex 15 of the GLWQA that deals with the atmospheric inputs ("loadings") of persistent toxic chemicals into the Great Lakes and the surrounding basin.

Work has been carried out to improve the current state-of-the-science sampling and analytical methodologies for airborne mercury, a chemical of prime concern in the Great Lakes ecosystem. Investigations are focusing on methods to reduce or eliminate sampling artifacts, such as memory effects exhibited by the sample collection media (noble metal adsorbents), or time-variant collector blanks. Experiments performed with nickel tubing have provided very encouraging preliminary results. They hold out the possibility of being able to replace the quartz tubing previously used in the fabrication of sample collectors with a construction material much more robust, durable and versatile -- characteristics of considerable importance during field measurements of atmospheric mercury.

The data obtained from daily (24-hour sample integration) measurements of atmospheric mercury concentrations and of related environmental parameters at CARE during a six-week period (March 15 to April 30, 1990), corresponding to the EMEFS Spring Intensive, were worked up. The data set will be used in the validation/calibration of numerical predictions (for ambient air concentrations of mercury) to be made with a modified version of ADOM.

### 2.3.4 Air-Water Exchange

- W.H. Schroeder

Annex 15 of the 1987 Protocol to the GLWQA of 1978 specifically calls for research on air-water exchange processes involving volatile inorganic and organic chemicals. This bilateral project has as its main objective the research, development, evaluation, and deployment in the field, of viable methods for in-situ investigations of air-water exchange phenomena, particularly volatilization of priority chemicals from lakes and rivers in the Great Lakes Basin. Two different, but complementary, technologies are under scrutiny: a flux chamber and a sparger system.

Prototype equipment designs were completed for the bubbling sparger at the University of Toronto and for the surface flux monitor at Concord Environmental Corporation. Target compounds chosen for this study were: chloroform, dichlorobenzene, Hexachlorocyclohexane (lindane) and 2,4,6-trichloro-PCB. Both devices have been tested simultaneously in a large tank (spiked with the target chemicals) at the University of Toronto's Institute for Environmental Studies and from a boat anchored in Hamilton Harbour during October. Preliminary results suggested that the overall method sensitivity, for both the sparger and the flux chamber technique, needed to be enhanced in order to detect the range of target chemical concentrations anticipated in natural waters. With this in mind, work was undertaken to improve the design of the prototype versions of the devices.

As a result of the work performed so far, it is expected that application of these two methods will yield a more definitive data set on the equilibrium status, or dynamic steady state partitioning, of contaminants between air and water, as well as on the likely magnitude and direction of chemical fluxes across the air-water interface. Following completion of the research and development phase of this project, the plan for the next 2 years calls for deployment of both devices at various locations for the purpose of investigating the extent and rate of volatilization of several persistent toxic substances of particular significance to Annex 15 of the GLWQA.

### 2.3.5 GAP Sampler Measurements

- D. Lane

This project was initiated to assess the present design and configuration of the GAP (Gas/Particle) sampler for the sampling and analysis of atmospheric polycyclic aromatic hydrocarbons (PAHs), a class of compounds arising from the incomplete combustion of virtually any material (gasoline, coal, tobacco, trees etc.) and listed under Annex 15 of the Canada/U.S. GLWQA.

This project will assess the efficiency of removal and retention of the vapours of several 3-ring (acenaphthylene, phenanthrene and anthracene) to 5-ring (perylene) PAHs in the annular diffusion denuder over the regular sampling time of 40 hours under a variety of simulated atmospheric conditions. Preliminary results showed that the vapours of anthracene, phenanthrene, pyrene (4-rings) and perylene were retained by the denuder at about 97% efficiency at a temperature of 26°C. Acenaphthylene was less efficiently retained. Results of tests carried out at 40°C are currently being assessed.

### 2.3.6 Polycyclic Aromatic Hydrocarbon (PAH) Transformations

- D. Lane

This project will identify the gaps in our knowledge about the concentration and distribution of each major toxic chemical compound class, about the chemical and physical processes which determine the concentration, distribution and fate of these species in the atmosphere, and about the human health and environmental impacts of exposure to these species.

A program has been defined to study the chemical processes leading to the decomposition of a representative PAH, such as naphthalene, and to carry out a complete identification of the products of the decomposition reactions.

A 10 m<sup>3</sup> photochemical reaction chamber was designed and is being built at York University. An Aadco pure air generation unit was ordered to provide a suitable source of clean air for the chamber. Equipment, such as a NO<sub>x</sub> monitor, a gas chromatograph, and sophisticated analytical services will be donated by various partners in the program. The Canadian Institute for Research in Atmospheric Chemistry (CIRAC) formally accepted this project as the first project in its Toxic Chemicals Program. Over the next few years, it is anticipated that this reaction chamber facility will become a major centre for research on atmospheric photochemistry.

### 2.3.7 Toxic Chemical Dry Deposition Project

- G. den Hartog and H.H. Neumann

The objective was to study the dry deposition of species relevant to the deposition of toxic chemicals to the Great Lakes. Development will be started on a tuneable diode laser for carbon dioxide (CO<sub>2</sub>) with the intent of using CO<sub>2</sub> as a tracer for atmosphere-lake interchange studies.

