

**AIR QUALITY
RESEARCH BRANCH**

ANNUAL REPORT

1998-99

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Compiled by
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October 2000

Air Quality Research Branch
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AIR QUALITY RESEARCH BRANCH

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1.0 FOREWORD

1.1 AIR QUALITY RESEARCH BRANCH

[D.C. McKay]

Even though the projects are described in the specific air quality issues, all these issues are related as they all concern the air in which we live. Furthermore, air quality issues are related to other environmental issues of our planet. In this report, we have indicated some new issues, i.e., particulate matter. Recently, the National Atmospheric Chemistry (NAChem) Database for Particulate Matter became fully operational, in which data from 14 regional-scale aerosol networks in Canada and the U.S. were placed.

In the past two years, the Branch formalized the CORE measurement program to determine the long-term impact of anthropogenic activities on atmospheric chemistry and radiation in five important airsheds of Canada. A five-year strategic plan for the Acid Deposition and Oxidant program is being used as a basis for a number of environmental initiatives across Canada. Analyses indicate that sulphate wet deposition decreased considerably from the early 1980s to the mid-1990s in both Canada and the U.S.

Modelling plays an important role in Branch monitoring and processes research activities as model representations can simulate the atmosphere after being evaluated against field and laboratory measurements. One such initiative is the AURAMS (A Unified Regional Air quality Modelling System) project, which is a multi-year effort to develop a new regional air-quality modelling system that will be used in Canada for studying and managing multiple regional tropospheric air issues. Another is the Canadian Hemispheric and Regional Ozone and NO_x System (CHRONOS) smog model, which can be used for smog and acid rain emission control scenario evaluations. Trajectory models have also proven to be valuable research tools in air quality research, particularly for pollutant transport issues.

The number of hazardous air pollutants detected has increased over the years so that the Branch has become involved in more varied aspects of these pollutants. The Branch continues to support the Great Lakes Water Quality Agreement, in particular Annex 15 that deals with airborne toxic substances. The major effort is the monitoring of air constituents to determine the atmospheric loading to the Great Lakes system. Besides the Great Lakes, the Arctic has been the recipient of pollution from other parts of the globe. The Arctic ecosystem exhibits increasingly evidence of contamination by persistent, bioaccumulating toxic

substances. To study this issue, the Northern Contaminants Program has just entered into a new five-year program, which includes the continued measurements of organochlorines and metals in the atmosphere that deposit in the northern latitudes.

High-resolution solar absorption spectra were recorded in order to monitor atmospheric gases implicated in stratospheric ozone depletion and the enhanced greenhouse effect. Some of these ground-based measurements are now being used in preparation for validation of space-based measurements, such as MOPITT (Measurements of Pollutants In The Troposphere).

Based on the Branch's Greenhouse Gases and Aerosols Program, which contributes to the understanding of greenhouse gases and aerosols, the first Baseline Program Report (Canadian Baseline Program Summary of Progress to 1998) is now available. For the future direction of the program, a five-year strategic plan and a scope document have been prepared.

1.2 AWARDS

[L. Kiely]

Since 1988, the Branch has presented the All-Seasons Research Award to members of the staff who have forwarded the goals of the Air Quality Research Program. To date, 35 such awards have been presented, including to staff from other sections of Environment Canada. In 1998, a Branch employee was recognized for his work:

Dr. William Schroeder who, with his colleague Julia Lu, completed the submission and acceptance of a major paper in *Nature* on the depletion of mercury in the Arctic boundary layer. This observation may be of global significance in determining a major sink for this important compound. Dr. Schroeder is to be complimented on his tenacity in pursuing this element throughout the global environment, and becoming recognized as an international authority on our understanding of mercury in the environment.

1.3 PROGRAM REPORT

[K. Ford]

On April 1, 1998, the Air Quality Research Branch (AQRB) began its fiscal year with a complement of 99 employees. Under the Workforce Adjustment Program two departed in mid year and two left on development leave. In 1998, the Branch hired an ozone and radiation trend research scientist,

an environmental analytical chemist, and a research analytical chemist. At the Centre for Atmospheric Research Experiments, an Integrated Atmospheric Deposition Network technician, an assignment technician and a computer scientist were hired. A site scientist commenced work at the observatory at Bratt's Lake in Saskatchewan.

In April 1999, AQRB started with a staff of 104 and by March 2000 will have a complement of 107. During 1999, two senior scientists left for positions in the U.S. The Branch also hired an air toxics research scientist, a trace organic chemist, a research chemist and a carbon cycle research physical scientist. A systems modelling analyst commenced work in the Branch's offices in Dorval, Quebec.

In each of the years, five post-doctorate fellows have been working on numerous Branch scientific programs. Also, during this period, several visiting scientists and guest workers from around the globe participated in the Branch's scientific studies. Each year, the Branch hired 22 students from colleges and universities for work terms.

In the first year, staff attended 67 international symposiums, conferences and business meetings. Of these, 22 were funded from outside agencies. One hundred and fifteen employees attended symposiums, conferences, and business meetings in the U.S. Twenty of these were funded from outside agencies. In the second year, 63 of the staff attended international symposiums, conferences and business meetings, 25 of which were funded from outside agencies. The attendance at symposiums, conferences and business meetings in the U.S. was at a level of 124.

1.4 BRANCH RESEARCH ACTIVITIES

1.4.1 AIRS Field Study [K.B. Strawbridge]

The Alliance Icing Research Study (AIRS) field study was operated out of the National Research Council's hanger in Ottawa with considerable ground installations located at Mirabel Airport, Quebec. Although there were several objectives behind the AIRS study, this description is limited to the simultaneous upward/downward airborne lidar system. The AIRS field study was divided into two field periods: December 1999 and January/February 2000.

The AIRS study provided an opportunity to compare the newly acquired 8mm Cloud Profiling Radar (CPR) with the results obtained from the lidar system. The CPR was very sensitive to ice crystal layers and less sensitive to water droplets. Two new log amps and detectors were purchased for the downward lidar system to provide more dynamic range when looking at cloudtop reflectivity. An attempt will be made at retrieving liquid water content information at the top of the cloud from the lidar return signal.

1.4.2 Evaluation of Unknown Sources [J. Pudykiewicz]

The development of methods was continued which were designed to locate clandestine nuclear testing in the context of the Comprehensive Test Ban Treaty (CTBT) debated by the United Nations in the past several years. The technique used for this purpose was based on the solution of the adjoint tracer transport equation with a properly defined forcing term. This technique is applicable for a large class of toxic materials either for the verification of the existing emission inventories or, as a sole method, for the assessment of the source term. In the research involving radionuclides observed in the atmosphere, the location of the source was estimated using the influence function obtained as a solution of the adjoint equation. The strength of the source is estimated from the Lagrange duality relation. The information obtained this way is important to enhance the ability to monitor nuclear testing. The general evaluation of the method indicates that it is more accurate than the traditional approach based on back trajectories.

2.0 THE ISSUES

2.1 ACID DEPOSITION and OXIDANTS

2.1.1 Acid Deposition and Oxidants [M. Lusic]

Broadly stated, the ultimate question posed in the Acid Deposition and Oxidants (ADO) Science Program is: "What is the reduction in emissions of acidic and smog-forming gases (in terms of magnitude, type, emissions sector and location) required to protect human health and the terrestrial and aquatic ecosystems?" ADO is the result of a merger of the former "NOx/VOC Science" and "Acidifying Emissions" programs, after some of the original resources in these programs were re-allocated to the present Particulate Matter program and Unified Model development efforts.

As in past years, about half of the resources went into long-term measurement, quality assurance/quality control, and database/analysis and reporting activities for acid deposition and smog-related constituents. The database/analysis and reporting activities were primarily in support of the Canadian Air and Precipitation Monitoring Network (CAPMoN) and the National Atmospheric Chemistry Database (NAtChem).

A notable development in long-term monitoring during the past two years was the formalization of the CORE measurement program, with regional cooperation. One of the main objectives of the CORE program is to determine the long-term impact of anthropogenic activities on atmospheric chemistry and radiation in five important airsheds of Canada (Pacific Coast, Prairies, Arctic, industrially impacted Eastern Canada, and East Coast).

Existing measurement stations, several of them supported by ADO, are used to provide the infrastructure for this program. Apart from long-term measurements, a number of method development and evaluation projects were also supported, including improved methods for determination of volatile organic compounds (VOCs) and oxygenated VOCs (OVOCs), and of nitrogen species (peroxyacetyl nitrate and nitrogen oxides). The formaldehyde intercomparison project was completed, and a report on the results was issued.

The modelling activities supported by ADO included the development of a model applications system, which encompasses an emissions preprocessing system and various off-the-shelf models for smog and acid rain emission control scenario evaluation purposes, in order to better serve the policy community. There was continued improvement and evaluation of the Canadian Hemispheric and Regional Ozone and NO_x System (CHRONOS) smog model. Significant resources were also devoted to the development of better methods for estimation of dry deposition rates of sulphur compounds at CAPMoN sites. Work was started to address the nitrogen dry deposition problem, including ammonia dry deposition.

Data analysis projects included the analysis of data from past field campaigns (notably NARSTO-CE, RACE and NARE). There were no major smog-related field studies in which the Branch participated in 1998 or 1999, but one exciting prospect for scientific research in the coming two years is PACIFIC 2001 (a follow-up field study to PACIFIC'93) in the Lower Fraser Valley that is planned for the summer of 2001. While particulate matter (PM) will be the primary focus of this study, the same smog-forming chemical mechanism leads to both PM and ozone formation.

With two major scientific assessments recently accomplished (for Acid Rain and Tropospheric Ozone), the ADO program strives to continue providing the best scientific support possible for policy development. A five-year strategic plan has been developed for ADO, and is being used as a basis for requesting additional resources to address some of the scientific information gaps that need to be filled if policy needs are to be met for a number of initiatives, including:

- Canada-wide Acid Rain Strategy for Post-2000
- Phase 3 of the Smog Management Plan
- Canada-wide Standards for ozone and PM
- Canada-U.S. Air Quality Accord Ozone Annex.

2.1.2 NAtChem Database [R. Vet]

The National Atmospheric Chemistry (NAtChem) Database and Analysis Facility focused on 3 areas related to precipitation chemistry: achievement of basic annual objectives, publication of analysis results, and NAtChem user support. The NAtChem/Precipitation Database was

updated to include 1996 data for all major Canadian and U.S. networks. All historical data were revisited and upgraded by adding missing and dry period records generated using climate data and scientific evaluation.

Research was carried out into the status and trends of aquatic critical load exceedances in eastern Canada. Maps were generated of critical loads, wet deposition fields, critical load exceedances, and trends in both exceedance areas and exceedance amounts. The results indicate that a very large area of eastern Canada still receives wet sulphate deposition in excess of the aquatic critical loads in spite of the fact that the area of exceedance has decreased.

Precipitation chemistry data from Canada and the U.S. were analysed to investigate the temporal changes in wet deposition patterns from 1980 to 1995, and to estimate the gross long-range transport of air pollutants from the U.S. into Canada. The analysis indicated that patterns of sulphate wet deposition decreased considerably from the early 1980s to the mid-1990s in both Canada and the U.S. In contrast, the patterns of nitrate wet deposition barely changed. Both results corresponded with changing sulphur dioxide (SO₂) and nitrogen oxides (NO_x) emission rates in eastern North America, i.e., a major decline in SO₂ emissions and a slight increase in NO_x emissions. A major shift in the ratio of nitrate to sulphate in wet deposition was found.

2.1.3 CAPMoN Data Quality [R. Vet]

The objective was to continue operating the quality assurance, data management and data analysis programs of the Canadian Air and Precipitation Monitoring Network (CAPMoN). In the Quality Assurance Program, CAPMoN sites were audited, data were quality controlled and an annual quality assurance report was designed. The U.S.-Canada air and precipitation sampling intercomparison studies were continued at the Pennsylvania State University, Sutton and Egbert sites. All parts of the CAPMoN sampling program were found to be in control, and the analysis of the intercomparison data is underway.

The CAPMoN Data Management Program continued operating normally. Precipitation and air chemistry data were quality controlled within 6 months of the end of each calendar quarter, and ozone data were quality controlled within 2 months of data collection. The CAPMoN air and precipitation chemistry data were submitted to the National Atmospheric Chemistry (NAtChem) Database, and the ozone data were submitted to the National Air Pollution Surveillance (NAPS) Database. Data quality control was done under contract using the Research Data Management & Quality Control System (RDMQ™) software package developed by Branch staff. The RDMQ™ software package was licensed to two external contractors and applied to a number of other measurement programs within the Branch.

The CAPMoN Data Analysis Program focused on publishing two papers, one on the precision of CAPMoN precipitation chemistry measurements and the other on the comparability of Canadian and U.S. precipitation chemistry measurements. Time series analyses continued including the development of a Kernel smoothing algorithm for presenting trends in CAPMoN data. The analyses show a decrease in sulphate concentrations in precipitation from the late 1980s through the late-1990s. Test programs were written to do cluster analysis of air mass trajectory data at CAPMoN sites.

2.1.4 CAPMoN [D. MacTavish]

The Canadian Air and Precipitation Monitoring Network (CAPMoN) is a non-urban air quality monitoring network with siting criteria designed to ensure that the measurement locations are regionally representative, i.e., not affected by local sources of air pollution. Scientists involved with the measurement of atmospheric pollution in urban centres would consider most CAPMoN sites to be remote and pristine. CAPMoN has four main objectives:

- to determine the spatial patterns and the temporal trends of pollutants related to acid rain and smog;
- to provide data for long-range transport model evaluations and effects research;
- to ensure compatibility of federal, provincial and international measurements; and
- to study atmospheric processes.

Between April 1, 1998, and March 31, 2000, CAPMoN made measurements at and reported data from 20 sites. These sites encompassed 18 precipitation chemistry measurement sites in Canada, 1 precipitation chemistry measurement site in the U.S., 10 air filter measurement sites, and 7 ozone measurement sites (Figure 1). The field component of CAPMoN, including site inspections, calibrations and contract administration, continues to be supported by Environment Canada's Meteorological Service of Canada staff in Pacific and Yukon, Prairie and Northern, Ontario, Quebec and Atlantic Regions. Overall network sampling integrity continues to be assured by auditing operations at a minimum of 13 sites yearly.

Laboratory credibility is maintained by participation in international Intercomparison studies. These include Environment Canada's NWRI/NLET Intercomparison, the WMO-GAW Laboratory Intercomparison, the United States Geological Survey Intercomparison, and the Norwegian Institute for Air Research's (NILU) Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) Laboratory Round Robin Study.

CAPMoN's infrastructure supports a variety of atmospheric research initiatives ranging from occasional use of the measurement site to the ongoing collection and analyses of

environmental samples. These cooperative ventures include various Branch programs, Environment Canada research initiatives, universities and other research-oriented networks, such as the Canadian Network for Isotopes in Precipitation.

2.1.5 HTM and GTM Trajectory Models [B. Pabla]

Trajectory models have long been proven to be valuable research tools in air quality research particularly for pollutant transport issues. The HTM (Northern Hemispheric Trajectory Model by Olson) has been operational for many years and has been widely used in data analysis and interpretations by Branch scientists, as well as by the scientists from MSC regional offices and from international institutions.

