AN AEROMETRIC PROGRAM

FOR

EFFECTS STUDIES

IN THE

ATHABASCA OIL SANDS REGION

by

R.B. CATON
C.S. DAVIS
M.J.E. DAVIES
D.L.M. STEVENS
Concord Scientific Corporation

R.R. WALLACE
Dominion Ecological Consulting Ltd.

G.A. YARRANTON
Yarranton Holdings Ltd.

R.A. CROWTHER
Aquatic Resource Management Ltd.

for

Alberta Environment

1990

EXECUTIVE SUMMARY

Alberta Environment is in the process of reviewing the scientific and technical basis for refinement of a regulatory approach to the environmental impact of present and future industrial development in the Athabasca oil sands region. The review has encompassed the results of 10 years (1975 to 1985) of studies conducted under the Alberta Oil Sands Environmental Research Program (AOSERP), as well as the results of other studies conducted in the oil sands region and elsewhere in the province. Reports in the international scientific literature were also considered in the review.

The result of this review was a plan for a five-year biophysical monitoring program to provide the necessary scientific and technical information upon which to base an effective regulatory approach. The documentation for the plan identified forest vegetation in the oil sands region as the most likely ecosystem component to show the effects of pollutant accumulation over the near-to-medium period of time, defined as 5 to 25 years. Aquatic ecosystems and soils were assessed as requiring longer periods of time to manifest detectable changes resulting from pollutant deposition.

In preparation for the biophysical monitoring program, a study was initiated to evaluate the requirements of an air quality and meteorological monitoring program to support the biophysical program, as well as the design of such an aerometric program. This study was carried out by Concord Scientific Corporation with assistance from Dominion Ecological Consulting Ltd., Yarranton Holdings Ltd., and Aquatic Resource Management Ltd. This report presents the results of the work and the recommendations of the study team.

Preliminary Review and Workshop

The study team conducted a literature review and consulted a number of knowledgeable scientists and program managers associated with the major air pollution/forest ecosystem effects studies in North America. The results of these activities were used to prepare a number of preliminary design options for an aerometric program. The major objective of this program would be to characterize the pollution gradient to which forest stands in the oil sands region are being exposed. The background material, the proposed options, and a recommended approach were presented for criticism and further development at a two-day workshop held in Edmonton in January 1987. The workshop was attended by Alberta Environment staff, invited environmental scientists from government, industry, and academe, and representatives of the study team.

The first day of the workshop focussed on the five-year plan, including the types of biological parameters and their response times that would probably be investigated in the biophysical monitoring program. These were considered on the second day in the context of a recommended aerometric program design option. The workshop addressed the feasibility and scientific defensibility of the recommendation, with the objective of determining the simplest air monitoring program that would be worthy of implementation.

The conclusion of the workshop was that air quality monitoring on a monthly time scale would be appropriate with respect to the annual time scale that is anticipated for the biological measurements. The preliminary aerometric program as defined by the workshop attendees was subsequently further developed by the study team to arrive at a recommended program.

Aerometric Parameters

A set of desirable aerometric parameters to be monitored was identified, based on the study team's review and on input from workshop attendees. This set was further reduced by the study team to a minimum defensible set based on the following criteria:

- association of contaminants with industrial emissions;
- potential biological significance of observed contaminant levels;
- technical ability to measure levels likely to occur at remote sites;
- potential biological significance of microclimate variability; and
- whether the parameter was needed to characterize pollution gradients.

Instrumentation and Methods

A measurement method was proposed for each desirable parameter. These methods were evaluated with respect to the following factors in deciding whether to retain the parameter or the method for the minimum list:

- adequacy of sensitivity/specifications;
- operational (logistical) suitability;
- validity and uncertainty of data produced; and
- general advantages/disadvantages.

Concentrations likely to be encountered in the study region were estimated from several sources: industrial monitoring data, Alberta Environment data (Sandalta and Fort McKay), and CAPMoN data from Cree Lake, Saskatchewan. Response times were related to the anticipated time scale(s) of the biological measurements.