Analysis of particle flux data collected over a leafless deciduous forest at CFB Borden, Ontario, during the Eulerian Model Evaluation Field Study 1990 Spring Intensive continued, and resulted in the report: "Particle Fluxes to a Leafless Deciduous Forest". Particles were measured using a high-flow PMS probe for a size range 0.2 to 12  $\mu\text{m}$  optical diameter. Particle fluxes were computed using the eddy correlation technique. The flux data were obtained for two days, April 23 and April 24, 1991, and flux was computed as averages over 4-hour periods. Computation of particle fluxes requires that enough particles are counted in each sampling interval (0.2 s in this case) and since particle counts decreased rapidly at the larger particle sizes, the analysis was limited to the size range 0.2 to 0.7  $\mu\text{m}$ . Results indicated that in a given size class, particle turbulence-driven deposition velocity was correlated with the variance of the tilt angle of the wind vector at the measurement height of 34 m. Particle deposition velocity due to turbulent transfer over the size range 0.2 to 0.7  $\mu\text{m}$  was found to have a maximum at a particle optical diameter of 0.4  $\mu\text{m}$ .

### 2.3.8 Size Distribution of Toxic Chemical Aerosol Particles

- G. den Hartog and H.H. Neumann

The objective of this project was to characterize the size distribution of atmospheric particles containing toxic chemicals at a site in the Great Lakes basin. This is to be accomplished by simultaneously measuring particle size distributions with an active scattering PMS aerosol probe and toxic chemical concentrations as collected on porous plugs; and then using time series analysis techniques to associate particle sizes and toxic chemicals.

A field experiment was conducted at CARE (Egbert, Ontario) from November to December 1991. Particle size distributions over the range 0.067 to 5.29  $\mu\text{m}$  were measured using two PMS probes (0.067 to 0.90  $\mu\text{m}$  and 0.12 to 5.29  $\mu\text{m}$ , each range divided into 31 logarithmically-weighted size classes). Particle filter data was collected at 10-second intervals using a high volume sampler for TOC (Total organic carbon) and for TSP (Total suspended particles) and using polyurethane foam plugs. Initial analysis shows a good correlation between estimated "mass" from the PMS probe results and filter TSP. The TOC/TSP ratio was negatively correlated with TSP, suggesting that most of the organic carbon was of local origin. Correlation analysis implied that the organic carbon was mostly found on particles in the size range 0.25 to 1.25  $\mu\text{m}$ .

### 2.3.9 Single Level Data Profile Method

- A. Lo

This project will develop a theoretical formulation on the methodology using single level meteorological data for extracting profile information and boundary layer parameters. This method is especially useful in deducing profile and boundary layer parameters from buoy data. Its greatest advantage is that it can generate boundary layer parameters, transfer coefficients, and wind and temperature profiles at all heights. The only input information that is required is the buoy data and the water surface temperature. This methodology has been tested successfully using the 1982/83 Great Lakes buoy data.

### 2.3.10 Aerial Application of Pesticides

- R.E. Mickle and J. Arnold

In September, AES conducted field trials jointly with other organizations to evaluate the effects of emission spectra coupled with wind meteorology on herbicide deposit and drift. The trials funded by the Ministry of Natural Resources were conducted in a clear cut area near Sevogle, N.B. Twelve spray trials (tracers only) were completed using three aircraft.

Deposit measurements were made in-swath and downwind to 600 m on natural foliage (raspberry, red maple, pin cherry) and on foliage simulators, while drift measurements to heights of 200 m were made at 300 and 600 m downwind of the spray line. It is expected that the interpretation of the data set will lead to recommendations to both industry and regulators on the impact of herbicide spraying from different industry standard nozzles.

Work continues towards testing a generic approach to be used in the registration of pesticides for aerial application. A contract has been issued to the New Brunswick Research and Productivity Council to develop a data base of existing research results upon which both a statistical and model evaluation can be carried out. Should the results be favourable, the models can then be used to assess potential environmental contamination from operational spray strategies and thereby assess impact from specific pesticide toxicity data.

#### 2.3.11 AES Rapid Acquisition Lidar (ARAL)

- R.M. Hoff

This system was used in 1990 for experiments in New Brunswick to measure the dispersion of pesticides sprayed from silvicultural (forestry) aircraft. The success of this experiment has prompted an improvement in the experimental setup to include the possibility of fluorescence lidar. The refit of the ARAL system involves the purchase of a new laser and a new mobile laboratory mounting. With this system in the fluorescence mode, the specific detection of Bacillus Thuringiensis (BT) pesticide and the detection of dyed pollen spores may be possible. Experiments are planned for the summer of 1992 to test these hypotheses.

#### 2.3.12 Atmospheric Sources

- E.C. Voldner

Characterization of emission to the atmosphere of acidifying and toxic chemicals is an essential component of Great Lakes Water Quality Program and programs under the Northern Contaminants Act. In this multi-year project global emissions inventories of SO<sub>x</sub>, NO<sub>x</sub> and VOC, use patterns of selected persistent organochlorines, as well as use patterns of current use pesticides in North America, will be compiled. From the latter emissions will be estimated.

#### 2.3.13 Regional Scale Modelling

- E.C. Voldner

Temporal variability in deposition of sulphur, nitrogen and metals to the Great Lakes has been estimated and reports are in progress. Results from a thirty day simulation of mercury transport and deposition, under the Canada/Germany project, was presented at an international workshop.