In order to compute trajectories on the global scale, the Global Trajectory Model (GTM) was modified to make it as user friendly as the HTM, and to run it on 1°x1° resolution as opposed to the original version developed for 2.5°x2.5°. The input databases (NCEP data base on 2.5°x2.5° from 1978 to 1998 and CMC database on 1°x1° from January 1999) were developed. The Graphical User Interface (GUI) was developed to submit trajectory jobs so that the user does not have to be familiar with all the technical details, e.g., CMC computers and their operating systems.

In anticipation that the HTM will be replaced by the GTM, some preliminary work has been performed to compare both trajectory models. Both the HTM and GTM models were modified to make them Y2K compatible and to output the data in a new improved format. In order to implement these changes, the trajectory plotting software "TrajPlot" is being modified. In addition to support for MSC users for trajectory computation, the trajectory data was computed for a fee for scientists from international organizations.

2.1.6 Modelling Atmospheric Aerosols [J. Pudykiewicz]

In the initial stage, the sulphate aerosol was studied with the help of a new mathematical formalization based on a continuous model. Unlike the existing bin models, the model solves rigorously the continuous dynamic equations for the aerosol (the space coordinates and the aerosol particle volume being the independent variables).

Three "types" of aerosol are taken under consideration: Aitken nuclei, sulphuric acid-water liquid drops, and sulphuric acid-water drops with solid cores inside. The initial physical and chemical processes affecting aerosol are homogeneous and heterogeneous nucleation of water and sulphuric acid vapours. The combined processes of condensation and coagulation assure further growth of freshly nucleated drops. The additional factors, which affect

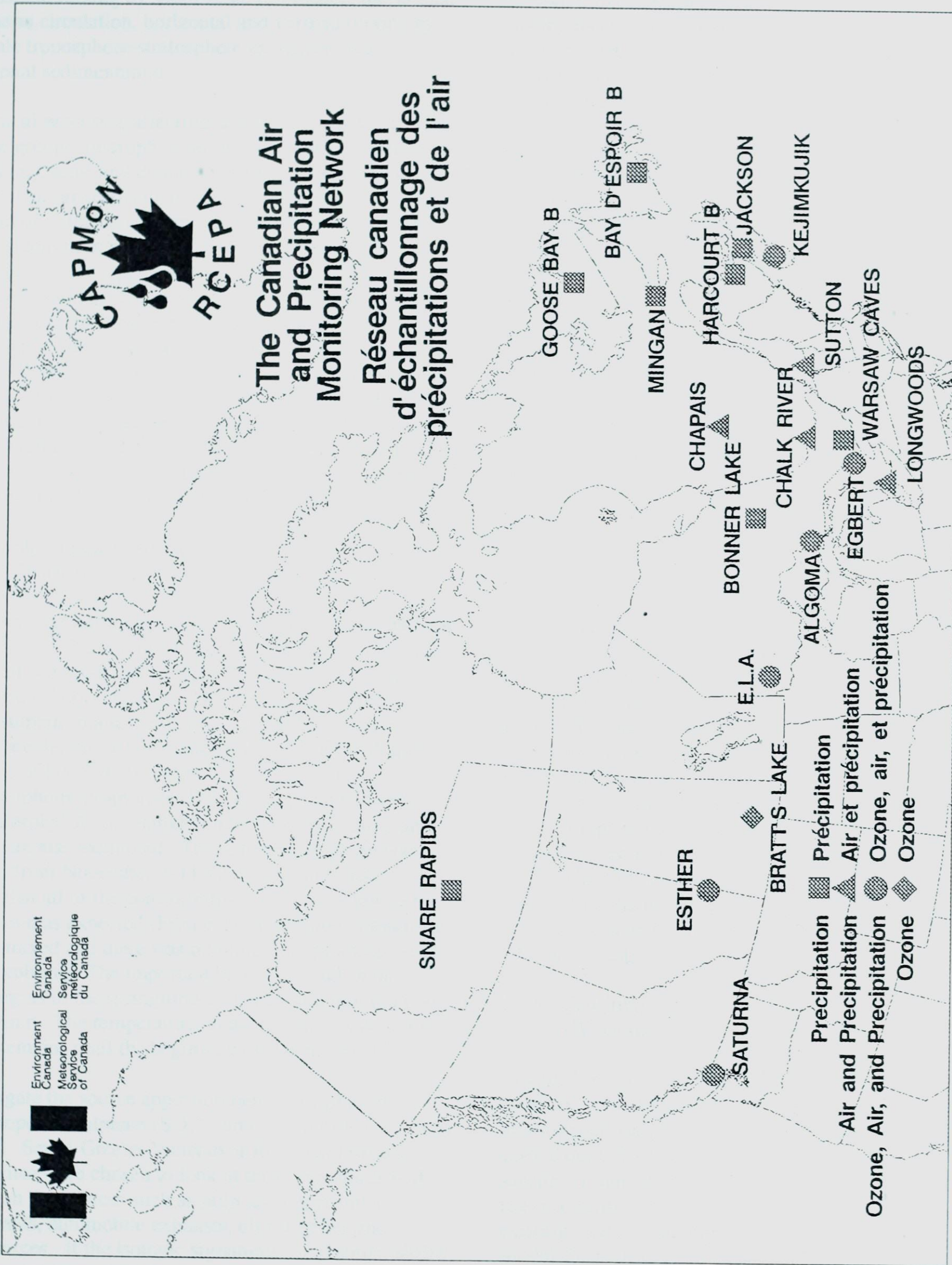


Figure 1: CAPMoN Sites

the aerosol growth, are of dynamic nature. These are vertical and horizontal mixing by small-scale turbulence, meridional hemispheric circulation, horizontal and vertical mixing by large-scale troposphere-stratosphere exchange, and gravitational sedimentation.

The physical processes affecting aerosol growth are divided into three groups: microphysical processes of the aerosol, chemical reactions, and dynamic processes. Among the microphysical processes there are the homogeneous nucleation of drops, heterogeneous nucleation on Aitken nuclei, condensation/evaporation of liquid aerosol, coagulation of each type of aerosol, and conversion of evaporating liquid aerosol with cores to Aitken nuclei. The chemical processes considered are those leading to the oxidation, and, subsequently, to the production of sulphuric acid, as well as those which produce sulphur dioxide through the photolysis of carbonyl sulphide (OCS). The sink/source of sulphuric acid through aerosol condensation/evaporation links the microphysical and chemical processes. The model was already tested for the stratospheric aerosol and results were reported in the scientific literature.

2.1.7 Sulphur in the Georgia Basin [S. Sharma]

A three-year study is being conducted in partnership with the Pacific & Yukon Region of Environment Canada. The main objective of this study is to determine the biogenic sulphur budget for the Georgia Basin. The seasonal and annual biogenic sulphur, mainly dimethyl sulphide (DMS), flux estimates are determined to achieve this. Along with this, the sources of DMS in the water column, such as dimethylsulphoniopropionate (DMSP_{particulate} and DMSP_{dissolve}), chlorophyll A, zooplankton mass and speciation, and nutrients, are also examined. The autumn campaign was conducted from November 3-11, 1999, and the results indicated that all of the concentrations were very low in the water column as expected (Figure 2). The water column was very well mixed and there was no biological productivity in the water column. The important biological and chemical activity begins in the springtime with the algal bloom in the water column. The temperature stratification sets in at this time and remains until the beginning of the autumn time.

To investigate the source apportionment of sulphur, the stable isotopes of sulphate (SO_4^{2-}) and sulphur dioxide (SO_2) were used. Seven Greater Vancouver Regional District (GVRD) sites were chosen to look at these signatures with the focus on the sources such as pulp and paper mills, cement plants, automobile exhausts, oil refineries and marine sources. If the isotopic signatures are distinguishable among these sources then the samples taken at a more polluted inland site will be compared with a site more influenced by the oceanic sources to determine the biogenic and anthropogenic contribution to the total sulphur.

Preliminary results indicate that the combustion sources (diesel + gasoline) from the seawater sulphate can be distinguished from the combined signature of sulphur from an oil refinery and the biogenic hydrogen sulphide from marshes and/or tidal flats. Data suggest very little presence of seawater sulphate in the GVRD relative to other sources.

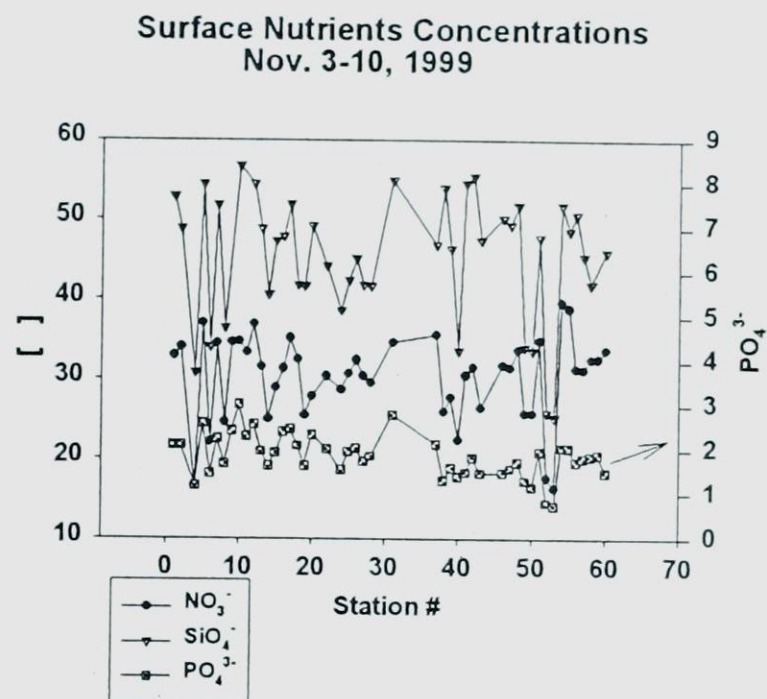
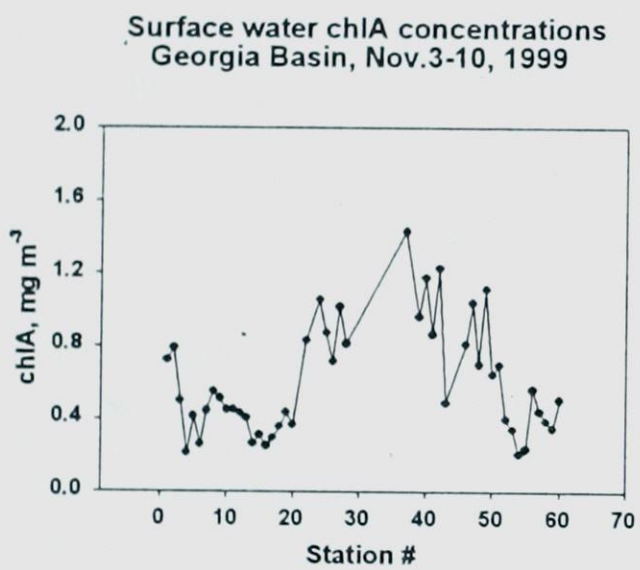
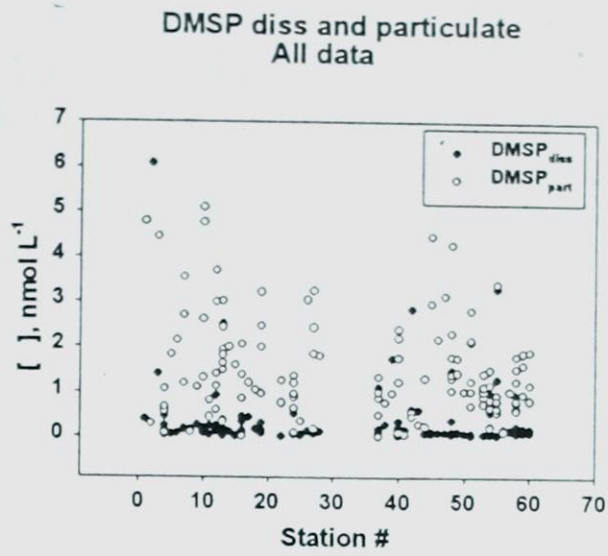
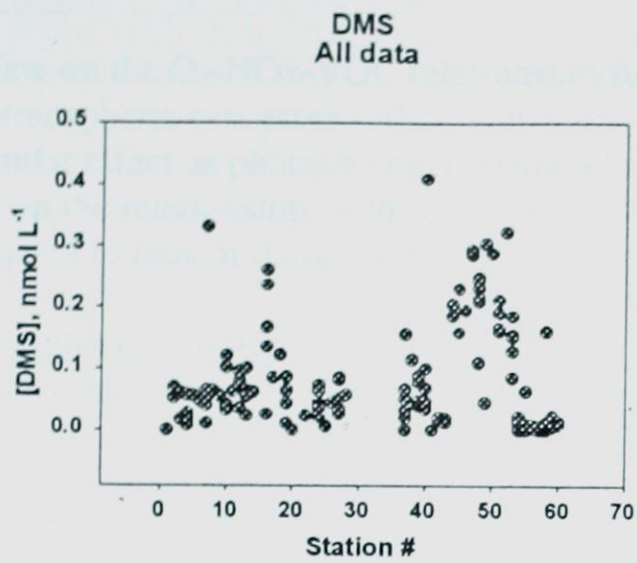
2.1.8 High Elevation Ozone and NO_x [K. Anlauf]

Continuous measurements of tropospheric ozone and supporting meteorology have been made on Mt. Sutton, a mountain top site near the rural town of Sutton, Quebec, since May 1986. The site is located at high enough elevation so that there is minimal influence on the chemical measurements from nocturnal inversions. A statistical analysis of the 1986-1998 ozone dataset has revealed no significant trend at the 2 sigma level; however, there was a small negative trend at the 1 sigma level. Sectoring the data, using the locally measured winds, shows that the 'background' ozone concentration varies seasonally with a maximum in springtime. The measurements also exhibit the expected summer-time hump related to anthropogenic emissions.

Detailed measurements of several reactive nitrogen oxide compounds (NO , NO_2 , PAN, HNO_3 , p-NO_3^- , NO_y) were made from February 1998 to October 1999 in order to determine their role in photochemical processes at this site. Preliminary analyses indicate that the site is frequently impacted by high concentrations of local nitrogen oxide (NO_x) emissions (>50 ppbv), particularly during the wintertime months (October through March). Partitioning the nitrogen oxides shows that HNO_3 , PAN and NO_2 are the major components. An intensive set of measurements was collected over a two-week period during July 1998 and July 1999. The NO_x median for the July 1998 period was 0.68 ppbv, while the medians for HNO_3 , p-NO_3^- , PAN and $\sum \text{NO}_y$ (sum of measured nitrogen oxides) were 0.42, 0.11, 0.35 and 1.87 ppbv, respectively.