Since air quality and precipitation samples would be integrated over monthly periods, certain parameters (soluble ions) had to be deleted from the final recommended list because of sample stability problems.

Few problems were anticipated measuring all of the desirable meteorological and climatological parameters at remote sites, since most of them are monitored routinely at remote sites at present.

Sampling equipment and power supplies were evaluated respecting performance in the oil sands environment. It was determined that the methods proposed, involving low-power DC active sampling or measurement and passive sample collectors, were feasible using existing technology.

The following table shows the minimum parameter sets resulting from the evaluation process.

Summary of minimum air quality and meterological parameter sets to be monitored in the aerometric program.

PARAMETERS	INSTRUMENTATION	TEMPORAL RESOLUTION
AIR QUALITY		
SO_2, TSP[a], $SO_4^=$, V, Ni (up to 18 elements)	Filter pack	Monthly
SO_2	Ontario passive sampler	Monthly
O_3	Continuous	Hourly
Dry Deposition Wet Deposition ($SO_4^=$)	Battery-powered. Aerochem Metrics sampler; ORNL collector	Monthly
Snow core	Manual snow core sampler	Monthly
Precipitation (amount)	Tipping bucket	Event
Bulk Deposition ($SO_4^=$, up to 18 elements)	Open bucket	Monthly
METEOROLOGICAL		
Wind (speed and direction)	Anemometer	Hourly
Temperature	Probes	
Air		Hourly
Soil		Hourly
Moisture	Probes	
Air (RH)		Hourly
Soil		Hourly
Radiation	Pyranometer	
Total		Hourly
Net		Hourly
Atmospheric Pressure	Barometer	
Upper Air Data	Various	Hourly

[a] Total suspended (airborne) particulate matter.

Implementation Strategy

The following factors to be considered in implementing a monitoring network of stations outfitted as proposed in the above tables are discussed:

- measurement approach - averaging period;
- protocols and documentation;
- siting - criteria, selection, specifications;
- data quality assurance and quality control; and
- data management and reporting.

In particular, pros and cons of making all of the measurements in forest clearings were considered in some detail. Siting criteria were developed to address the following requirements:

- permanence of the site (redevelopment);
- location along the pollution gradient;
- meeting the needs of the biological measurements; and
- satisfying the needs of all aerometric instruments.

Recommendations

The principal recommendations are as follows:

1. Air quality measurements should be made on a monthly-average time scale at each site selected for biophysical monitoring.
2. Meteorological measurements should be made on an hourly-average time scale at each biophysical site.
3. Both air quality and meteorological measurements should be made in a clearing that is within or near the forest stand.
4. All instrumentation, methods, and protocols should be based on those already developed and available for established networks or studies. The equipment recommended meets this criterion.
5. Implementation of the network should be phased, concentrating on establishing a small number of sites in the first year, (e.g., two sites at the extremes of concentrations expected in the study area). During the first year, operational details and protocols would be developed and the feasibility of proposed methods and parameters could be evaluated.
6. If financial feasibility turns out to be a serious limitation, consideration should be given to the following program reductions, in order of priority:
    a. delete the AC-powered master site;
    b. reduce the number of aerometric monitoring sites (but not the number of biophysical monitoring sites); and
    c. delete the DC-powered components at the remote sites (i.e., completely passive sites).
7. The minimum number of aerometric sites should be six, three at each of two impingement zones (high and low). The number of biophysical sites could be larger, if the additional sites are near aerometric monitoring sites and there are no significant differences in site characteristics.

8. An additional research priority should be to obtain good quality emission data for the existing oil sands plants. Specifically, characterization of particulate emissions would allow receptor modelling/source apportionment calculations on the filter pack TSP catches (using chemical mass balance methods, for example).
9. Perhaps most important, care should be taken at the early stages of planning the aerometric network to integrate planning for the biophysical studies to follow, including aquatic and soil studies that may be relatively far in the future.

TABLE OF CONTENTS

Continued . . .