### 2.4 CLIMATE CHANGE

#### 2.4.1 Polar Sunrise 1992 - Gas/Particle Measurements

- S.M. Li

During the Polar Sunrise Experiment of 1992, a series of experiments were carried out so as to understand the interactions between different phases in the winter-spring arctic atmosphere -- particle gas, precipitation-gas, and precipitation-particles -- and their roles in the spring tropospheric ozone depletion processes. The experiments include denuder-filter pack sampling for determination of gaseous HONO, HNO<sub>3</sub>, HBr, and hopefully HCl in the arctic atmosphere along with their counterparts in the aerosol phase; filter pack charcoal trap sampling for aerosol particles, as well as total organic bromine in order to close the total bromine system; CAPMoN style filter sampling for different species along with SO<sub>2</sub> on impregnated W41 and HNO<sub>3</sub>, on nylon filters; snowfall sampling for the various chemical species; and cascade impactor sampling to determine the particle size distribution of these chemical species.



In addition, di-chot high-volume samples are also being collected. From the samples collected, we will also determine the organic methanesulfonate in particles and in snow in order to understand the biogeochemical cycles of sulphur in the arctic spring atmosphere.

To complement the experiments being carried out in the field, we are planning a laboratory experiment designed to test the collection efficiency of several filter media for various gaseous chemical species. This will be carried as a joint project between York University and AES. The aim is to be able to differentiate the chemical species collected on the filters from the field so as to understand what chemical forms of these species are involved in a number of atmospheric processes, including the ozone destruction processes.

#### 2.4.2 Polar Sunrise 1992 - Arctic Aerosol Measurements

- G. den Hartog, R. Staebler, H.H. Neumann and J. Deary

The objective of our project was to fully characterize the arctic aerosol from sizes in the nanometer range to 10 microns. To achieve this we operated three optical aerosol probes during the period January 15 - April 22, 1992. In addition, measurements of wind speed, air temperature and humidity were also obtained. Our experiment was a collaborative effort with the University of Hanover who operated high-volume impactors to provide chemical composition of the aerosols in different size ranges, a PAH sensor, a CNC counter and a differential mobility analyzer. Except for the impactors, the data have a time resolution of 1 minute; therefore, a very large data base exists. The short time resolution allows for the removal of the effects of vehicle emissions from the aerosol data.

#### 2.4.3 Gas Standards Laboratory - Program Review

- N. Trivett, D. Ernst, D. Worthy, J.F. Hopper, M. Rauh, S. Racki, V. Hudec, L. Leeder, V. Chorney and E. Wallgren.

In May, 1991, a peer review of the Canadian Baseline Program was undertaken on the on-going monitoring of atmospheric trace gases with special emphasis on the work being done in the Arctic. The review evaluated the quality and the effectiveness of the scientific, technical and operational aspects of the Program, and the interaction between the Program and collaborating groups. In addition, the review meeting served as a forum for the exchange of information among the various investigators present. The peer report submitted in November 1991, summarized their conclusions and recommendations.

#### 2.4.4 Gas Standards Laboratory - Carbon Dioxide

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

Several carbon dioxide (CO<sub>2</sub>) standard intercomparisons have been carried out between agencies from Italy, Germany, the C.I.S. and recently between 12 international laboratories as part of a NOAA/GMCC round robin schedule. The results should validate a recent calibration of BAPMoN's best CO<sub>2</sub> standards by the Scripps Institute of Oceanography (SIO). SIO determines the international scale on which the majority of atmospheric CO<sub>2</sub> concentrations measured are based.

A computer database was constructed which enables an organized cataloguing of CO<sub>2</sub> calibration data and the ability to automatically re-adjust CO<sub>2</sub> standards data to account for changes in concentration (due to drift) with time. All calibration data from 1986 to present has been edited and entered into the database. Graphical representation of concentration drift in the standards is a powerful feature of the database.

#### 2.4.5 Gas Standards Laboratory - Methane

- D. Worthy, R. Staebler, M. Rauh and M. Junop

The calibration gas chromatographic (GC) system was modified to enable the analysis of grab flask samples for methane and carbon dioxide. A report outlining the results of the development and evaluation of the calibration GC system has been written.

A methane standard inter-calibration study was performed between AES and NOAA/CMDL. Three cylinders were used in the experiment. Two were provided by NOAA and one by AES. The results clearly revealed that there is approximately a 23 ppb methane concentration difference between the NBS methane scale and the NOAA methane scale. Presently, a round robin methane calibration intercomparison is taking place between the U.S., Japan, Australia and Canada. The results will allow the agencies to intercompare their data more accurately.

A tunable diode laser methane absorption spectrometer, built on contract for AES at the University of Guelph, was evaluated by extensive in-lab experimentation. The system displayed fast response times (up to 6.6 Hz) and immunity to interference from other radiatively active atmospheric gases. Absolute methane concentration readings were repeatable to only about 50 ppbv due to zero drift. However, readings relative to a fixed standard agreed with simultaneous GC readings to a precision of .005 ppmv over the range of 1.8 to 2.5 ppmv (using 2 minute averages). Similar TDL systems for N<sub>2</sub>O, CO and CO<sub>2</sub> are currently being tested at the University of Guelph.

Extensive laboratory tests were also carried out using NBS and in-house standards to evaluate a commercially modified NDIR-CH<sub>4</sub> analyzer for low concentrations (0 - 2 ppmv). The results of the tests revealed the noise level to be too high to obtain the required precision and accuracy for ambient monitoring. Typical precision levels were approximately 30 ppbv over a 3 minute time interval (GC system 3 to 5 ppbv precision).