2.1.9 Sensitivity of O₃-NO_x-VOC [W. Gong]

Regional ozone, nitrogen oxides and volatile organic compound (O₃-NO_x-VOC) sensitivity in eastern Canada was investigated using a model-based approach. Analysis was carried out to look at the regional variability of the sensitivity, and at indicator ratios and their applications in regional sensitivity evaluation. These were based on the existing model simulations of one week during the Eulerian Model Evaluation Field Study (EMEFS) and one month during summer 1996. Additional scenario simulations (i.e., 35% reduction in anthropogenic NO_x emissions alone; 35% reduction in anthropogenic VOC emissions alone; and 35% reduction in both) were considered.



Flux estimations of DMS in the Georgia Basin using Liss Merlivat's flux estimation Model

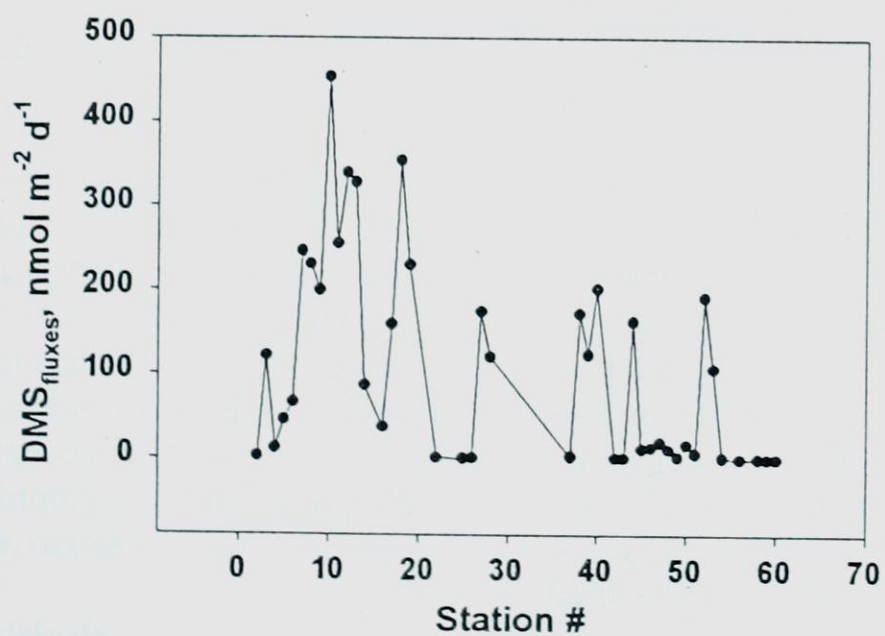


Figure 2: DMS in the Water Column

Recent review on the O₃-NO_x-VOC relationship suggests that some atmospheric processes (other than chemical) may have the similar effect as photochemical aging which will in turn impact on the relationship. Additional model runs are being conducted to look at these issues.

2.1.10 Tropospheric Nitrate Chemistry [P.A. Makar]

The aim was to create a smog chamber data set to be used in evaluating models of the heterogeneous chemistry of particle nitrate formation. The KFA particulate chamber in Juelich, Germany, was to be used for the experiments, with the contribution of active scattering probes and an Anderson Impactor from us to complement the instrumentation already in the KFA chamber. The measurement program planned would have included different sets of initial conditions of particulate ammonium nitrate and ammonium sulphate, and the precursor ammonia and nitric acid gases. Resulting changes in particle size, number and composition would then be used for model verification.

Unfortunately, there were a number of technical difficulties once the program got underway. The scattering probes were not designed for use with the high number densities present in the smog chamber. Some experimentation on changing the flow rates was attempted, but it eventually became clear that the probes would not be able to accurately measure the observed number densities. The Anderson impactor was used for a number of sampling periods, although it was noted that there were some problems with its operation. There were also problems with the use of ammonium sulphate as an initial condition in the chamber. The experimenters preferred to start with salts such as potassium nitrate since they had more experience with potassium salts. Also, there was concern that the ammonium sulphate would clog their aerosol creation system. However, some sulphate measurements were taken. Data are to be analyzed.

2.1.11 Sensitivity Study of NO_x and VOC Data [P.A. Makar]

The intent was to continue earlier work begun with the NAPS (National Air Pollution Surveillance Network) database, using the NAPS measurements of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) to suggest local sensitivities of the ozone concentration to changes in VOC and NO_x concentrations. Earlier work showed those differences in the relative importance of different hydrocarbon classes across the country, although particular classes had the greatest impact on ozone levels.

2.1.12 Measurements of Formaldehyde [A.M. Macdonald]

Continuous measurements of formaldehyde (HCHO) were made with the Hantzsch-coil method for an intensive measurement period July 12 - 29, 1998, at Mt. Sutton and

August 3-19, 1999, at Egbert. At Mt. Sutton, measurements of HCHO by DNPH cartridges (4-hour integrated samples, 12-16 LT, analysis by EPS) provided an additional opportunity to compare the methods under field conditions. Volatile organic compound canister samples were also collected (six 4-hour samples over 24 hours) and analyzed.

The 1998 Mt. Sutton data set was relatively polluted and contrasts with the clean measurements of the North American Research Strategy for Tropospheric Ozone-Canada East (NARSTO-CE) 1996 campaign. The anthropogenic influence was clearly seen during periods of southwesterly flow when ozone reached 90 ppbv and HCHO exceeded 4 ppbv (the mean concentration of HCHO over the period was 1.8 ppbv). A pollution event sampled during the first part of the study was a regional event with high ozone concentrations observed also at Egbert and at Kejimikujik. The Egbert 1999 period was very clean (45% of the data were collected under northwesterly flow) with a mean concentration of HCHO for the entire period of 1.1 ppbv.

Several precipitation events occurred with a related loss of HCHO. Little information is available in the literature on HCHO deposition rates, primarily because high-resolution measurements are not available. These periods are being examined to determine the wet removal rates of HCHO and to compare them with current model parameterizations.

2.1.13 Formaldehyde Measurement Techniques [A.M. Macdonald]

Six methods to measure gas-phase formaldehyde (HCHO) were compared over a one-week period in the spring 1998. These methods included the TDL (York U), two methods based on the Hantzsch reaction (AES and Purdue U), and three methods based on HCHO reaction with DNPH (MSC and EPS). The study was divided into two phases. On two days of the experiment, participants sampled a series of air mixtures containing known amounts of HCHO. Tests were also conducted for influences of ozone, sulphur dioxide and isoprene on the techniques.

Ambient HCHO measurements were made from May 27 until June 1. Meteorological conditions varied widely over this 5-day period providing a range of HCHO concentrations (~100 pptv to 3 ppbv) for testing the methods. The continuous methods (Hantzsch-coil, Hantzsch-nafion, and DNPH-coil) agreed well with the TDL. The DNPH-mist and DNPH-cartridge methods showed both a non-zero background and the highest degree of scatter with the TDL. The higher degree of uncertainty for the cartridges was attributed to blank levels for the high-resolution one-hour samples.

Two data workshops were held - one in September for a submission of the data sets and one in March 1999 to finalize discussions for a journal article and a technical report. Experiment results and preliminary conclusions were presented at the 1998 Fall AGU meeting. A technical report

that expands on the individual methods and the performance of the techniques compared to the TDL has been published as an AES internal report. Examination of the ambient data will focus on three aspects: (1) washout/wet deposition of HCHO; (2) dry deposition; and (3) response of HCHO to radiation changes.

2.1.14 Formaldehyde Chemistry Modelling [A.M. Macdonald]

A four-day period from the North American Research Strategy for Tropospheric Ozone-Canada East (NARSTO-CE) data set was chosen to model formaldehyde (HCHO) concentrations and sources at Mt. Sutton. During this period, HCHO reached its highest concentrations of the study. Clear skies, elevated temperatures, and a light to stagnant southwesterly flow characterized the meteorology. The chemistry at the site was relatively clean with low ozone, carbon monoxide and anthropogenic volatile organic compounds, but isoprene peaked during this period. A box model was run to investigate the impact of biogenic hydrocarbons to the site.

Improvements in the model included an update of the numerical scheme with the Sparse Matrix Vectorized GEAR (SMV-GEAR) solver, the ability to track any chemical constituent of interest, and an update of the chemical mechanism for biogenic hydrocarbons. Base and sensitivity runs were completed for the case study from the summer 1996. Results show a significant contribution to HCHO concentration from biogenic hydrocarbons. The overall pattern of the HCHO measurements is well produced but the model underestimated the absolute HCHO values. Uncertainties in the model's chemical input could not account for the difference. A radical source approximately equal to the photolysis of 2 ppbv of nitrous acid was added to the model - this improved the magnitude and time dependence of the modelled formaldehyde relative to measurements, but a net HCHO deficit in the model results still occurred.

The box model HCHO deficit may be due to the effects of advection (not included in a zero-dimensional model of this nature) or the presence of other, unmeasured sources of HCHO at the measurement site (e.g., higher monoterpenes). The model (without the extra radical source) was used to determine the relative contributions of different precursor hydrocarbons to the net HCHO concentration of the resolvable chemistry. Overall for these selected days, approximately 58 % of the HCHO could be accounted for from oxidation of biogenic hydrocarbons, 29% from methane, and 8% from anthropogenic sources.

2.1.15 Southern Atlantic Region Transport [W. Gong]

An investigation of the roles and mechanism of transport and chemical transformation affecting ground-level ozone in the

Southern Atlantic Region (SAR) of Canada, based on the Acid Deposition and Oxidant Model simulation of an Eulerian Model Evaluation Field Study case, was carried out.

Past observations have shown that the area is strongly influenced by the marine environment over the Gulf of Maine, and that pollutants transported at high levels do not always reach ground level.

From the reconstructed time history of various processes along modelled back trajectories originating from a site in Nova Scotia, the analysis clearly shows that the elevated ground-level ozone in the SAR during the study period was associated with transport at low levels. Also, the high ozone levels brought to the site were mostly produced within the stable marine boundary layer from precursors picked up earlier over the emission area on the east coast of the U.S.

2.1.16 Canopy Emissions Modelling [P.A. Makar]

The objective was to construct a 1-dimensional canopy model of the Borden forest, and use the model to study the interactions between anthropogenic species and local biogenic emissions at the Borden site. A number of important discoveries were made. The development of a new dispersion parameterization resulted in greatly improved simulations of the observed levels of isoprene.

In the real canopy, the net rate of change of isoprene will be due to the effects of emissions less diffusion less chemical removal as formulated below:

$$\partial C / \partial t = E_{\text{real}} - D - L_{\text{chemistry}}$$

Measurement campaigns to determine biogenic emissions (E_{real}), which rely on flux measurements above the canopy frequently, make the assumption that the chemical loss term is negligible, hence:

$$\partial C / \partial t = E_{\text{measured}} - D$$

The canopy modelling work suggests that the emissions (E_{real}) and diffusion terms, although large, come close to cancelling out, with the result that the chemical losses have a significant effect on the net rate of change. The standard measurement practice of using the net rate of change and turbulence parameters to estimate emissions may therefore underestimate the calculated emission fluxes ($E_{\text{measured}} = E_{\text{real}} - L_{\text{chemistry}}$). This work suggests that this underprediction may be on the order of 40% of the total emission, if the emitted hydrocarbon of interest is the most reactive one at the measurement site. Ozone oxidation of biogenic and anthropogenic alkanes was a source of hydroxyl radicals during the night and morning.

Subsequent work extended the model to estimate the production of particulate forming condensable gases, with the conclusion that biogenic emissions of alpha-pinene may be a significant source of aerosol mass. The model has also been used in graduate thesis work at the University of Virginia, where the addition of anthropogenic emissions has been used to show the interactions between anthropogenics and biogenics under higher nitrogen oxides conditions. The model has been well received by the research community, and several collaborative projects are planned.

2.1.17 Speciation in Chemical Mechanisms [P.A. Makar]

This project started as part of the Eurotrac-2 GLOREAM (Global and Regional Atmospheric Modelling) subproject - a continuation of work on the mathematical techniques used to compress chemical reaction mechanisms into smaller numbers of variables. This in turn reduces the processing time required to perform a simulation of complex chemistry. The current work has resulted in techniques using integrating factors that can reduce processing time by a factor of 3.7 relative to standard codes.

2.1.18 Chemical Transport Modelling [J. Pudykiewicz]

The Canadian Hemispheric and Regional Ozone and NO_x System (CHRONOS) for prediction of atmospheric oxidants on regional and hemispheric scales was developed and evaluated. The model simulates dispersion and complex chemistry of nitrogen oxides and volatile organic species. The meteorological data for the model is provided by the Mesoscale Community Model (MC2), and alternatively, by the Global Environmental Multiscale (GEM) model. The results provided by CHRONOS show the increased performance of the model when compared to other similar numerical models.

The most important feature of the new model is its ability to predict very high ozone concentrations that are observed during smog episodes. CHRONOS was employed for evaluation of emission control scenarios and for international assessments involving transboundary pollution issues under Canada/U.S. Air Quality Accord. Currently, the model is used by the Canadian Meteorological Centre to issue the regional air quality forecast. The future development of CHRONOS will extend its ability to forecast particulate matter, and subsequently, will permit regional simulations of tropospheric chemistry with very high, of the order of 1 to 2 km, horizontal resolution.

In order to prepare the model for runs with very high resolution, mathematical methods have been employed which can increase the understanding of the formation of complex subgrid-scale structures in the tracer distribution, as well as permit the realistic parameterization of mixing coefficients on a grid of an Eulerian model.

2.2 HAZARDOUS AIR POLLUTANTS

2.2.1 Hazardous Air Pollutants [K. Puckett]

The Branch continues to support the Great Lakes Water Quality Agreement (GLWQA), in particular Annex 15 that deals with airborne toxic substances. Research is directed towards addressing the significance of atmospheric loadings to the Great Lakes system relative to other pathways and sources outside of the Great Lakes system. The major effort is in the surveillance and monitoring of air constituents to determine the atmospheric loading to the Great Lakes System by quantifying the total and net atmospheric input, and by defining the temporal and spatial trends in the deposition of toxic substances.

The Northern Contaminants Program entered into a new five-year program, which included the continued measurements of organochlorines (OCs) and metals in the atmosphere. Measurements continued at Alert, Nunavut, and steps have been taken to initiate similar measurements at Amderma in Russia and also to re-establish measurements at Cape Dorset. Measurements of total gaseous mercury (TGM) were made year round at Alert and special emphasis was placed on the Polar Sunrise period. TGM depletions were observed again in keeping with similar measurements in previous years.

The Canadian Atmospheric Mercury Measurement Network (CAMNet) was initiated with measurements of total gaseous mercury (TGM) being made at various locations across Canada, in addition to the ongoing measurements at Alert. The intent of this measurement program is to quantify the short-term temporal and spatial changes in TGM levels with a view to understanding the processes influencing the levels seen across Canada and in source identification.

2.2.2 Great Lakes Water Quality Program [K.J. Puckett]

The Canada-U.S. Great Lakes Water Quality Agreement (GLWQA) contains Annex 15, which deals with airborne toxics. The Branch's prime obligation under this annex is the operation of the Integrated Atmospheric Deposition Network (IADN), initiated in 1990 with a six-year plan (IP1). The results of this first phase have been analyzed and published. Measurements show that target chemicals are still detectable in air and precipitation. Based on this experience, a further plan (IP2) was developed and signed in 1998.