TABLE OF CONTENTS (CONCLUDED)

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

A recommended design has been developed for an air quality and meteorology monitoring network in the Athabasca oil sands region of Alberta. The objective of the network is to provide data to support biophysical studies of boreal forest ecosystems.

The design options considered address the following aspects of an aerometric program:

- pollutant measurements necessary to characterize forest exposure;
- meteorological/climatological parameters;
- technical and logistical capability to monitor aerometric parameters with appropriate accuracy, precision, and time response;
- availability of appropriate forested sites and requirements of biological studies;
- cost; and
- operating protocols.

A review of the international literature was carried out, with emphasis on post-1980 reports of studies or programs in which aerometric monitoring was integrated with biological-effects research. Researchers and program managers of key current studies were canvassed for additional unpublished information.

The results of the review formed the basis of approaches to the design of a scientifically valid, affordable monitoring network. Preliminary proposals were evaluated by a workshop attended by representatives of government, industry, academe, and the contract study team.

A recommended network design was prepared which takes into account the workshop results and the specific constraints imposed by technical ability, logistical feasibility, and budget. The recommended program comprises a minimum of six non-AC-powered monitoring sites - three at each of two plume impingement zones (high and low) - to characterize the gradient of pollutant exposure of forest stands in the region. Each site is recommended to be equipped with low-power, battery-operated equipment, or passive contaminant samplers, combining air quality and meteorological measurements at each site. An additional master site is recommended for more extensive monitoring with AC-powered equipment.

The recommended air quality parameters are sulphur dioxide, sulphate (in solution in wet deposition and in dry-deposited particles), and vanadium and nickel (in wet- and dry-deposited particles). An extensive set of standard meteorological parameters is recommended.

ACKNOWLEDGEMENTS

The study team thanks Ms. Bonnie Magill, the Project Officer, and Dr. Glen Singleton of Alberta Environment for their guidance and criticism during the course of this work. Special recognition is given to the contributions of the participants in the January 1987 workshop which evaluated the study team's preliminary design proposals. Concord Scientific particularly thanks its collaborators: Dr. Ron Wallace, Dr. Tony Yarranton, and Dr. Roy Crowther for bringing an informative, biological perspective to the development of an aerometric program. Ms. Linda Fulford provided her always excellent word processing skills.

1. INTRODUCTION

1.1 BACKGROUND

The Alberta Oil Sands Environmental Research Program (AOSERP) sponsored studies of the state of the environment and the impact of development in the Athabasca oil sands region between 1975 and 1985. Alberta Environment has recognized that research to establish the basis for regulatory approaches to current and future development in the oil sands region will have to be carried out for an extended period beyond the initial 10-year mandate of AOSERP. This conclusion is based on a review undertaken by Alberta Environment of the results of the AOSERP program, other Alberta-based environmental studies, and of studies outside of Alberta documented in the international literature. During 1985/86, Alberta Environment undertook a technical review of the atmospheric and terrestrial effects research related to acid-forming emissions in the oil sands area. The results of that review are presented in the report "An Acid Deposition Research Program for Alberta Environment, 1986/87 to 1990/91" (RMD 1986), which proposes a research program.

Studies in the oil sands region have demonstrated few measurable biological effects from emissions due to the relatively low ambient concentration of pollutants in the region (compared with levels at which observable effects occur) and natural ecosystem variability. These findings imply that effects research in the forest ecosystem of the oil sands region must be carried out over an extended time period to permit valid inferences of potential chronic, cumulative impacts.

The five-year research program proposed by Alberta Environment will form the basis of a long-term monitoring program to identify and quantify changes in terrestrial and aquatic systems resulting from anthropogenic emissions in the region.

An "atmospheric and source studies" component has been defined within the proposed research program to provide the models and data necessary to interpret, with confidence, the potential effects of emissions from current and future oil sands development on forest ecosystems. One of the identified research needs is the determination of atmospheric deposition, specifically, quantification of pollutant loading at selected receptor sites.