#### 2.4.6 Gas Standards Laboratory - Freon

- D. Worthy and M. Rauh

A GC system has been developed and tested for the analysis of F-11, F-12 and F-113. The stability, sensitivity, linearity and precision of the GC system was optimized over a 6 month period. The precision ranges of the system compare favourable with the precision ranges attained by the NOAA GC system. The gas standards were purchased from Scott Specialty Gases and calibrated by NOAA. This system will be installed in the Alert BAPMoN station in the fall of 1992.

#### 2.4.7 Aerosol Program

- J.F. Hopper and E. Wallgren

A comparison of annual cycles of black carbon (BC), CO<sub>2</sub>, CH<sub>4</sub> and SO<sub>4</sub> at Alert showed that there were extensive correlations between BC and gaseous species in the winter, confirming earlier reports from Barrow, Alaska.

A project was initiated to develop a method for the analysis of BC in glacial ice and snow samples. Results have been quite encouraging. A comparison between aerosol SO<sub>4</sub> at Alert with BC in ice from the Agassiz Glacier on northern Ellesmere Island has shown excellent agreement in the two time series. This development opens up substantial new investigative possibilities for extending the historical record of aerosol species in the northern Ellesmere region, and linking these data to current ambient measurements.

#### 2.4.8 Flask Sampling Program

- V. Hudec, M. Rauh and N. Trivett

Weekly flask sampling continued at Sable Island, Cape St. James and Alert. The Weather Station at Cape St. James will be closed in October 1992, and an automated weather station will be set up. This situation will make it impossible for us to collect further flask samples from the site. As a result, in early spring of 1992, two sites were investigated as replacement sites. The sites are Cape Scott on the Northern tip on Vancouver Island, and Estevan Point on the west coast of Vancouver Island. Flask samples will be collected at both of these sites and compared to those collected at Cape St. James until October 1992. The replacement station will be chosen at this time.

Modifications were made to the existing flask extraction and analysis system, and extensive testing was carried out to evaluate the accuracy and efficiency of the system. The existing flask evacuation system was also upgraded by incorporating an oven into the system for "baking out" moisture from the flasks. A new double stopcock flask was designed for use in the flask sampling program for the purpose of obtaining pressurized samples. The pressurized air flask will now have enough sample collected so that some of the air can be analyzed for CO<sub>2</sub> and CH<sub>4</sub> as well.

The international flask program was expanded to include a joint Russian-Canadian flask sampling cooperation for Alert and the Russian flask sampling station Teriberka.

#### 2.4.9 Alert Operations

- N. Trivett, J.F. Hopper, D. Worthy, D. Ernest, V. Chorney, V. Hudec, M. Rauh, S. Racki and L. Leeder

Improvements to the CH<sub>4</sub> integration on the GC were carried out and resulted in an improvement of the precision in the analysis by a factor of two. Most of these data were presented at the Program Review Meeting in May, 1991.

The carbon dioxide isotope program for carbon-14 has been in place for 2 years. Weekly samples are collected by passing air through a sodium hydroxide solution. The samples and filters are sent to Germany for analysis.

The Alert radon program has generated some very interesting data. Preliminary analysis indicates that the radon levels are lowest when the air parcels arrive at Alert from over the frozen ocean and highest with southerly winds. However, the radon levels never reach the very low concentrations expected when the air masses have been in contact with the open ocean for long periods of time. More data are required before characteristic levels of radon can be established for Alert "continental" and "maritime" air masses.

The Alert methane 14C and 13C and 85Kr isotope programs were established in August, 1990. For this program, special sample bags are slowly filled over a period of 2 weeks to get an integrated sample of the ambient air. This sample is then extracted from the bags into 14.7 litre aluminum tanks using a compressor. These tanks are sent monthly to Toronto where the methane and krypton are cryogenically extracted and transferred into smaller 2 litre aluminum tanks to be sent to Germany for isotope analysis.

A second aethalometer was operated at Alert from January to July 1991. Data from the two instruments generally compared favourably, despite a high noise level in the second instrument, but a detailed investigation is still in progress.

A flask sampling system to take air samples on board an aircraft was designed. The system was successfully tested during a flight into Alert in April 1991. Samples which were taken at eight different levels ranging from the ground level to 3000 metres were analyzed for CO<sub>2</sub> and CH<sub>4</sub> on the GC and NDIR systems. As expected, the results revealed the atmosphere to be well mixed. Within the atmospheric boundary layer, the decrease in concentration was 27 ppbv for CO<sub>2</sub> and 6 ppbv for CH<sub>4</sub>.

In August and September, 1992, the existing laboratory facility will be expanded by approximately 4 times. The extra space will be used to facilitate the installation of more gas analysis equipment for AES operations, as well as for international agencies.

#### 2.4.10 Sable Island Operations

- N. Trivett, D. Ernst, J.F. Hopper and D. Worthy

Plans are currently under way for a pilot study to evaluate Sable Island as a possible future background air chemistry monitoring site. This will be a cooperative effort between AES and NOAA/GMCC. The NOAA group will be responsible for the aerosol program and AES will be responsible for the greenhouse gas program.

An initial pilot study was started for the greenhouse gas program with the August 1992 installation of continuous CO<sub>2</sub> monitoring equipment on the second floor of the Sable Island weather office. Air was sampled from the top of a 10m tower approximately 30m southwest of the main office. Special conditioning of the sample was required due to the high amount of moisture at this Maritime location.

#### 2.4.11 Fraserdale Operations

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

Preliminary examination of the ambient methane data for 1990 and the beginning of 1991 suggests that air masses arriving from the wetland regions are about 10 ppbv higher in CH<sub>4</sub> concentrations than those air masses arriving from non-wetland regions. The highest concentrations of CH<sub>4</sub> were observed from the southern sectors indicating a probable anthropogenic origin.