Branch management objectives of signing off the plan and of hiring a data officer has been completed. Other objectives are discussed in the relevant reports. Other agencies participating are the National Water Research Institute (NWRI) and the Ontario Ministry of the Environment (OME). NWRI is collecting and analyzing precipitation

samples, analyzing buoy samples, and assessing the NWRI plume for determination of mass transfer coefficients. One of OME's tasks is to conduct round-robin intercomparisons between the participants.

2.2.3 IADN Station Operation [F. Froude]

As part of the responsibility under the Great Lakes Water Quality Agreement (GLWQA) Annex 15, the Branch operates the Canadian stations in the Integrated Atmospheric Deposition Network (IADN). There are three sites located at Point Petre, Egbert and Burnt Island. The data from these sites, in conjunction with data from the U.S. sites, aid in the understanding of the atmospheric loadings to the Great Lakes.

Operations and data analyses are continuing but difficulty has been experienced with the supply of acceptable polyurethane (PUF) cartridges. On a temporary basis, PUF cartridges are being cleaned in-house to augment the supply. Data have been placed in the Branch's Research Data Management and Quality Control System (RDMQ) for quality control. At the moment, Egbert data have been logged on to an intranet site which includes tabular and graphical displays. Graphs can be configured for fixed time periods from hourly to annually. Also, the package has the ability to average data over periods from seconds to weeks. Data from the other sites are being added.

2.2.4 IADN Laboratory [K. Brice]

The trace organics analytical laboratory supports Annex 15 of the Great Lakes Water Quality Agreement (GLWQA), particularly the analysis of air samples from the Canadian sites of the Integrated Atmospheric Deposition Network (IADN). Emphasis has been placed on the targeted polychlorinated biphenyl (PCB) congeners, organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs). Other activities include support for special studies, continued method development for laboratory analyses, and participation in inter-laboratory intercomparisons.

As previously mentioned in the report on IADN operations (see 2.2.3), the laboratory has been involved in the preparation of polyurethane (PUF) cartridges. Problems have been identified with the manufacture and, based on the investigations, the laboratory has assumed responsibility to prepare PUF cartridges.

Due to the large throughput of samples from the network and other studies, both sample analysis and data delivery are continued extensive workloads. Sample analysis includes sample extraction, cleanup, instrument calibration and data reduction on blank samples, as well as field samples. Only after a complete data review to ensure that all samples are correctly assigned are the data placed in the Research Data

Management and Quality Control System (RDMQ) as a laboratory-validated data set.

2.2.5 Toxaphene and PCBs at IADN Sites [K. Brice]

The purpose is to gather data on the atmospheric concentrations (gas and particle phase) of toxaphene congeners at Point Petre, which is one of the sites of the Integrated Atmospheric Deposition Network (IADN). Multi-day (5 days) sampling at this site has produced a three-year data set that can be analyzed in conjunction with data from other locations.

Analysis procedures have concentrated on investigating the compositional complexity of some of the specific peaks and clusters observed in the gas chromatographic analysis of the technical toxaphene standard. Investigations into the composition of the constituents in background ambient air have shown clear differences relative to the technical toxaphene standard. The air sample displays reduced complexity with fewer components identified.

To obtain improved data on the atmospheric concentrations (gas and particle phase) of toxic co-planar polychlorinated biphenyls (PCBs), extracts can be taken from the air samples obtained at Point Petre. There are three years of data available.

2.2.6 IADN Data Analysis [R. Hoff]

The Integrated Atmospheric Deposition Network (IADN) data analysis group is responsible for inputting the IADN data into the Research Data Management and Quality Control System (RDMQ) after the principal investigators have assembled the data. This group performs first-level quality control, i.e., detection of outliers, addition of flags and recommendations for field or laboratory remedial action, and then assembles the data into its relevant program focus. This step is carried out with the involvement of the principal investigator. The final data sets are then placed in the National Atmospheric Chemistry (NAtChem) database. Finally, the group is responsible for the scientific data analysis and the presentation of these data.

Processing of the entire IADN data set is progressing well but delivery schedules are slipping due to the extensive work to be achieved in the quality control and analysis of this large data set. New computer programming is progressing in extracting data to calculate loadings of all chemicals measured by IADN.

2.2.7 Northern Contaminants Program [L. Barrie]

One of the objectives of this program is to measure and understand the occurrence and trends of selected

organochlorines (OCs) and polycyclic organic hydrocarbons (PAHs) in the Arctic atmosphere. Other objectives are to provide insight into contaminant pathways and to enable validation of models of contaminants in the northern environment with atmospheric observations. An archive of organic extracts of Arctic air samples is being maintained for retrospective investigation for contaminants of the future. A major long-term trends measurement station is being operated for the Arctic Monitoring and Assessment Programme (AMAP) at Alert, Nunavut, in parallel with a western Russian Arctic station funded by the Canadian International Development Agency, and the Departments of Indian and Northern Affairs, and of Foreign Affairs and International Trade.

Since January 1992, measurements of airborne persistent organic pollutants (POPs) including herbicides, pesticides, synthetic industrial compounds and PAHs have been made on a weekly basis in the Canadian and Russian Arctic. At Tagish, Yukon, concentrations of hexachlorocyclohexanes (HCHs), chlordane, DDT, and other OC pesticides were measured in ambient air samples on a weekly basis between December 1992 and January 1995. Mean concentrations of chlordanes and DDT were $<1.5 \text{ pg.m}^{-3}$, while other OCs were observed at mean concentrations of $<6 \text{ pg.m}^{-3}$.

These measurements were analyzed with air parcel back trajectories and other meteorological information to provide insight into the sources, transport, and chemical transformation of OC pesticides to the western Canadian Arctic. In winter, unusually high air concentrations of HCHs, DDT and chlordanes were predominantly influenced by trans-Pacific long-range atmospheric transport from eastern Asia that generally occurred within five days. HCH concentrations were correlated with the time that air spent over eastern Asia prior to arrival at Tagish. However, chlordane and DDT, which also increase with trans-Pacific transport, do not show a correlation with time, as these pesticides can undergo partial degradation in soils prior to transport. Trans-Pacific transport from Asia did not result in exceptional levels of other OC pesticides such as dieldrin and endosulfan. Air masses originating predominantly from North America had the highest concentrations of HCHs, chlordanes and endosulfan when the five-day upwind airshed included the western United States. Endosulfan concentrations may also be influenced by suspected usage of endosulfan in the west coastal and prairie regions of Canada. When the occurrence of long-range transport from Asia was low, such as in the summer, most OC pesticides exhibited a significant dependence of atmospheric concentration on land surface temperature.

2.2.8 New Persistent Chemicals in the Arctic [T. Bidleman]

The focus is to determine "new" chemicals in the Arctic environment that have not been monitored previously. From a national and international perspective, finding new

chemicals in the Arctic implies that these compounds are sufficiently persistent in the atmosphere and seawater to be transported to the Arctic. If found in Arctic food webs, there is the added threat that these compounds are bio-accumulative and are contaminants of human food.

Many studies have reported the presence of pesticides in seawater or fog water samples in the Bering Sea and other areas of the Arctic. It has been noted that the degradation rates of pesticides, which could be regarded as non-persistent in temperate environments, are much slower in the Arctic. Organochlorine pesticides are already being monitored but monitoring pesticide enantiomers could enhance the understanding of the source of the pesticides. Looking at these enantiomer ratios can indicate the age of the pesticide, i.e., is it from present usage or is it recycled due to volatilization from contaminated soils? Industrial chemicals are another area requiring investigation and, at present, knowledge of their presence in the Arctic environment is limited or non-existent.

A pilot study has been carried out on samples from Arctic air in an effort to identify these "new" chemicals and to improve analytical methods.

2.2.9 Metals in the Environment [MITE] [K. Puckett]

The Canadian Atmospheric Mercury Measurement Network (CAMNet) was established to improve our understanding of the processes governing the atmospheric concentrations of mercury, of the temporal and spatial variability of atmospheric mercury, and of sources and sinks of atmospheric mercury. CAMNet currently consists of 11 monitoring sites across Canada, chosen to represent major geographical and ecological regions. Each site was classified as either rural-remote or rural-affected. The latter category applies to sites that are expected to be significantly impacted by nearby anthropogenic mercury emissions.

Mean total gaseous mercury (TGM) concentrations ranged from 1.3 to 1.9 ng/m^3 . The spatially averaged median concentration among all sites was $1.60 \pm 0.15 \text{ ng/m}^3$. Seasonal variations in TGM concentrations were observed at all sites. At most sites monthly median concentrations were highest in late winter and lowest in fall.

Diurnal variations in TGM concentrations were also observed at most sites. The most common pattern of diurnal variability was minimum concentration just before sunrise and maximum concentration around noon. The diurnal variability was seasonally modulated, reaching maximum amplitude during spring or summer. Diurnal variability was affected by local wind patterns and mixed layer development.

2.2.10 Atmospheric Mercury at Alert [W. Schroeder]

At Alert, measurements are being made of ambient air concentrations of total gaseous mercury (TGM) to establish the variability and the trend. Also, these measurements are used to investigate the linkage with the Arctic food chain and to study the transport of mercury into the Arctic. The Arctic ecosystem exhibits increasingly evidence of contamination by several persistent, bioaccumulating toxic substances, including heavy metals such as mercury. Mercury vapour has a residence time of 0.5 to 2 years in the atmosphere, which renders it susceptible to long-range transport into the Arctic.

Due to continuous measurements at Alert since 1995, significant advances have been made in the knowledge of atmospheric mercury in the arctic environment. The quality of data being obtained has improved each year. As a participant in the Canadian Atmospheric Mercury Measurement Network (CAMNet), the data complies with the network's QA/QC data protocol. The Branch's Research Data Management and Quality Control System (RDMQ) is used for data quality control. Once the data have been thoroughly quality controlled, it is submitted to the Branch's National Atmospheric Chemistry Database (NAtChem).

Data have shown distinct seasonal patterns, including the perennial springtime mercury vapour depletion, an increase in TGM in summer, and a decrease in fall to a steady background level. Investigations as to source contributions have indicated anthropogenic contributions from the populated areas of Europe and North America. Elevated summer concentrations appear to be of geological origins.

Because of these findings, various other international organizations are preparing to install similar TGM measurement systems in other arctic regions. These efforts will lead to a better understanding of the sources, occurrences and atmospheric fate of mercury in the Arctic.

2.2.11 Smog Chamber Studies [D.A. Lane]

The objective is to advance the knowledge of the gas phase reactions of various polycyclic aromatic compounds (PACs) and other gas phase compounds with the hydroxyl (OH) radical and other oxidants. A new smog chamber was built in the Thomson laboratory and instruments to monitor the reactions in the chamber were obtained, set up and calibrated.

Reactions of various PACs with the OH radical were carried out in the chamber to determine the products of the reactions. After introducing the reactants to the chamber, the lights were turned on for a specified time, then turned out. A sample was collected and the process continued. By turning off the lights, the reactions were instantly stopped.

Samples collected at that point were representative of the extent of the reaction to that point.

Initially, air samples drawn from the chamber were passed over a liquid nitrogen cooled cold finger. Products were analyzed after the sample was warmed to room temperature. Because this method also removed oxygen from the air and retained it as liquid oxygen, it was suspected that some product might originate from the reaction of the PAC with liquid oxygen. To alleviate this, a technique was developed using Solid Phase Micro Extraction (SPME) fibres to collect air from the chamber. This technique eliminated sampling artifacts and had the added advantage that the SPME fibre could be directly introduced to the injector of a gas chromatograph/mass spectrometer (GC/MS) for analysis.

Utilizing this technique, many of the reaction products of naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, 2,3-dimethylnaphthalene, acenaphthene and phenanthrene were determined by both GC/MS and by HPLC/MS techniques. Products detected were the hydroxy, quinone, nitro, hydroxynitro, dinitro derivatives of the parent PAC, as well as ring opening products. Many of the hydroxynitro-, nitro and dinitro products are known to be direct acting mutagens. Reaction rates for the parent compounds have been calculated. In addition, these studies have shown that particles are formed during the chamber reactions and several of the compounds associated with the particles have been identified. These include, primarily, the oxidized PAC.

2.2.12 Denuder Development [D.A. Lane]

The objective is to advance diffusion denuder technology for the determination of the gas and particle partition ratios of airborne polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) as a function of temperature and relative humidity. During this period, laboratory equipment was moved from the old laboratory at York University to the new Thompson laboratory, as well as new equipment was installed. Two commercial Integrated Organic Gas & Particle Samplers (IOGAPS), designed by D.A. Lane and L.A. Gundel, were acquired and utilized in air sampling programs at Pt. Petre (Ontario), at Lancaster (England), at Egbert (Ontario) and at the Atlanta supersite (Atlanta, GA).

To permit air samples to be taken at a high flow rate, a High Capacity IOGAPS was designed to draw air at 100 L/min, compared with 16.7 L/min for the standard IOGAPS. Air sampling was carried out for either 23 or 46 hours. Results from these sampling programs have revealed that gas/particle partition measurements clearly demonstrated that the conventional sampler geometry (filter followed by adsorbent) suffers significant blow-off artifact errors for the semi-volatile organic compounds. Accurate gas/particle partitioning was observed with the IOGAPS for a number of polycyclic aromatic compounds. Total suspended particle measurements made using glass fibre filters (GFFs) may

suffer as much as 40% positive ("blow-on") artifact errors. The compounds adsorbed may be organic or inorganic in nature. There are no positive artifact errors when using a denuder in front of a GFF.

Sorbent impregnated filters, conceived by L.A. Gundel and D.A. Lane, and developed at the Lawrence Berkeley National Laboratory, were first used in the Atlanta intensive study in August 1999. These filters were designed to eliminate the problems of large adsorbent traps necessarily placed downstream of the particle filter in the IOGAPS and to allow immediate total organic carbon measurements to be made on the filters.

A program has been initiated to develop a new denuder that will have very thin walls and will never need to be coated. Other features will be that it can be desorbed without solvents, can be desorbed in less than 5 minutes, and will allow direct injection of the entire sample into the front end of a gas chromatograph. A prototype denuder has been designed and obtained for preliminary investigation.

2.2.13 Transport of Metals to the Great Lakes

[S. M. Daggupati]

One objective is to provide estimates of seasonal and annual concentration and deposition of lead and cadmium to the Great Lakes and, in particular, to Lake Ontario and surrounding area through atmospheric pathway from Ontario, Canadian and U.S. metal smelting industries (1994-1996). This will be achieved through high-resolution mesoscale and regional scale numerical modelling. The other objective is to compare model results with the monitored Integrated Atmospheric Deposition Network (IADN) data of the Great Lakes region.