To address that identified need, a study entitled "Design and Development of an Air Quality, Deposition and Climate Monitoring Program in Support of Terrestrial and Aquatic Effects Research" was initiated. This study, carried out by Concord Scientific Corporation in conjunction with Dominion Ecological Consulting Ltd., Yarranton Holdings Ltd., and Aquatic Resource Management Ltd., is the subject of this report.

1.2 PROJECT OBJECTIVES AND WORK PROGRAM

The initial objective of this project was to design a detailed monitoring protocol that would:

1. Characterize and quantify total (relevant) pollutant loading and climate for selected terrestrial and aquatic receptor sites in the oil sands region; and
2. Discriminate between the pollutant loadings at the selected sites in low, medium, and high plume impingement zones and in a control area.

In order to address this objective, a work program was devised to undertake the following tasks:

1. Review the literature on aerometric measurements carried out or planned in conjunction with the studies of effects of atmospheric deposition of aerosols containing acidic (or acidifying) and phytotoxic substances, including metallic substances;
2. Interview key researchers and program managers familiar with the field of ecosystem effects of atmospheric deposition;
3. Assess the air quality and meteorological parameters to be measured and determine the most appropriate set;
4. Review instrumentation and methods for the required aerometric measurements, concentrating on those that would be appropriate for use in remote (powerless) locations;
5. Produce a preliminary aerometric program design, outlining options;

6. Conduct a workshop to review proposed program options; and
7. Prepare a program design, including detailed operational protocols, for an aerometric monitoring network at biophysical study sites.

The review of effects programs and related aerometric measurements was to concentrate on forest (vegetation) studies, but was not to ignore soils and aquatic receptors, recognizing their importance as components of forest ecosystems.

Based on this review, the design, equipment, and protocols comprising a generic aerometric program that would be sufficient to support as broad a range as feasible of the terrestrial (principally, vegetative) and aquatic effects studies would be specified (RMD 1986).

Since a number of strategies for effects studies had to be accommodated, a workshop was convened to review several possible approaches and recommendations from the study team. The workshop was held on January 14 and 15, 1987 in Edmonton. The documentation prepared for the workshop is given in Appendix 8.2, and the list of attendees is given in Appendix 8.3. Following the workshop, the study team incorporated the results of the workshop with additional analysis and revision of the preliminary proposals, and recommendations to produce the program design described in this document.

1.3 SCOPE OF WORK

The study team's priority was to provide substantiation for a number of approaches to aerometry that would address various scenarios of effects studies, aiming toward a practical, scientifically defensible aerometric program. In recognition of the time and resources available, the scope of work was focussed strategically on key papers, programs, and researchers, principally in North America and since 1980, to maximize the collection of directly applicable information and ideas. This approach is intended to achieve timely design of a program that will work for northern Alberta over an extended monitoring period.

1.4 REPORT OUTLINE

Section 2 of this report summarizes the major points considered in the portion of the January 1987 workshop that addressed the aerometric program, and discusses the recommendations which arose from the workshop. This section concludes with an outline of the proposed field program based on these recommendations and subsequent deliberations.

Section 3 sets forth the basis and results of the study team's assessment of the air quality and meteorological parameters, identifying those that are desirable or feasible to include in the field program.

Sections 4 and 5 address, respectively, the selection of equipment for the proposed program and implementation strategies, including logistics and data handling.

Section 6 comprises conclusions and recommendations.

Section 7 provides a list of references cited in this report. A more complete bibliography may be found in the Workshop Document (Appendix 8.2).

The appendices (Section 8) contain supporting information, particularly as documented for the workshop, including protocols for various components of the recommended field installations in use in existing networks or programs and which will provide the basis for developing operational, site-specific protocols once monitoring sites are selected by Alberta Environment.

2. WORKSHOP SUMMARY AND PROPOSED PROGRAM

2.1 WORKSHOP

The workshop was held on January 14 and 15 at Alberta Environment, Oxbridge Place, Edmonton. The first day was devoted to presentations by Alberta Environment of their proposed five-year work-plan: "An Acid Deposition Research Program for Alberta Environment" (RMD 1986), which was subsequently reviewed by the attendees. During the second day, the study team presented the proposed design options for an aerometric program to support the anticipated effects studies described on the first day with respect to the workshop. The attendees contributed their comments and criticisms with respect to those proposals. This section summarizes the results of the first day, but addresses in detail only the deliberations and conclusions of the second day.