Breakdowns caused both CNC instruments to be removed from service for several weeks in the summer of 1991. Preliminary examination of the data reveals generally good agreement between the two instruments. Since they have different response functions, some of the observed differences may be of use as qualitative indicators of the particle size distribution.

Analysis of 1990 data suggested that black carbon (BC) concentrations were dominated by episodic events of long-range transport from southern areas. These events were superimposed on summer and winter increases in the background (non-transport event) BC concentration. At present, the winter increase appears to be either an extension of Arctic Haze or some sort of analogous phenomenon. The summer increase is believed to be partly due to emissions from wildfires in northern areas. Wildfire statistics from provincial agencies are being collated and will be examined in conjunction with the data.

Plans are under way to measure the carbon isotopes for methane. This is a cooperative program between AES and the University of Heidelberg. The air will be sampled only from the wetland sector. This monitoring should help define the isotopic fraction of the CH<sub>4</sub> emitted from the wetland areas.

#### 2.4.12 Data Analysis and Capability

- N. Trivett, D. Worthy and S. Racki

Alert and Fraserdale data analysis procedures were modified to improve the method of quality control for the data. A new software package called FLAGGER was created with its purpose to graphically present collected data and allow flagging of bad or questionable data.

The computer operation of the Downsview laboratory has been continually upgraded to extend data handling and storage capabilities. The current system in the CO<sub>2</sub> laboratory consists of a NEC 386 computer acting as a server for a Novell local area network (LAN) that connects all the personal computers. All the computers are linked via thin Ethernet cabling and are equipped with personal productivity software for stand alone use. A recent addition of a transceiver box has allowed for the seamless connection of the CO<sub>2</sub> laboratory network to the 'backbone', allowing for much needed quicker access to mainframes in the Downsview building and across Canada. Currently, the laboratory communicates regularly to Russian sites via SOVAM, other worldwide agencies via Internet, and the Alert station via EOS (Unitel service). With the growing need for data storage facilities and zero-wait processing power, the current server will be replaced in September 1992. To complement the system, a 4 Gb backup unit will be installed to allow for inexpensive and reliable data backup.

## 2.5 STRATOSPHERIC STUDIES

### 2.5.1 Ozone Monitoring

- J.B. Kerr, C.T. McElroy, W.J. Clark, J.J. Bellefleur, F. Karpenic, R.H. Hoogerbrug, H. Fast and D. Tarasick

The Experimental Studies Division organized and conducted the WMO International Ozonesonde Intercomparison which was held at Vanscoy, Saskatchewan from May 13-24, 1991. This intercomparison was attended by researchers from six countries: Canada, Finland, Germany, India, Japan and USA. The purpose of the intercomparison is to compare and evaluate the performance of the different types of ozonesondes which are presently in operational use in the Global Ozone Observing System.

In July-August, 1991 the Experimental Studies Division conducted the WMO International Intercomparison of nitrogen dioxide (NO<sub>2</sub>) measuring instruments at Mount Kobau, British Columbia. This intercomparison was attended by scientists from Canada, Germany, New Zealand and USSR. A Brewer ozone/NO<sub>2</sub> instrument was tested at Mount Kobau in August for eventual remote operation in the stratospheric monitoring network.

Airmass extrapolation measurements were carried out on several Brewer instruments at Mauna Loa Observatory in Hawaii. In November and December, 1991, calibrations were carried out on two of the Brewer triad reference instruments based in Toronto, the Canadian travelling standard and the WMO travelling standard. In February 1992, the third instrument in the triad was calibrated.

As a result of the heightened concern regarding depletion of stratospheric ozone, the OZONE WATCH program was initiated in March, 1992. This is a weekly bulletin which is released to the Canadian public and describes the present state of the ozone layer over Canada.

### 2.5.2 Stratospheric Research

- H. Fast, D.I. Wardle, R.H. Hoogerbrug, J.J. Bellefleur, F. Karpenic, C. Midwinter, W.J. Clark and A. Ullberg

Data obtained from the 6th Canadian Ozone Experiment (CANOZE 6) was analysed for ozone, nitric acid and polar stratospheric clouds (PSC) aerosols. In August, a stratospheric balloon campaign was conducted at Vanscoy, Saskatchewan, in preparation for CANOZE 7 at Alert. New miniradiometers, backscatter sondes, and nitrogen dioxide sondes were test flown along with ozonesondes on two balloon payloads. To accelerate the development of the nitrogen dioxide sondes, an additional two balloon flights were carried out in November at Vanscoy.

To track Mount Pinatubo volcanic aerosol to northern latitudes, University of Wyoming backscatter sondes were launched from Vanscoy on September 25, from Resolute Bay on October 9, and from Alert on December 2.

The CANOZE 7 winter campaign at Alert was conducted from December 1991 to March 1992. It was coordinated with NASA's second Airborne Arctic Stratospheric Expedition (AASE 2) in order to maximize the number of simultaneous measurements of various constituents that are important for a better understanding of ozone depletion in the arctic winter and early spring. Ozone data exchange was also carried out between Canada's ozone monitoring network and the European Arctic Stratospheric Ozone Experiment (EASOE) to further optimize the benefits gained from three simultaneous ozone research campaigns in the arctic.

For CANOZE 7 a total of nine balloon payloads were launched from Alert with miniradiometers and ozonesondes on board. The radiometer data yield information on the altitude distribution of trace gases, such as nitric acid, which play an important role in the ozone chemistry.