Two modelling systems were used: one on mesoscale domain (400 km x 400 km) and the other on regional scale domain (3,000 km x 3,000 km). The Boundary Layer Forecast Mesoscale model and Air Pollution Prediction System (BLFMAPS) for passive pollutants with a fine grid resolution of 5 km was used for the mesoscale studies of transport and deposition of heavy metals. The impact of Ontario industrial sources of lead on Lake Ontario was investigated with the mesoscale model. An efficient Eulerian model with very high order accuracy, known as the Discrete Ordinate dispersion model (DO model), was the transport, dispersion and deposition module for both mesoscale and regional scale models. The Global Environmental Multiscale model (GEM) and the DO model were applied for regional scale impacts.

Recent improvements in sub-grid scale terrain heterogeneity effects on boundary layer dynamics and in accurate estimation of dry deposition with sub-grid scale effects were included in both models. As a reliable and quality-controlled lead emission inventory for North America was not available, it was developed with data from the National

Pollutant Release Inventory (NPRI) of Environment Canada for Canadian sources and from the Toxic Release Inventory (TRI) of the U.S. EPA for U.S. sources.

A significant result that is expected is a quantitative estimate of monthly, seasonal and annual lead loading to Lake Ontario and other Great Lakes through atmospheric pathway as a result of emissions from Ontario, U.S. and Canadian smelter industries. From regional scale modelling studies, loading of lead and seasonal variation to each lake are being investigated. Contribution of Ontario sources versus Canadian and U.S. sources to the loading is a significant by-product of the study. Results will be of value to the Great Lakes Water Quality Agreement and science policy issues.

Preliminary analyses of results indicate, as shown in Figure 3, that model simulated air concentrations (solid lines) compared well with the IADN monitored air concentrations (dotted lines). Lead emissions from sources in the U.S. made major contributions (about 90%) to the lead loading to Lakes Erie, Michigan and Superior, whereas 90% of total deposition to Lake Huron and 70% to Lake Ontario are due to Canadian sources. Figure 4 shows total deposition for 1995 due to North American lead emissions. Further analysis will study seasonal variations and comparisons with IADN estimated lead loadings to the lakes, and the effects of mesoscale dynamics on large-scale transport and deposition.

2.2.14 Atmospheric Heavy Metals Model

[A.P. Dastoor]

The Global/Regional Atmospheric Heavy Metals Model (GRAHM) is a 3-dimensional Eulerian multi-scale meteorological and chemical processes model. The model was developed starting with the Canadian Meteorological Centre operational weather forecasting GEM (Global Environmental Multiscale) model. It has variable resolution in the vertical as well as in the horizontal, and uses hybrid vertical levels with 3-dimensional finite element spatial discretization. The time discretization is performed by a two-time-level semi-Lagrangian scheme. The transport scheme for the tracers is a mass conserving quasi-monotonic semi-Lagrangian scheme.

At present, the objective of the model is to understand the transport, transformation and loss of mercury in the atmosphere. Therefore, it integrates dynamic equations for all meteorological processes, and a comprehensive set of physio-chemical processes for mercury species in gas and aqueous phases. Anthropogenic global emissions for 1990 for point and area sources of mercury have been introduced into the model.

In recent years, several regional models have been developed to simulate the fate of mercury in the atmosphere but, unlike other heavy metals, mercury has a long residence time in the atmosphere (order of one year), which makes it a global pollutant. GRAHM is one of the first comprehensive

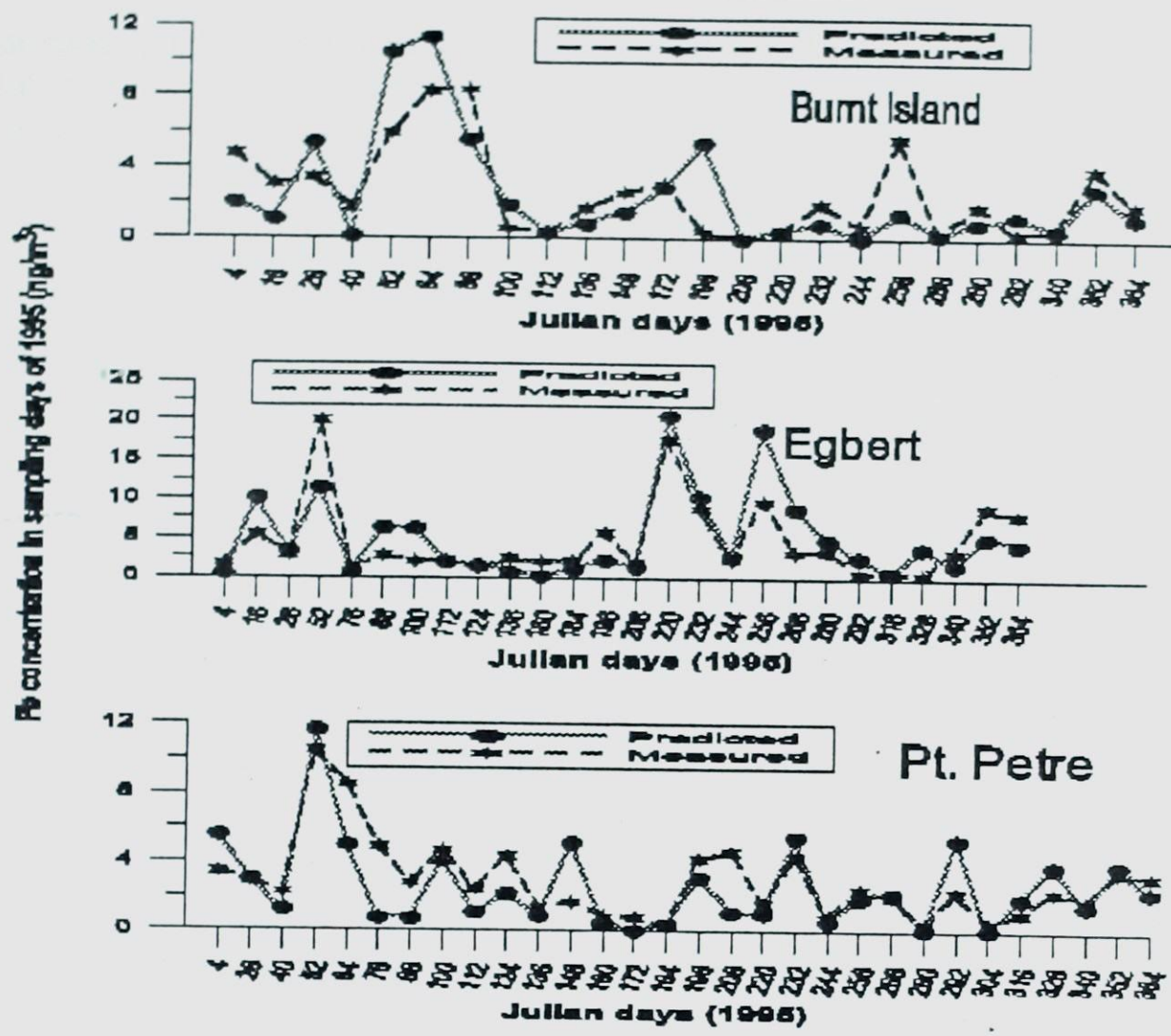


Figure 3: Modeled and measured concentrations in 1995 at Burnt Island, Egbert and Pt Petre

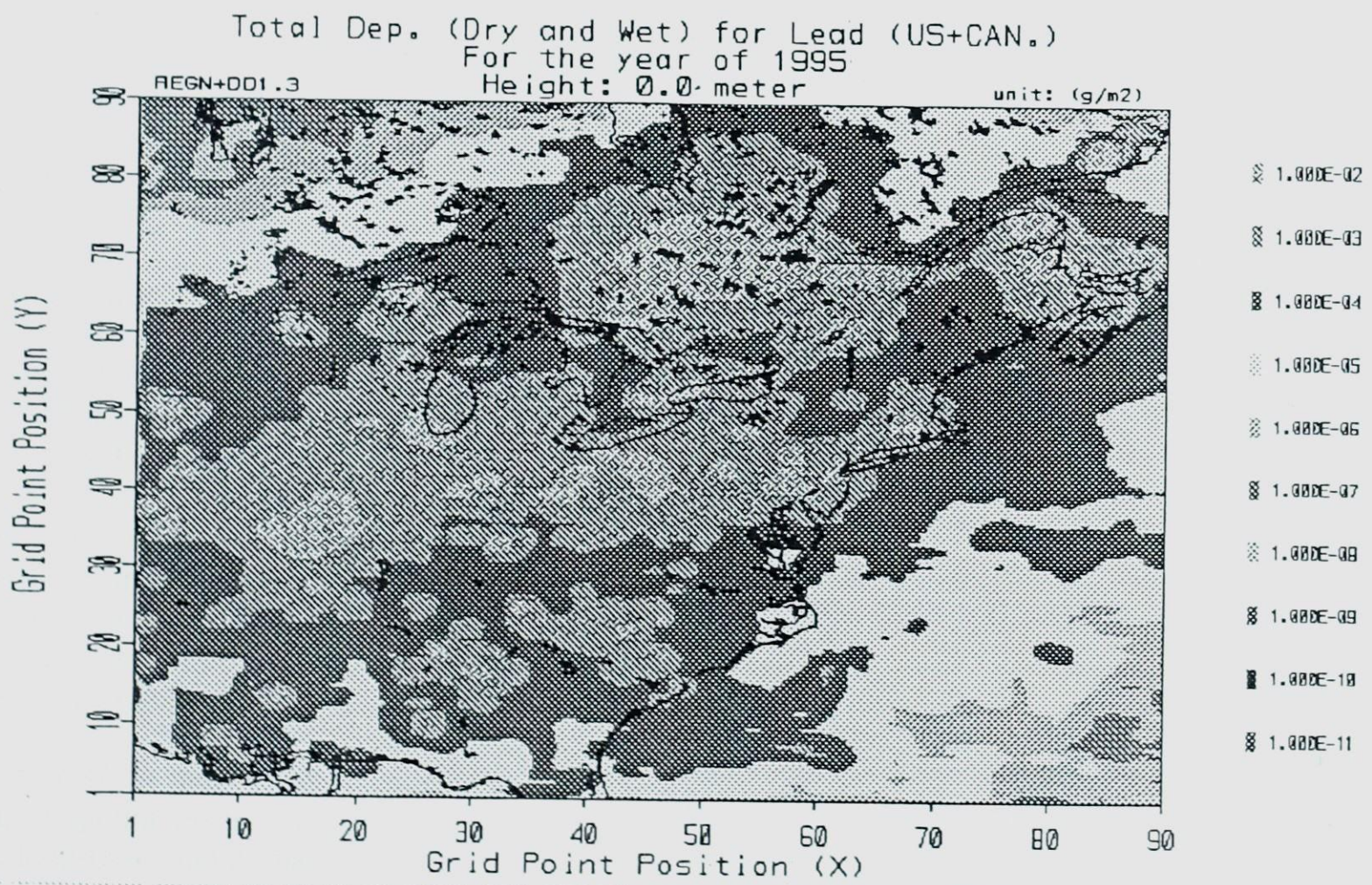


Figure 4: Total deposition (dry+wet) in 1995 due to North American lead emissions

global models developed for understanding the atmospheric cycling of mercury from global to urban scales. The model will be applied to simulate and understand global mercury budgets, residence time of mercury in the atmosphere, global background concentrations, trans-boundary exchanges and polar mercury pollution.

2.2.15 Atmospheric PCB Transport [S.L. Gong]

The objective is to develop and improve the model for atmospheric polychlorinated biphenyl (PCB) air-surface exchange, incorporate it into the 3-D version of the Northern Aerosol Regional Climate Model (NARCM), and to test it using air concentration data. The long-term objective is to develop modelling capacity to study the transport of persistent organic pollutants (POPs), particularly in relation to determining the degree to which domestic and international sources are contributing to observed levels of POPs in Canada and, in the case of international sources, their countries of origin.

Excellent progress has been made. After a detailed critical literature review of the physical/chemical characteristics of PCBs, parameterizations of Henry's law constants, vapour pressures and diffusion coefficients in air and water were developed. A critical review of air water and of air-aerosol partitioning and exchange was undertaken. Results were put into an operational column version of NARCM and demonstrated to perform realistically. Implementation of the PCB parameterization scheme into the 3-D regional NARCM framework is well under way to test the transport patterns of PCB in the Northern Hemisphere.

2.2.16 Chemical Transport Modelling of HCH [J. Pudykiewicz]

A global three-dimensional multicompartiment environmental model based on the advection-diffusion equation in the terrain-following spherical coordinates was developed and applied for simulation of global scale transport of hexachlorocyclohexane (HCH). The atmospheric part of the model is coupled with the realistic description of the soil, the cryosphere, and the aquatic systems. Such a model is applicable to a wide variety of atmospheric tracers including greenhouse gases, radioactive tracers, atmospheric oxidants, heavy metals, and other toxic and hazardous airborne substances.

Initially, the application of the model was considered to study persistent organic pollutants because of their significance for the long-term contamination of the environment. To obtain realistic results, the modelling system included atmosphere, soil and water driven by the objectively analyzed meteorological data. Therefore, the results could be verified against actual observations. By the same token, the evaluation of the source-receptor relationships and the emission control scenarios based on the

adjoint model could be considered as an accurate and useful one for the evaluation of the policies regulating the usage of pesticides.

2.2.17 Global Emissions Inventories [Y.-F. Li]

The objective is to create a database of historical, present, and predicted global emissions of the organochlorine (OC) pesticides with 1° X 1° latitude/long resolution, enabling interpretation of long-term trends of OC pesticides in air, water and the food chain in the Arctic. This project also contributes to the United Nations Economic Council of Europe's Task Force on Persistent Organic Pollutants and Heavy Metals; the UN ECE Expert Panel on Emissions; the Global Emissions Inventory Activity (GEIA) of the International Geosphere/Biosphere Program; and the United Nations Environment Programme (UNEP).

Global technical hexachlorocyclohexane (HCH) usage and α -HCH emissions have been studied and estimations of gridded global α -HCH emissions in 1980 and 1990 due to 15 consecutive years of application of technical HCH are shown. Total global α -HCH emissions in 1990 (Figure 5) were 44 kt (93% contributed by current use and 7% by the residues due to the use of technical HCH since 1976). The data can be obtained from the Canadian Global Emissions Interpretation Centre (CGEIC) website.

By considering emissions and degradation of pesticides in soil, we developed a simple model to calculate pesticide residues in agricultural lands. Study of trends of α -HCH residue shows that α -HCH can remain in the soil for more than 10 years. The trends of α -HCH concentration in the soils in the Kitakyushu District, Japan, and Taihu Lake basin, China, estimated from our model fit the monitoring data in the same areas quite well (Figure 6). The two curves show the trends from the model. The curve labelled "Japan" is for a grid cell located in the Kitakyushu District of Japan and the one labelled "China" is for a grid cell located in the Taihu Lake basin, China. The squares represent the measurements of the concentration of α -HCH from soil samples taken from Kitakyushu District, Japan, and the diamonds represent the measurements of α -HCH concentration in the soil samples from Taihu Lake basin, China.