2.1.1 Workshop Summary - First Day

The presentations on the first day of the workshop addressed the following subjects:

1. objectives, scope, and background of Alberta Environment's Acid Deposition Research Program;
2. landscape/response monitoring and modelling studies; and
3. air/source monitoring and modelling studies.

The ensuing discussion addressed all three subjects, but the critical result for consideration on the second day was an indication of the biological parameters that were expected to be important in future

Table 1. Biological parameters of potential interest.

PARAMETER (trees)	TEMPORAL SCALE
Bark acidity (or other matter)	Annual
Foliar sulphur concentration[a]	Annual
Seedling establishment	Annual
Seed germination[a]	Annual
Shoot growth[a]	Annual
Needle retention/mass[a]	Annual
Understory cover	Annual
Leaf decomposition rate	Annual
Tree rings (growth)	Every 5 to 10 years

[a] Possibly at more than one vertical level.

studies. Most importantly, the temporal scales of the biological responses were needed to evaluate the response required of the proposed aerometric monitoring. Table 1 lists the biological parameters of potential interest, along with their respective temporal scales. These parameters were recommended by the workshop, based on material presented by C. Powter. They are, for the most part, measures of forest productivity, which was identified as the indicator most likely to show the earliest effect of pollutant deposition (RMD 1986).

Another important conclusion of the first day's discussion was that the terrestrial and aquatic effects studies should be integrated with the aerometric program in the planning stage, without waiting until the implementation stage. The incorporation of the requirements for parameter measurements implied by Table 1 into the evaluation of the proposed aerometric program designs during the second day of the workshop was intended to achieve part of the necessary integration.

The attendees concluded that aerometric measurements were necessary to support interpretation of any biological observations. It was also agreed that climatological and meteorological measurements would be as important as air quality measurements.

2.1.2 Workshop Summary - Second Day

The objective of the second day of the workshop was to address the project's terms of reference by:

1. determining the feasibility of any aerometric program, should the biophysical studies proposed by Alberta Environment be carried out; and
2. recommending the simplest, scientifically defensible approach determined by consensus if an aerometric program were found to be meaningful and feasible.

The Workshop Document (Appendix 8.2) provided background information from the literature review conducted by the study team and presented a number of design options for an aerometric program.

The design options relied heavily on information from several key current programs which combine aerometric and biophysical studies of forest ecosystems. These programs are:

1. Integrated Forest Study (Oak Ridge National Laboratory/ Electric Power Research Institute);
2. Acidic Precipitation in Ontario (Ontario Ministry of the Environment);
3. Mountain Cloud Chemistry Program/Chemistry of High Elevation Fog Program (US Environmental Protection Agency/ Environment Canada); and
4. National Forest Response Program/Atmospheric Exposure Cooperatives - particularly by Western Conifers Research Cooperative (US Environmental Protection Agency).

More information about these programs may be found in Appendix 8.2.

The following subsections present a summary of the design options offered to the workshop attendees for evaluation prior to the workshop, the rationale for the option considered in greatest detail during the second day of the workshop, and the results of the attendees' evaluation of that option.

2.2 DESIGN OPTIONS

Five design options (scenarios) based on various combinations of time resolution and frequency of aerometric measurements were offered for consideration. The design options for the aerometric program are described in terms of the time scale (interval) over which aerometric measurements are integrated (short, medium, or long interval) and in terms of the intensity of the measurements, namely, intensive (continuous, frequent), or campaign (periodic, highly intensive measurements). These options were identied as:

- short-term interval, intensive;
- medium-time interval, intensive (with special or campaign studies);
- long-time interval;
- no aerometric measurements (i.e., biophysical observations only, plus existing climatological and meteorological measurements); and
- a hybrid of the first three options.