The radiometer flights were made a few hours after launching Canadian and University of Wyoming backscatter sondes. The backscatter sondes were used to monitor the transport of Mount Pinatubo volcanic aerosols into the polar vortex and to detect and determine the distribution of PSC's.

To improve the signal to noise ratio of atmospheric absorption spectra obtained by the high-resolution interferometer at CARE, a contract was awarded to upgrade the hardware and software. The development of ground-based measurements of trace gases was continued with the low resolution interferometer. A meeting with Japanese scientists concluded with a plan for a joint research program at the ASTRO facility being built at Eureka.

### 2.5.3 Aircraft and Space Experiments

- C.T. McElroy, D.I. Wardle, L.J.B. McArthur, C. Midwinter, A. Ullberg, D.V. Barton, W.J. Clark, J.B. Kerr, D. Tarasick and R.H. Hoogerbrug

Equipment for the SunPhotoSpectrometer Earth Atmosphere Measurement (SPEAM-2) experiment is nearly ready for flight. The SPEAM-2 experiment uses two instruments: the Airglow Imaging Radiometer (AIR) and the SunPhotoSpectrometer (SPS). The AIR will observe light emitted by excited oxygen and the SPS will make measurements of the amount of ozone, nitrogen dioxide and aerosol in the stratosphere. A new development in the project has the side-hatch window of the orbiter Columbia being changed out for a quartz version. This will give the SPEAM experiment the opportunity to make observations in the ultraviolet part of the spectrum. The SPEAM-2 Shuttle flight is now scheduled for mid-October. Steve MacLean, the Canadian Payload Specialist who will operate the experiment on-orbit, is now undergoing training at the Johnson Space Center in Houston, Texas.

Bristol Aerospace is continuing work on the Brewer Earth Atmosphere Measurement (BEAM) experiment hardware. The BEAM project will see the Brewer launched in the Shuttle Payload Bay as a Get Away Special (GAS) Payload in 1993. The experiment focuses on the problem of the long-term calibration of satellite-based ozone measuring instruments. Recent work by Bristol has resulted in the completion of control software and the construction of some hardware for the ground-checkout equipment for BEAM.

AES has been invited to participate in the NASA ER-2 high-altitude ozone research program. The SunPhotoSpectrometer is being adapted to fly in a wing pod on the ER-2 aircraft. The data collected will be used to verify the atmospheric light-scattering codes used in photochemical models of the ozone layer chemistry. Work is now under way at an accelerated pace to meet a September 1 delivery commitment for the installation of the equipment on the ER-2 at the NASA/Aimes Research Center at Moffet field in San Francisco, California.

Discussions are proceeding between scientists at AES and the Institute of Atmospheric Physics of the Academy of Sciences of Russia which will lead to the installation of an AES Brewer Ozone Spectrophotometer on-board the Aeroflot flight which goes between Montreal and Moscow three times per week. The purpose of the project is to provide comparison data for the Total Ozone Mapping Spectrometers (TOMS) instruments which are on-board the US NIMBUS and Russian METEOR satellites and the SBUV instrument on-board NIMBUS.

### 2.5.4 National Atmospheric Radiation Centre

- L.J.B. McArthur, T. Grajnar, A. Ullberg and R.H. Hoogerbrug

The National Atmospheric Radiation Centre (NARC) hosted the final meeting of the International Energy Agency Task 9. This brought experts on the measurement and modelling of solar radiation for solar energy uses from nine countries together to complete a task that was begun 3 years earlier. The major findings of the task were better characterization methods for pyranometers and the design of a typical solar radiation year, including prototype design years for Germany and the United States.

In cooperation with Task 9 and the beginning of the new IEA TASK 17 (in which the NARC is also a member), a second field comparison of Global Radiation Reference Radiometers (GRRR) was held at CARE (Egbert, Ontario). Canada, Sweden and Germany participated in this field test which was run in its entirety by NARC from the months April through August. A second set of comparisons was initiated with the Australian Bureau of Meteorology. These were to test for differences in the calibration responsivities of pyrgeometers. The preliminary results found that the differences were small and probably due to spectral shifts between the blackbodies because of different calibration temperatures. NARC participated in a third multi-national comparison of radiometers at the FIRE II experiment at Coffeyville, Kansas, during November 1991. The results from these measurements are being used to support work in the Atmospheric Radiation Measurement Programme and the Baseline Surface Radiation Network. The main goal of the radiation portion of the experiment was to determine how to improve measurements of broadband infrared radiation.

The laboratory facilities at both NARC and the Radiatively Active Gases (RAGS) site in Asquith, Saskatchewan, have been further upgraded. The data from this latter site has been used to validate satellite model work conducted at McGill University. NARC has begun an investigation into developing a measurement site south of Regina.

## 2.6 CORE RESEARCH

### 2.6.1 Wind Flow in Complex Terrain

- J.L. Walmsley

Continuing efforts in collaboration with Prof. S. R. Karpik, University of Toronto, have led to a PC version of the MSFD model. Considerable attention has been given to ensuring that the model will be easy to use on this new platform. It should not be difficult to convert the code for use on a UNIX-based mainframe, should that prove necessary. Although the model requires a powerful PC (e.g., 486/33 MHz) and FORTRAN compiler (Lahey F77L 32/EM) to produce results in a reasonable time (hours rather than days), we believe that it will be of interest to research users inside and outside AES.