Toxaphene usage and residues in the U.S. have been studied extensively since toxaphene from the U.S. is the major source of toxaphene in the Canadian environment. The total production in the U.S. between 1946 and 1983 was 700 kt, and the total usage (Figure 7) between 1947 and 1986 was about 480 kt, more than one third of the total global usage. The majority of toxaphene was used in the Southeast Delta states regions. Using gridded cropland, cotton land, and soybean land datasets as surrogate data produced qualified toxaphene usage distribution within NAPAP grid system.

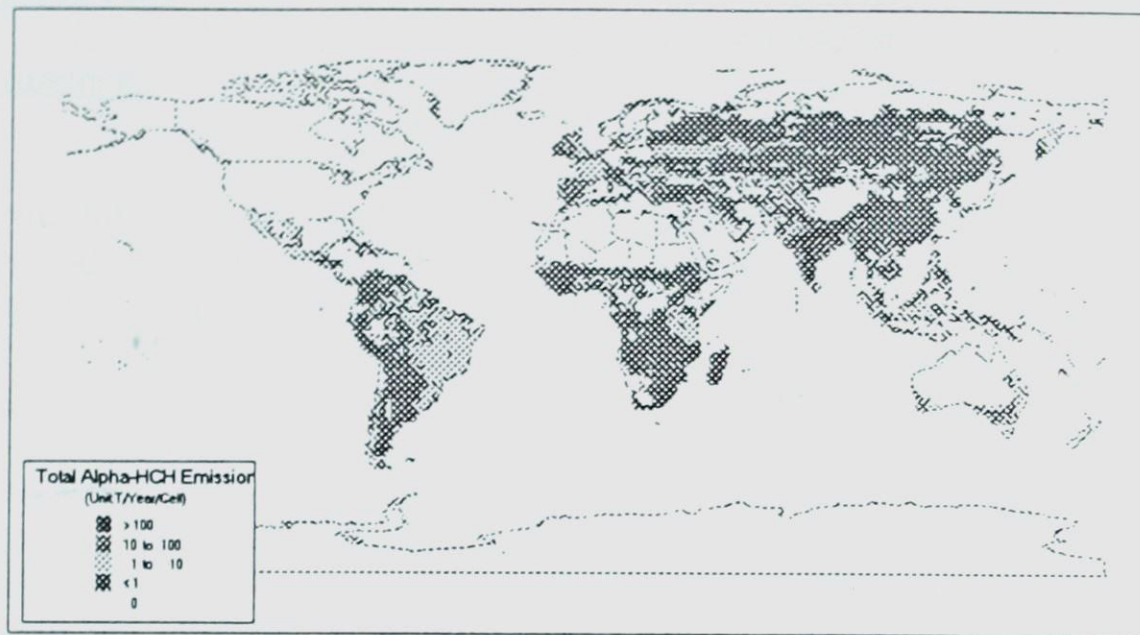


Figure 5. Gridded global annual emissions for α -HCH in 1990

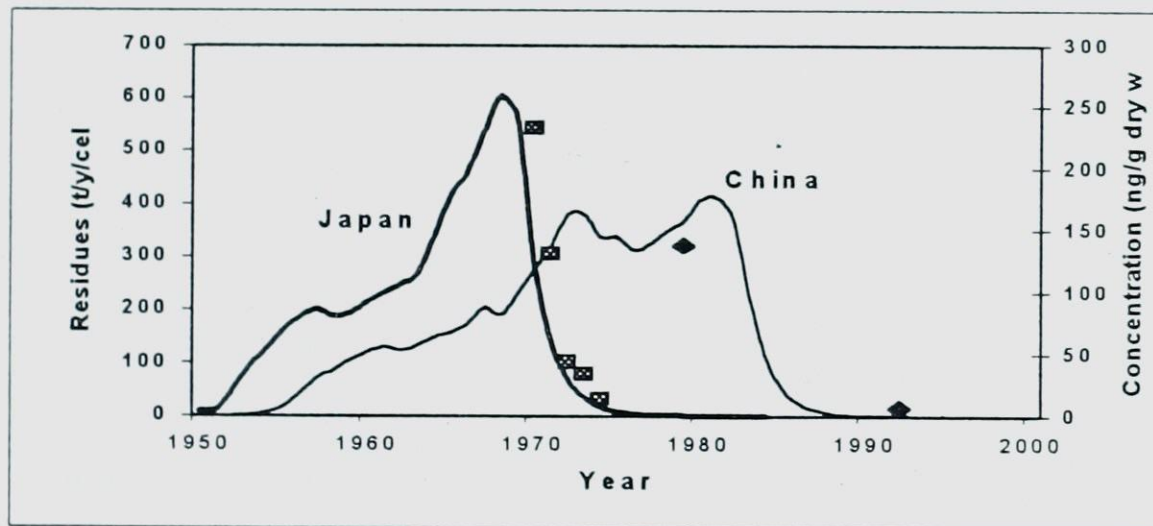


Figure 6. Trends of accumulated α -HCH residues in soil since 1950

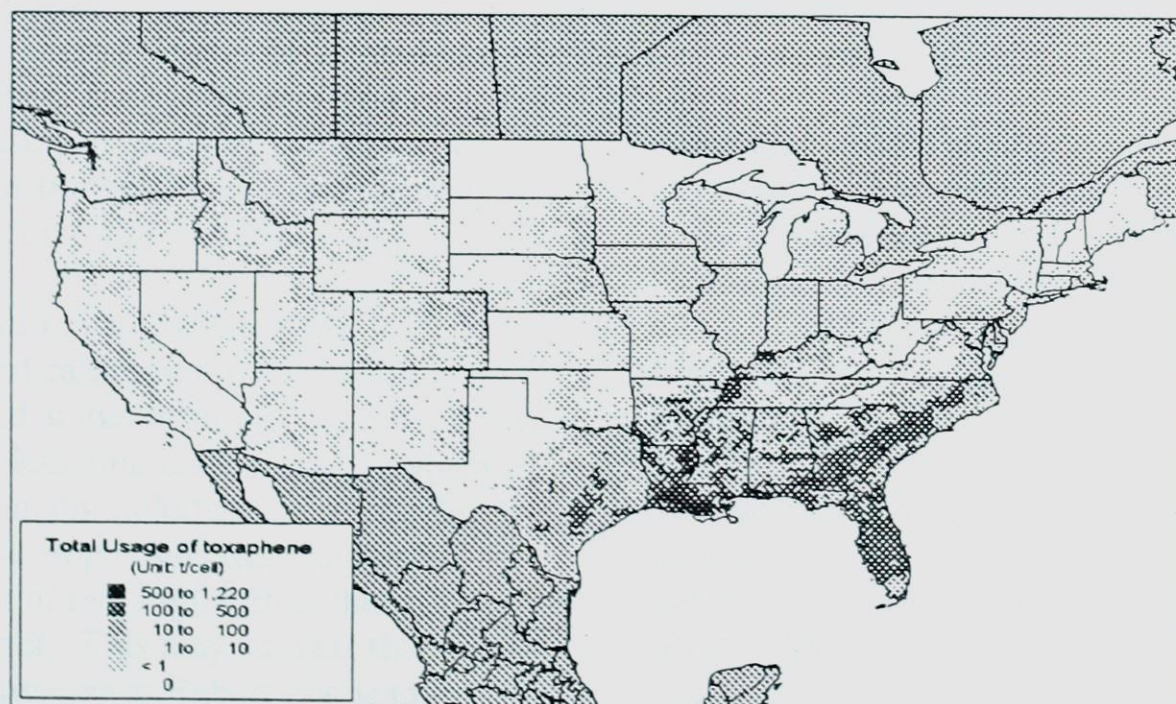


Figure 7. Total toxaphene usage in the U.S.

2.3 PARTICULATE MATTER

2.3.1 Black Carbon Measurements

[S. Sharma]

A study was conducted during July 1998 to size characterize the inorganic portion of fine and coarse particles and measure their optical effects. Measurements of black carbon were a small component of that study. The main thrust has been to become familiar with the operation of aethalometers. The Particle Soot Absorption Photometer (PSAP) was operated side by side with an aethalometer for comparison. Several techniques for measuring black carbon (BC) were also compared. Instruments such as an aethalometer, the PSAP, and the Guelph Aerosol and Visibility Monitoring (GAVIM) network's Laser Integrated Plate Method (LIPM) were used to obtain the absorption on a filter. DRI's Thermal Optical Reflectance (TOR) method for measuring absolute BC concentration was used to confirm the manufacturer recommended specific attenuation cross section to convert the extinction coefficient due to absorption to the black carbon mass.

The extinction coefficient (b_a) due to absorption by the particles was calculated using the signal and reference recorded from the aethalometer output. In the PSAP, the calculations were made by the built-in microprocessor and the output already had these parameters. Figure 8 shows the comparison of the sigma calculated by PSAP versus black carbon concentrations using the aethalometer at Egbert in 1998. The BC concentrations were calculated by applying the specific attenuation cross section of $19\text{m}^2/\text{g}$ to the extinction coefficient due to absorption (α) by the aethalometer. A slope of $9.9\text{m}^2/\text{g}$ was obtained with a good correlation coefficient ($r^2=0.87$). This is the manufacturer recommended value for the PSAP.

Figure 9 shows aethalometer data in comparison to GAVIM's LIPM method. There is some correspondence between the two data but there are not enough data points to show a significant relationship. This again reflects on the optical differences in the instruments and does not imply that the aethalometer data is incorrect or correct.

However, the questions still remain whether the manufacturer recommended calibration values of 19 and $10\text{m}^2/\text{g}$ and BC mass are valid at this location. To investigate this, Figure 10 shows the elemental carbon (EC) analysis of filters from the DRI TOR method plotted versus the BC data from the aethalometer. The slope indicates that the EC analysis results are a factor of two higher than the BC measured using aethalometer. This may suggest that either that there are aerosol constituents at Egbert that lead to artifactual errors in the TOR analysis or that the specific attenuation of this aerosol differs from the value conventionally used in the aethalometer to convert the optical signals to BC mass. If the latter is true then the

specific attenuation of 9.5 for the aethalometer and $5\text{m}^2/\text{g}$ for the PSAP should be used at Egbert.

Two other studies are being conducted at a remote site at Alert and an urban site at Evans Ave. to see how the above mentioned relationships hold as the composition of the aerosols mixtures change.

2.3.2 NAtChem Database

[R. Vet]

The National Atmospheric Chemistry (NAtChem) Database for Particulate Matter (PM) became fully operational. Data from 14 regional-scale aerosol networks in Canada and the U.S.A. were placed in the database. The networks include:

- Canadian Air and Precipitation Monitoring Network (CAPMoN)
- Clean Air Status and Trends Network (CASTNet)
- Atmosphere/Ocean Experiment (AEROCE)
- Atmosphere Integrated Research Monitoring Network (AIRMoN)
- Acidic Precipitation in Ontario Study (APIOS) network
- Canadian Arctic Aerosol Program (CAAP)
- Canadian Acid Aerosols Monitoring Program (CAAMP)
- Eulerian Model Evaluation Field Study (EMEFS)
- Fine Particulate Network (FPN)
- Guelph Aerosol and Visibility Monitoring (GAVIM) network
- Integrated Atmospheric Deposition Network - Canada (IADN-C)
- Integrated Atmospheric Deposition Network - U.S. (IADN-US)
- Interagency Monitoring of Protected Visual Environments (IMPROVE) network
- Canadian National Air Pollution Surveillance (NAPS) network

A number of data quality assurance (QA) checks were developed and applied to the NAtChem/PM data. Included in the QA checks were several graphical data visualization techniques for identifying potential problem data. Feedback on problem data was given to the data submitters, and corrected data sets were re-entered and checked in the database.

Several data analysis and presentation tools were developed including statistical summaries, time series plots and spatial distribution maps. A World Wide Web site was developed and NAtChem products were made available through the site. The database was used to produce maps of PM and sulphate distribution for verification of the NARCM-LITE experiments and for evaluation of large-scale PM episodes in eastern North America.

Outputs of Aethalometer vs PSAP

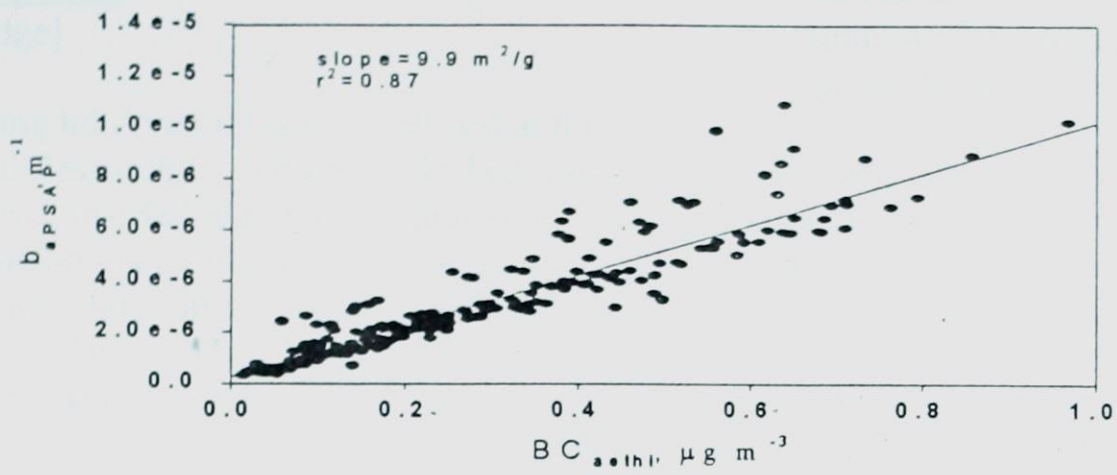


Figure 8: Extinction coefficient (b_a) due to absorption

INTERCOMPARISON OF AETHALOMETER DATA WITH B_a OBTAINED BY LIPM

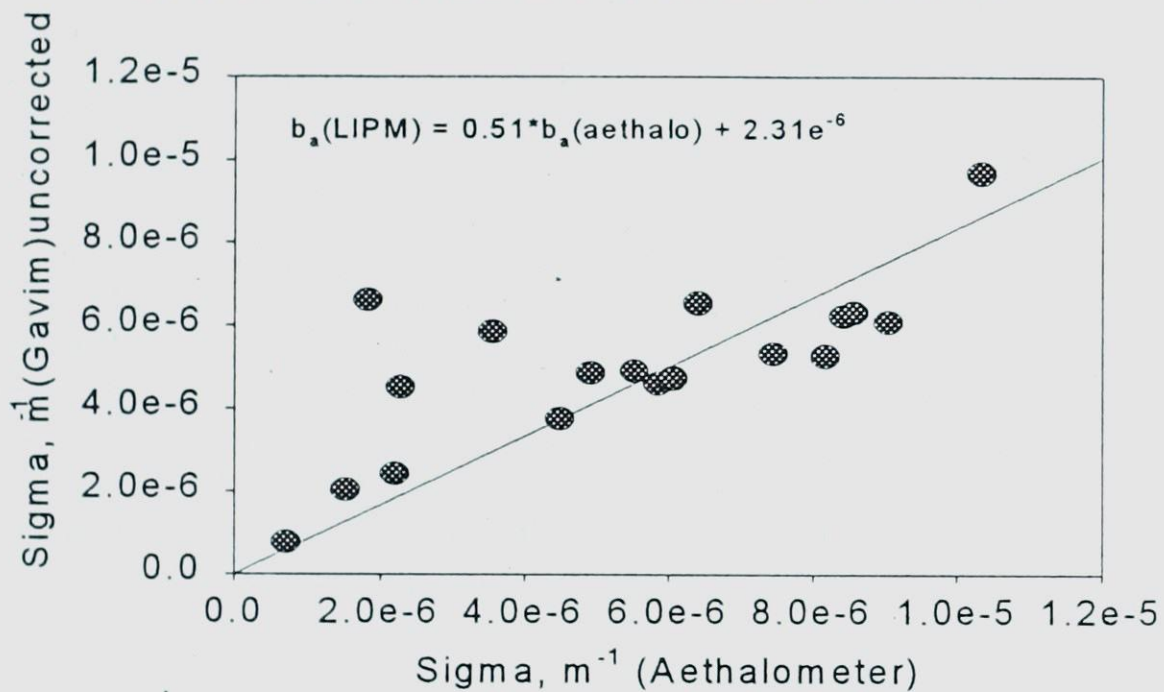


Figure 9: Extinction coefficient comparison (LIPM/aethalometer)

Measurements of black carbon using thermal method and aethalometer (conversion of 19 m²/g used for BC_{aeth})

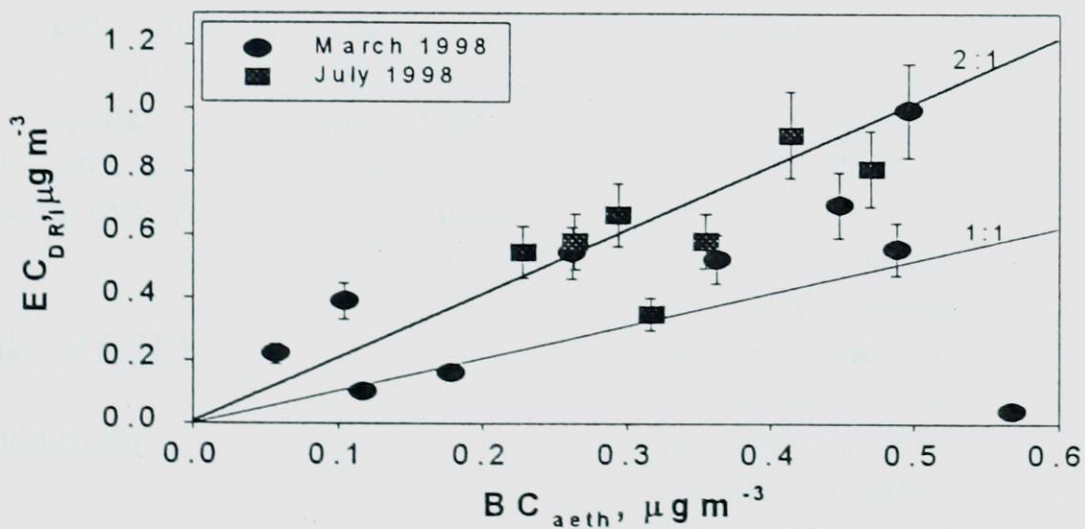


Figure 10: Black carbon concentration 1998 at Egbert

2.3.3 Mobile Scanning Lidar [K.B. Strawbridge]

Recently, a new scanning lidar facility was developed at the Centre for Atmospheric Research Experiments. In February 1999, a motorhome was converted to a mobile laboratory to allow for the remote operation of a ground-based scanning lidar system. The scanning lidar operates at a wavelength of 1064 nm and is capable of fast azimuthal and elevation scanning profiles of the lower troposphere.

The system is based on a two-mirror design with the first mirror being fixed and the second mirror rotating in both the azimuth and elevation. The optical axis allows for full 180-degree azimuthal operation and elevation scans of up to 100 degrees. The exception to this is a small "dead" zone surrounding the first mirror. Lidar scan speeds of up to 24 degrees per second are obtainable but operational scan speeds typically range between 0.2 - 2 degrees per second. A high power optic was placed at the optical centre of both mirrors in support of a co-axial design.

The detector was a 35.6 cm Celestron Schmidt-Cassegrain telescope with an 8 mrad field-of-view, which focused the captured light on a 3 mm RCA 30956E avalanche photodiode (APD) and pre-amplifier. The signal was then digitized to a 3 m resolution, stored and displayed in real-time. The laser was a Continuum NY-61, Nd:YAG, operating at the fundamental wavelength (1064 nm) with an output energy of approximately 650 mJ and a repetition rate of 10 Hz.

To aid in the safe operation of the lidar system, a marine radar was placed on the roof of the vehicle. The radar was modified with a flexible waveguide in order to reduce ground clutter and improve its ability to detect aircraft.

In order to prepare for two large upcoming field studies, the lidar system was field tested in November 1999 to verify the "in-house" control software developed for data acquisition, motion control of the new rotation mirror and data playback. This allowed an opportunity to test the optical sensitivity of the scanning lidar system. The field test was performed downwind of the stacks at Nanticoke's Coal-Fired Generating Station with initial results being very promising.

2.4 STRATOSPHERIC OZONE

2.4.1 Arctic Stratospheric Ozone [H. Fast]

The 1999/2000 winter measurement campaign at Eureka started in September with the recording of solar absorption spectra using the Bomem DA8 Fourier Transform Infrared (FTIR) spectrometer whenever the sun was visible. The University of Denver FTIR system recorded atmospheric emission spectra throughout the winter. Data from both

FTIR instruments will yield information on the concentration of many gases above Eureka, which are essential for the analysis of ozone chemistry in the Arctic.

The ozone LIDAR was operated by CRESTech for most of the nights from November to March to obtain high-altitude ozone, temperature, aerosol, and tropospheric water vapour profiles. Japanese scientists (MRI, CRL and the University of Nagoya) used the aerosol LIDAR for measuring polar stratospheric clouds, as well as background aerosol in the troposphere and stratosphere.

The modified Brewer ozone spectrophotometer, which is capable of using the visible as well as the conventional UV ozone bands, was operated remotely from headquarters for downloading of data and diagnostic tests. A zenith-sky spectrometer was installed by the University of Toronto in February to study the feasibility of measuring gases such as bromine oxide and chlorine dioxide which are important in the ozone chemistry but not yet measured by other instruments at the observatory.

Ozonesondes were launched from Eureka in support of the various measurements at the observatory and in collaboration with the European Match ozonesonde campaign, which also involved the other five Canadian ozonesonde stations.

2.4.2 Ground-based FTIR Measurements [H. Fast]

High-resolution solar absorption spectra were recorded approximately twice per month, using the Bomem DA8 Fourier Transform Infrared (FTIR) spectrometer, in order to continue the monitoring of atmospheric gases implicated in stratospheric ozone depletion and the enhanced greenhouse effect. Some of the measurements obtained at the Centre for Atmospheric Research Experiments are now being used in preparation for validation of space-based measurements such as MOPITT (Measurements of Pollutants In The Troposphere).

2.4.3 WOUDC Activities [E.W. Hare]

The World Ozone and Ultraviolet Radiation Data Centre (WOUDC) continued to process, archive and publish ozone and ultraviolet (UV) radiation data reported by 400 stations, worldwide. Ozone data have traditionally been published in hard copy form in the EC/WMO publication entitled "Ozone Data for the World" commonly referred to as the "redbook". The redbook has been replaced with an annual report and printed data being available on CD-ROM.

Since late 1994 the WOUDC has been Internet accessible and continued this tradition of providing data sets of processed ozone and UV data on a regular basis. The WOUDC also continued to archive primary data and

provided the service of processing these data on behalf of the submitting agency if so requested.

The WOUDC web site was updated and is the focal point for WOUDC information dissemination. Information about data sets (revision history, updates, metadata, etc.), data submission/retrieval documentation, analysis software and general information of interest to the ozone/UV community is posted on this site. The WOUDC ftp site contains the entire ozone and UV inventory, which provides data clients with output products and data originators with personal ftp accounts for easy data submission. Since 1998, over 50 new stations were added to the WOUDC.

Data analysis and quality assurance software was developed for spectral UV data and ozone quality assurance programs continued to be updated. An examination of the entire WOUDC inventory of total column ozone data was undertaken and the results were published.

Development continued with the new data inventory archival and retrieval system, which uses the newly developed data submission file format called the extended comma separated values (extCSV) format. The new inventory database is now in use. This new format is currently being considered for use within the World Meteorological Organization/GAW World Data Centre network for representing metadata in a common file format template. The WOUDC released Version 5.1 of the UV Guidebook and continued updating the Ozone Guidebook.

2.4.4 MODE Experiment [D.W. Tarasick]

The Middle Atmosphere Ozone, Dynamics and Energetics (MODE) Experiment is a small satellite payload proposed for the first mission of the Canadian Science Satellite (SCISAT1) program. It consists of three small instruments: the Mesospheric Imaging Michelson Interferometer (MIMI), the Ozone Backscatter Observation Experiment (OBOE), and the Mesopause Oxygen Imager (MOXI).

MIMI is a near-IR field-widened Doppler imaging Michelson interferometer. It will use six lines in the $O_2(^1\Delta)$ band at 1.27 microns on the limb to measure winds, temperatures and ozone concentrations, globally from 45 to 100 km altitude. The data will be unique, as wind measurements at this altitude have never been made from space.

OBOE, a development of the AES SunPhotoSpectrometer that has flown on the U.S. Space Shuttle and aboard the NASA ER-2 high-altitude research aircraft, will make measurements of total column ozone and its vertical distribution via backscattered ultraviolet and visible radiation. It will measure nitrogen oxide, stratospheric aerosols, and other species important to ozone chemistry,

such as bromine oxide, which is detected in the arctic troposphere in spring and in polar stratospheric clouds.

MOXI, a nadir-pointing CCD imager with the prime purpose of measuring small spatial scale intensity fluctuations (gravity waves) in the $O_2(^1\Sigma)$ band airglow, will study the characteristics, sources and climatology of this important middle atmosphere energy transport mechanism.

The experiment also includes extensive ground-based observations and the assimilation of these and meteorological data to produce a global data set from the ground to 100 km. MODE received Phase A funding during 1998 but was not selected for SCISAT1. Currently bridge funding is being provided by the Canadian Space Agency to develop further the instruments while launch opportunities are sought.

Our interest in MODE was quite strong, particularly because of the OBOE ozone measurements, but also because of the mesospheric wind and ozone measurements from MIMI, which would be very valuable to the Canadian Middle Atmosphere Model (CMAM) and the Middle Atmosphere Initiative (MAI) projects. The gravity wave data would also be valuable to CMAM.

2.4.5 Middle Atmosphere Initiative [D.W. Tarasick]

Currently the Middle Atmosphere Initiative (MAI) comprises two main projects. One focuses on improving long-range forecasting while the other addresses the circulation of the stratosphere and lower mesosphere, in order to better understand ozone change (particularly transport) and climate change problems.

The project to assimilate ozone data in real time using the new operational Global Environmental Multiscale (GEM) model and the 3-dimensional Variational Data Assimilation (3DVAR) system is well-embarked and it has produced some results, using the TIROS Operational Vertical Sounder (TOVS) total ozone retrievals, that appear reasonable. Comparison with the Total Ozone Mapping Spectrometer (TOMS), Brewer and ozonesonde data is underway.

In order to assimilate at least one year of data from the UARS satellite, the CMAM and 3DVAR systems have been interfaced. Successful assimilation runs using standard meteorological observations have been completed. Current work focuses on the elimination of an anomaly in the tropical wind field, on the calculation of proper background error covariances for CMAM, on the modification of the 3DVAR system to operate on a much larger number of vertical levels, and on assimilation runs with TOMS data.

2.5 GREENHOUSE GASES AND AEROSOLS

2.5.1 Greenhouse Gases and Aerosols Program

[M. Lusic]

The overall objective of the Branch's Greenhouse Gases and Aerosols Program is to contribute to the understanding of greenhouse gases and aerosols - their trends, budgets and role in climate change - by carrying out measurements, modelling and process studies with a Canadian focus, and by interfacing with other major international programs.

Long-term measurements of greenhouse gases and aerosols are currently being made at Alert, Fraserdale, Estevan Point and Sable Island, as part of the Canadian Baseline Program. This is Canada's contribution to WMO's Global Atmosphere Watch (GAW) Program, and the Global Climate Observing System (GCOS).

Support for the Branch's global warming-related work also came from outside sources, such as the Panel on Energy Research and Development (PERD) and the Canadian Climate Research Network. The support was used for the carbon flux study at Fraserdale and the Northern Aerosol Regional Climate Modelling (NARCM) Project. The objective of this study is to determine the role of the eastern Canadian "wet" boreal forest in sequestering anthropogenic carbon dioxide emissions. The objectives of NARCM are to further our understanding of how Canadian climate is affected by anthropogenic aerosols by incorporating size-distributed aerosols as active constituents in Canadian global and regional climate models. Then these models are used to understand the role of aerosols in radiative forcing and climate feedback.

Data sets for 1998 and 1999 have been submitted to the WMO/GAW World Data Centre for Greenhouse Gases at the Japan Meteorological Agency, and the Carbon Dioxide Information Centre at the Oak Ridge National Laboratory. There have been a number of notable accomplishments including:

- A regular analysis program was designed and implemented for carbon and oxygen isotopes in flask samples from Estevan Point and Alert, and regular laboratory intercomparisons were continued with CSIRO (which now show good agreement for C but some problems still to be resolved with O);
- Evaluation has begun on various methods for measurement of carbonaceous aerosols;
- The first Baseline Program Report (Canadian Baseline Program Summary of Progress to 1998) is now available; and
- For the future program direction, a five-year strategic plan and a scope document have been prepared.

The last two items are a result of recommendations made during the 1997 Canadian Baseline Program Peer Review.

2.5.2 Ozone Measurement at Alert

[K. Anlauf]

At the Global Atmospheric Watch (GAW) laboratory, twin TECO Model 49 photometric ozone analyzers continuously measured ozone. This Alert ozone measurement program started in 1992 and considerable data has been incorporated into joint scientific publications on Arctic chemistry. A statistical analysis of the 1992-1998 ozone data using the ozonesonde statistical model has revealed a positive trend of about 2.5% per year (with 95% confidence); on a seasonal basis, only the March-May period showed a significant trend at 5% per year.

2.5.3 Arctic Aerosol Chemistry

[S.L. Gong]

This project is undertaking to understand the long-term trends, composition and role of aerosols on Arctic climate. The major objectives are to continue 19 years of baseline aerosol chemistry observations at Alert, to analyze and report results of the aerosol data, and to continue to use the aerosol archive to initiate and support new investigative studies of arctic processes.

This project is an ongoing one that provides a long time series of observations at the baseline observatory at Alert against which to check climate models of aerosols, such as the Northern Aerosol Regional Climate Model (NARCM). This work yields the seasonal variations of anthropogenic, sea salt, soil dust, marine biogenic and photochemical aerosol components.