The time spent in developing the PC version of MSFD has resulted in delays in extending the range of applicability of MSFD. Progress has been made, nevertheless, in incorporating thermal stability effects; preliminary results were presented at a conference on air pollution. Work on continuing development of the MSFD-concentration model is also planned for 1992/93 in collaboration with Dr. J. Padro. We hope to restructure the code so that the pollutant concentration and flux can be driven by either the neutral or stable MSFD model. If this proves feasible, it should be possible to include equations for more than one species, provided that all terms can be linearized.

A new method of formulating the PBL Resistance Laws that relate external (geostrophic wind speed, Coriolis parameter and surface roughness length) to internal (friction velocity and cross-isobar angle) parameters has been proposed.

### 2.6.2 Wind Energy

- J. L. Walmsley

PERD funding over the past several years has been used in developing and refining the MS-Micro model, our first-generation model for wind flow in complex terrain. We have a modest marketing strategy for MS-Micro that has led to sales in 1991 alone to 17 groups in 10 countries, generating over \$3,000 in revenue. (Sales of our Wind Correlation model produced an additional \$2,000.) MS-Micro is being used by research groups in the wind-loading and wind-energy fields. Many of the 1991 sales were in the United Kingdom where activity in wind energy is at a new high. In Canada, the main interest has been in southwestern Alberta and Quebec; however, there are indications of new activity in wind energy in Saskatchewan and Manitoba. In 1992/93, we intend to prepare for an anticipated revival of wind energy in Canada by producing a report on the Canadian wind resource and by documenting a Recommended Practice for Canadian Standards Association.

In 1991/92 we acquired the Pixeltrak software that now enables us to digitize topographic contours and surface land-use boundaries much more accurately and quickly than manually tracing lines with a digitizer. The software manufacturer also provided us with a program that converts Pixeltrak's standard output to a form that can be easily processed by either MS-Micro or MSFD to produce input fields for those two models.

As a spin-off to wind-energy modelling activity, several chapters were written for a book on modelling of atmospheric flow fields and a chapter was written for a wind-diesel guidebook. A further spin-off involved assistance to Canadian Climate Centre in forest management at CARE. MS-Micro was used to provide wind speed estimates for deciding whether to thin the red pine forest. The model will also be used in several forestry projects regarding seed orchard management, windbreaks and pollen flow.

### 2.6.3 Gaussian and Heavy Gas Research - C.S. Matthias

A model has been developed which describes several important features of the flow of a pressurized fluid from a punctured tank. Model results are being compared to experimental results received at a conference in New Orleans (May, 1991) and which were gathered by Quest Consultants in Norman, Oklahoma. The present model falls closer to the data than the RELEASE model developed by CREARE, Inc. The features which are described are the release rate (kgm/s) of a superheated liquid from a pressurized container, the instantaneous boiling of a fraction of the liquid to a gas, the rapid evaporation of some of the remaining liquid, the production of suspended droplets by the vigorous boiling, and the extreme cooling of the liquid-gas mixture.

The variables which are compared are the liquid flow rates, quantity of liquid falling from the jet, and low temperatures resulting from evaporation. The chemicals are water, freon, methylamine, cyclohexane, and chlorine. The results suggest that the model may be applied to any pressurized liquid.

## 2.7 AIR QUALITY SERVICES

### 2.7.1 Modelling for Air Pollution Emergency Response - S.M. Daggupaty

The PC-Version of AQPAC's (Air Quality Package of Programs), containing Heavy Gas plume model codes, and Neutral gas plume and puff model codes, were modified with the implementation of variable step size Runge-Kutta 4th order scheme. This made the run time for the models much faster. The PC version of AQPAC development has been completed, through a joint venture and cost sharing project with MEP. It has been undergoing final touches with regards to bullet-proofing and to smoothen out their performance and to integrate model results with a report writing capability. Now the graphical output with a specified option of scale is colour coded to depict different levels of toxic or flammable limits.

As a member of working group of MIACC (Major Industrial Accidents Coordinating Committee) AQPAC results for specific accidental releases of some selected toxic chemicals were presented for the risk analysis studies.

### 2.7.2 Mesoscale Boundary Layer Forecast Model (BLFM) - S.M. Daggupaty

The three dimensional mesoscale boundary layer forecast model was further modified for use on our IBM-PC 386 machine. A paper describing the simulation of boundary layer circulation with a gradual development of lake breeze over southern Ontario and its comparison with a special mesoscale network of observed data has been completed. Preliminary experiments with simple surface characteristics were performed to compare with an earlier study in which the land is assumed to have uniform roughness length.



Further work is under progress with the inclusion of detailed surface temperature prediction using "Force - restore" method of Bhumralkar and Deardorff. Work has also been initiated to include land use data into the model at 1 km resolution.

It is encouraging to note that an independent evaluation of results of our earlier version model compared favourably with the sophisticated and much complex model of Pielke's group at Colorado State University. Potential applications with this model include prediction of pollution episodes, detailed forecast of hourly circulation and turbulence information (hazard areas) over complex terrain, coastal and marine areas for oil and chemical spills.