2.5.4 Atmospheric CO₂ Ratios

[L. Huang]

In order to understand the mechanism of long term carbon dioxide (CO₂) increase in the atmosphere, the objectives are threefold:

- to participate in international intercomparison programs to achieve high accuracy and precision in measurement of $\delta^{13}\text{C}$ (Ratio $^{13}\text{C}/^{12}\text{C}$) and $\delta^{18}\text{O}$ (Ratio $^{18}\text{O}/^{16}\text{O}$) in flask-air CO₂;
- to measure $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO₂ at each baseline station (Alert and Estevan Point) to determine long term trends; and
- to analyze isotope data to constrain the relationship between sources and sinks (i.e., ocean and terrestrial biosphere) for CO₂ in its seasonal and annual changes.

The laboratory has extracted about 180 flask-air CO₂ samples for Alert (AES and CSIRO samples) and about 170 samples for Estevan Point (AES and CSIRO samples). Also, about 430 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data (from Alert & Estevan Point) were obtained by infrared mass spectrometry. Data have

been analyzed for Alert up to June 1998, and for Estevan Point up to June 1998.

In the intercomparison with CSIRO (Australia) for both Alert and Estevan Point data (June 1996 to June 1998), results obtained were:

- Intercomparison one (same samples measured by CSIRO and AES) showed $0.1 \pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $-0.5 \pm 0.5\text{‰}$ for $\delta^{18}\text{O}$
- Intercomparison two (samples from different sampling ways measured by AES) showed $0.014 \pm 0.015\text{‰}$ for $\delta^{13}\text{C}$ and $-0.426 \pm 0.513\text{‰}$ for $\delta^{18}\text{O}$

The results indicate that there are some systematic biases both from different sampling methods and from different laboratory procedures.

2.5.5 Isotope Composition of Atmospheric CO₂ [L. Huang]

To understand the global biogeochemical cycle of carbon, especially the interaction processes between atmosphere and biosphere at continental mid-latitudes, $\delta^{13}\text{C}$ (Ratio $^{13}\text{C}/^{12}\text{C}$) and $\delta^{18}\text{O}$ (Ratio $^{18}\text{O}/^{16}\text{O}$) of carbon dioxide (CO₂) are measured. These ratios are measured both in flask-air (-0.3 m and 20 m), and in aircraft flask samples at different heights close to the boundary layer. Also, carbon and oxygen isotope data are sampled to constrain the relationship between sources and sinks for CO₂ in its diurnal cycle processes (i.e., photosynthesis, respiration and mixing).

Five intensive campaigns (from October 1998 to August 1999) have been conducted at Fraserdale. From about 200 flask samples taken at 20 m and at the subsurface (-0.3 m), and from about 150 flask samples from an aircraft, CO₂ values have been obtained. Using infrared mass spectrometry, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for CO₂ have been obtained. Results show that the carbon isotope signature of source CO₂ from the biosphere is relatively stable, around -27‰ (to VPDB scale), whereas, the oxygen isotope signature of source CO₂ from the biosphere changes at different seasons and different days in the range of about 70 ‰ (to VSMOW scale). This indicates that the processes corresponding to oxygen isotope signature change may vary with time.

2.5.6 Isotopic Composition of VOCs [L. Huang]

It is known that volatile organic compounds (VOCs) emitted from different sources or through different processes may carry characteristic isotopic compositions with special fractionation patterns. Thus, it is possible to obtain source apportionment and process mechanism by measuring stable isotope composition of VOCs in air. In order to understand the role of VOCs in the atmospheric processes, $\delta^{13}\text{C}$ (Ratio $^{13}\text{C}/^{12}\text{C}$) of VOCs in polluted urban air, global background, e.g., in Arctic air, will be measured to investigate the

distribution of sources of VOCs in the atmosphere. Also, the $\delta^{13}\text{C}$ of VOCs in physical (e.g., evaporation) and chemical (e.g., reaction with OH) processes will be measured to understand the isotopic fractionation of VOC in different processes.

The construction of a VOC extraction line for conventional isotopic analysis has been only partially completed. The $\delta^{13}\text{C}$ of tetrachloroethylene has been analyzed (about 15 analyses) by infrared mass spectrometry. The fractionation factors from the kinetic experiments for 11 compounds (C₃-C₆ alkanes etc.) have been obtained out of about 200 analyses. Also, the $\delta^{13}\text{C}$ of VOCs in ambient air from 30 different sources and biomass burning samples have been analyzed.

2.5.7 Carbonaceous Arctic Aerosols [S. Sharma]

This project is a component of the regular monitoring in the Canadian Baseline Program at Alert, Nunavut, established since 1989. The main objective is to understand the occurrence, atmospheric chemistry and potential impacts on climate of the black carbon and organic carbon fraction of Arctic aerosols.

Historically, ten years of light absorption measurements cannot be converted into black carbon mass with confidence because the operational absorption coefficient, determined by making independent measurements of black carbon, is unknown. Thus, to establish this calibration factor, a one-year method intercomparison study has been conducted at Alert for the collection of black carbon. Among the methods are the thermal method (H. Cachier, CNRS, Paris), the integrated plate/Raman Scattering technique, the thermal/laser (P. Chylek/G. Lesins), and the thermal technique for total carbon and water soluble organic fraction (D. Toom-Saunty/S.M. Li). The project is expected to produce a quality-controlled and quality-assured dataset for the 10 years of black carbon measurements.

2.5.8 DMS in Lakes of the Canadian Boreal Region [S. Sharma]

A two-year study was conducted in 1995 and 1996 to determine the natural sulphur input, mainly dimethyl sulphide (DMS), from the lakes of the Canadian Boreal region to the atmosphere. Ten different lakes of different sizes and depths (1-56 ha in area and 1-32 m in depth) were surveyed during the growing seasons to measure surface concentrations of DMS, chlorophyll A, sulphate, nitrate, phosphate, silicate, other nutrients, and metals. A Liss and Merlivat model was applied to the concentrations of DMS to estimate the fluxes.

Concentrations of DMS varied from 0.1 nmol L^{-1} to 100 nmol L^{-1} (geometric mean = 1.2 nmol L^{-1}) during the ice-free season. The higher concentrations of DMS were found in

the shallow and mid-sized lakes (less than 15 ha in area and 5-10 m in depth). During the fall in the medium size lakes, DMS concentrations increased markedly by a factor of as much as 100 because of circulation of deeper, high-DMS water from the hypolimnion (lake turnover). The estimated seasonal mean fluxes of DMS from the shallow and medium depth lakes tend to release higher DMS than the large and deeper lakes. The estimated seasonal mean fluxes of DMS from the shallow and medium size lakes to the atmosphere ranged from 0.058 and 15 mmol S m⁻² d⁻¹.

Extrapolation of flux estimates indicates that the lakes of the Canadian Boreal region emit 1.5 Gg yr⁻¹ biogenic sulphur (DMS) to the atmosphere, this is approximately 83% of the total annual biogenic sulphur (DMS) emissions from the Canadian Boreal Shield (lakes plus terrestrial). Compared to the annual anthropogenic emissions by five smelters in the boreal region, these emissions are small (0.08%).

2.5.9 Flux Estimation of Oceanic DMS [S. Sharma]

This was a joint study between Canada and the U.S. conducted from July to October 1994. Simultaneous measurements of atmospheric and surface water dimethyl sulphide (DMS) concentrations were taken aboard the icebreaker USCGC Polar Sea. The expedition included circumnavigation of North America with the Arctic Ocean transect.

Atmospheric DMS concentrations around North America varied between 0.25 and 50 nmol m⁻³ (mean = 5.1 nmol m⁻³) with highest values in the western Arctic Ocean and off the U. S. east coast near the Sargasso sea. In the Arctic Ocean, maximum concentrations in the air and water were found along the ice edge in the Chukchi Sea region. Atmospheric DMS decay rates of 68% per day and 38% per day were deduced from observations between 70° and 76°N on the west side and between 80° and 90°N (central Arctic Ocean) for the east side of the Arctic Ocean, respectively. Ocean to atmosphere flux estimates of DMS were determined using the Liss-Merlivat empirical dependence of exchange coefficient on wind speed, DMS air concentrations, Henry's law constants and DMS water concentrations. DMS fluxes varied between 0.0017 and 30 μmol m⁻² d⁻¹ with higher fluxes in the regions with open water. The Arctic Ocean contributed 0.063 Tg S (DMS) (0.4% of DMS from the world oceans) during the summer of 1994.

A simple one-dimensional (1-D) photochemical box model, applied to six case studies, showed that the atmospheric lifetime of DMS in the high Arctic was 2.5 to 8 days, whereas at 16-33°N it was 1 to 2 days. Modeled DMS decay rates for these regions, using the 1-D model, accounted for only 33% of the measured decay rate. This result also suggests that halogen chemistry, reactions with bromine and bromine oxide, may be an important sink for DMS in the Arctic atmosphere.

2.6 UNIFIED MODEL

2.6.1 AURAMS [S. Venkatesh]

The AURAMS (A Unified Regional Air quality Modelling System) project is a multi-year effort to develop a new regional air-quality modeling system that will be used in Canada for studying and managing multiple regional tropospheric air issues, including particulate matter, acid deposition and photochemical oxidants. This emerging modeling system includes a size-resolved, composition-resolved representation of atmospheric particulate matter. Progress on a few of the sub-projects under AURAMS is described below.

2.6.2 Canadian Aerosol Module [S. Gong]

A size-segregated multi-component aerosol algorithm CAM (Canadian Aerosol Module) is being developed for use with climate and air quality models. It includes major aerosol processes in the atmosphere (production, growth, coagulation, nucleation, condensation, dry deposition, below-cloud scavenging and activation), and an explicit micro-physical cloud module to treat the aerosol-cloud interactions and chemical transformation of sulphur species in clear air and in clouds.

A unique numerical method is being developed to efficiently solve the complicated size-segregated multi-component aerosol system to be included in global and regional models. Emissions to the atmosphere of anthropogenic and natural aerosols are simulated for five aerosol types: sea-salt, sulphate, soil dust, and black and organic carbons. CAM implementation in AURAMS is being carried out to simulate particulate matter (PM_{2.5} and PM₁₀) in the unified modelling system.

2.6.3 Cloud Chemistry Modelling [W. Gong]

As part of the AURAMS development effort, the existing Acid Deposition and Oxidant Model (ADOM) aqueous-phase chemistry module has been adapted to a size-resolved representation in order to deal with size-dependent and inhomogeneous chemistry in cloud.

Preliminary tests with the stand-alone, size-resolved, aqueous-phase chemistry model were carried out, and the results were compared to those with the original bulk module. It was shown that activated aerosols (cloud droplets) with similar wet size could be chemically inhomogeneous due to the difference in chemical composition in the dry aerosols prior to activation. This is seen to introduce inhomogeneity in the aqueous phase oxidation of S(IV) process and will affect the final mass distribution over the size spectrum.

2.6.4 Chemical Sensitivities using SMVGEAR

[P.A. Makar]

The aim was to modify Jacobson's Sparse Matrix Vectorized GEAR (SMVGEAR) gas-phase chemistry solver, so as to include the calculation of sensitivity coefficients. These are derivatives of the model final results with respect to initial conditions; for example, the derivative of the model-predicted ozone with respect to the initial concentrations of all of the gas-phase species.

Relevant mathematics was determined for the alterations to the SMVGEAR code, which uses a substantially different means of implementing Gear's multiple-step backward difference algorithm. A number of comparisons were made to simple chemical systems for which the analytic solution could be calculated – the model derived sensitivities were accurate for less reactive species, but the accuracy decreased as the reaction rates were increased. Further analysis work is required to determine whether the accuracy may be improved. An error analysis of the results has indicated several potential avenues for investigation.

2.6.5 Secondary Organic Aerosol Formation

[P.A. Makar]

A modified version of the "two-product" model of secondary organic aerosol formation was incorporated into the AURAMS code. Significant effort was spent in determining the correct aerosol partitioning. The first stage version of the AURAMS model uses the Acid Deposition and Oxidants Model II (ADOM-II) mechanism, in which several potential aerosol precursor gases are lumped into a smaller number of model hydrocarbons. The ADOM-II mechanism was designed to preserve hydrocarbon reactivity, not aerosol precursor mass.

An analysis of the NAPAP32 (National Acid Precipitation Assessment Program) speciation upon which ADOM-II is based was performed, in order to determine the relative fractionation of the aerosol precursor components of the ADOM hydrocarbons. The resulting modified two-product model was included as a new subroutine within the AURAMS code, and run for the first day of the EMEFS-II (Eulerian Model Evaluation Field Study) measurement intensive (July 30/31, 1988). The model results compared well with expected secondary organic aerosol mass found within urban areas.

2.6.6 Gas-Phase Mechanism Development

[P.A. Makar]

A modelling system allowing the fast simulation of a large number of smog chamber experiments was created to aid in the evaluation of gas-phase mechanisms for regional modelling. The system has three components: a combined database of UNC (U. North Carolina) and SAPRC (Statewide Air Pollution Research Center, U. California)

smog chamber experiments, the SMVGEAR (Sparse Matrix Vectorized GEAR) chemistry solver, and a post-processing package to calculate statistics of a large number of model runs. The SMVGEAR code was modified to allow for smog chamber simulations. Its usual configuration is for use in integrating chemical equations in a regional model context. The new system allows for the very rapid comparison of complex model results against a large number of experimental measurements, and is an invaluable tool for chemical analysis.

2.6.7 Canadian Emissions Processing System

[P.A. Makar]

The first stage version of AURAMS makes use of the Acid Deposition and Oxidants Model II (ADOM-II) gas-phase reaction mechanism. The second stage will use a revised chemical reaction mechanism (See 2.6.6: Gas-Phase Mechanism Development). The new mechanism has approximately twice as many species as ADOM-II, with most of the new speciation being in the hydrocarbons. In order to use the new mechanism within the regional model, the Canadian Emissions Processing System had to be re-run with a revised set of emissions processing rules. The Chemical Abstract Service (CAS) codes were added to all species, to allow for easy cross-linking to chemical databases. These databases included ones with reactivity information and vapour pressure.

The NAPAP32 (National Acid Precipitation Assessment Program) intermediate emissions classification was revised and expanded to allow for the creation of lumped hydrocarbons, which have a significant direct or secondary product fractionation to the aerosol phase. The NAPAP32 classification was designed solely to preserve reactivity, and the aerosol-forming potential for the species was not considered. During the course of the analysis, it was discovered that the vapour pressures of broad classes of hydrocarbons might be accurately predicted as simple functions of carbon number and temperature. The completed speciation was delivered to Canadian Ortech Environmental to generate the emissions files for the new speciation.

2.6.8 Heterogeneous Chemistry Module Development

[P.A. Makar]

This project deals with the development of a heterogeneous chemistry module for the AURAMS model. The current version of the heterogeneous chemistry module includes SO_4^- , NO_3^- , NH_4^+ , HSO_4^- , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, NH_4HSO_4 , NH_4NO_3 , gas and aqueous phase ammonia, and nitric acid. The module is designed to allow for the transfer of mass between particle bins in the same distribution, an improvement over the usual approach of a bulk calculation across all size bins. Coding and testing of the components of the module are currently underway.

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