### 2.7.3 Hemispheric Tracer Model & Its Applications

- J. Pudykiewicz

The objective of this project is to generalize the hemispheric tracer model developed in AES to study the movement and transformation of toxic chemicals, sulphur species and heavy metals on the scale of the Northern Hemisphere. The proper generalization of the model will provide unique capability to investigate different problems related to atmospheric environment. The most important applications of the model will include:

- (a) studies of the transport of various contaminants to Northern Ecosystems
- (b) studies of the atmospheric input of contaminants to Great Lakes
- (c) investigation of atmospheric transport of heavy metals
- (d) investigation of atmospheric oxidants on regional and hemispheric scale

During the first stage of this project, attention will be focused mostly on appropriate modifications of the modelling system and application of the model for studies of the transport of various contaminants to Northern Ecosystems. The model runs will provide the rational base for identification of pollutant sources affecting Northern Ecosystems, and are also essential for determination of the levels and trends of contamination in arctic ecosystems.

### 2.7.4 Global Tracer Model with Complex Chemistry

- J. Pudykiewicz

The global scale predictive tracer model designed to simulate atmospheric transport processes, as well as tropospheric and stratospheric chemistry, will be addressed. The model consists of a global spectral model and a set of the mass conservation equations coupled through the chemistry terms. The model was tested in both diagnostic and fully predictive mode simulating the global scale dispersion of atmospheric tracers. Attention will be focused on two major topics:

- (a) development of the parameterization method for mass fluxes of tracers associated with convective clouds; and
- (b) continuation of work on the numerics of the model.

### 2.7.5 Canadian Nuclear Emergency Response Model (CANERM)

- J. Pudykiewicz

The development of CANERM was initiated by AES in response to the Chernobyl accident in order to create an operational capability to analyse and predict the environmental effects of accidental releases of radioactive and toxic materials. The present version of CANERM is a sophisticated computer system consisting of the 3-Dimensional eulerian dispersion model simulating transport processes and of numerical weather prediction models providing information about the state of the atmosphere. The dispersion model is based on a system of the advection-diffusion equation transformed to the terrain-following coordinate system  $\sigma$  in order to incorporate effects of the topography.

The operational version of the system is very flexible and could be executed either in diagnostic mode using objectively analysed meteorological fields or in predictive mode. The predictive mesoscale version of the system is run on a grid with spatial resolution from 5 to 15 km using output from a fine resolution Regional Meteorological Model. The meteorological fields from the hemispheric spectral model are used for the simulation of extended range regional dispersion on grid with resolution from 20 to 50 km.

The description of the source term is provided by the expert computer system. In the most general case, the accident scenario is derived from a separate computer model simulating the dynamics of the discharge of the radioactive or chemical species. A simpler solution is related to the use of the accident scenario from "look up tables" containing descriptions of the most typical potential accidents. The CANERM is capable of treating stationary sources as well as moving sources of different origins located within the Northern Hemisphere. The discharge of the radioactive material is represented using the Particle In the Cell (PIC) method. A second alternative description of the release is based on the multi-grid method. The release in this method is simulated on a series of nested grids with increasing resolution. The multi-grid method is particularly attractive in context of the simulation of local and mesoscale transport where detailed information about the deposition pattern in the vicinity of the source is important.

Since the implementation of CANERM in 1988, the system has been applied to several environmental emergencies involving nuclear power plants. The system was also used on several occasions to assess the environmental impact of the reentry of nuclear powered satellites.

#### 2.7.6 Air Quality Services - M.E. Still

During 1991, a review of the Services portion of the Air Quality Services and Research Program (AQS RP) was undertaken to determine from the Regions how the Air Quality Research Branch could best support the Program. The review recommended that:

1. AES undertake a review of AES responsibilities in the federal Environmental Assessment and Review Process (EARP);
2. The Branch hire an applied scientist to assist the Regions in the operation of dispersion models;
3. The Branch arrange training sessions in the operation of dispersion models for the regional air quality specialist;
4. CMC with the assistance of the Branch assess user needs for the Environmental Emergency Response (EER) program;
5. The Branch hire a meteorologist to provide a national focal point for the implementation of smog advisories and ultra-violet radiation warnings;
6. The Branch hold a workshop to review regional, national and international experience in providing smog advisories and ultra-violet radiation warnings, and to develop a plan for their implementation;
7. The Branch regularize or cancel the Acid Rain Report Program;
8. The Branch encourage cooperative research projects between the Branch and the Regions;
9. The Branch organize conference calls to involve the regional SSD Chiefs in the planning of the Air Quality Services and Research Program; and
10. The Branch allocate a budget to cover costs of appropriate regional information and advice activities.

The Regions commented that the review could have also looked at how the Regions could support the AQS RP and at what were the roles and responsibilities of the Regions in this Program. A draft document detailing the roles and responsibilities of all components of AES in the delivery of the AQS RP has been completed and is being reviewed by the management of the Research Directorate.

Some of these recommendations have been initiated. A workshop was held to review the expertise available in providing smog advisories in the designated areas of Canada (6). The Regions and the Branch agreed that the Acid Rain Report should be continued under the leadership of the Quebec Region (7). The Branch has encouraged the Regions through its workplanning exercise to enter into joint projects that have a regional emphasis (8). When the draft workplans are prepared, the Regions will be included in the finalizing of the regional portion and in commenting on the regional applicability of other projects (9).

The Annual Climate and Air Quality Services meeting was held in November. The main discussion in the Air Quality session centred around the priorities of the AQSRP and the relationship between the Regions and the Branch in the Program delivery.

## 2.8 REGIONAL AIR QUALITY REPORT

### 2.8.1 AES Regional Activities

Information on the AES regional activities that support the delivery of the AES Air Quality Services and Research Program in the Regions can be found in the combined Quarterly Reports (Volume 9, Number 1 to 4) of the AES Regional Scientific Services Divisions.

## 2.9 BRANCH PUBLICATIONS

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