These scenarios are described in the Workshop Document (Appendix 8.2) and are summarized here for convenience.

2.2.1 Short-Interval, Intensive Option

This option assumes that only short-interval (hourly and/or event) responses are appropriate to indicate existing or future effects on forest vegetation. It also assumes that the biophysical measurements require detailed within-canopy measurements, namely, vertically and horizontally resolved air concentration and meteorological measurements, the measurement of event wet deposition, and throughfall and stemflow measurements.

In this option, the selection of sites with similar aerodynamic features will be necessary in order to facilitate inter-site comparisons. Factors such as elevation, slope and aspect, and canopy height and density will have to be taken into consideration.

The requirements for pollutant monitoring are extreme in that hourly measurements would likely be desirable. The shortest time interval for ambient concentration measurements using passive or battery/solar operated active samplers is daily integration using multi-day samplers that incorporate a sample changer. In principle, low-volume samplers based on filter pack methods for gases and particles could be used provided suitable power supplies (battery, solar powered, etc.) are available.

Meteorological measurements (wind speed and direction, temperature, relative humidity) with hourly integration of measurements are feasible through the use of solar/battery operated equipment that stores data electronically and transmits data at preselected intervals via telecommunications or satellite. The provision of hourly-integrated meteorological data is technically feasible and the costs of providing longer-interval measurements are not likely to be significantly different.

2.2.2 Medium-Interval Option With or Without Campaign Studies

This options assumes that medium-interval (weekly or monthly) site-specific ambient concentration measurements are needed.

This option may be consistent with a planned medium-term (10 to 25 years) study which may yield definitive answers relatively early, such that more or less intensive biophysical and/or aerometric monitoring may take place. In this option, it is assumed that above-canopy measurements only will suffice for concentration and meteorological measurements. The air quality and meteorological measurements would be required to establish seasonal and longer-term means.

This option may or may not include campaign and/or shorter-term studies as are appropriate. The campaign studies could, for example, incorporate within- and below-canopy measurements (multiple sites per stand), throughfall and stemflow measurements, and shorter-interval concentration measurements.

2.2.3 Long-Interval, Regional-Scale Monitoring Options

In this option, measurements integrated over long time periods (monthly or longer) are appropriate for the effects studies which would likely be based on a long-term (20 to 25 years) program. Site-specific measurements for particulate concentrations and monthly wet deposition measurements would be sufficient.

Only regional climate monitoring is required for characterizing meteorological conditions at or near plume heights and/or for establishing weather conditions that are representative of the region. Available meteorological data from the region clearly indicate that significant differences in microclimate are likely at different study sites within a 20 km radius of either major emission source in the study area. Regional climate monitoring options therefore will focus on the choices for characterizing plume-level meteorological conditions.

2.2.4 Hybrid Option

This option would include above-canopy site-specific measurements consisting of medium- and long-interval measurements for some pollutants, and selected meteorological parameters. In addition, regional-scale measurements of ozone would be made and existing meteorological measurements would be used to complement the site-specific measurements. Other air quality measurements would include passive samplers for SO_2 and H_2S, on monthly sampling intervals, and suspended particles (TSP) monthly using low-volume active sampling and dustfall devices.

The meteorological measurements would include a limited number of sites at which hourly meteorological data are obtained. The site selection process would ensure that at least two pairs of sites have features likely to result in similar microclimates. Meteorological data would be acquired by above-canopy sensors for wind, temperature, and relative humidity, and by ground-based sensors for soil temperature. Data from these sensors would be stored electronically and telemetered periodically. Additional measurements would include snow depth and snow core sampling in winter and battery-operated wet deposition collectors would be used in the summer (only for collecting rain samples integrated over 28 days).

2.2.5 No Aerometric Measurements: Use Existing Climatic Data

One option is not to make any site-specific aerometric measurements. Existing climatic information alone would be used to complement observational or biophysical/biomonitoring studies.

2.3 RATIONALE FOR SELECTION OF RECOMMENDED DESIGN OPTION

In evaluating these options, the workshop participants addressed the following principal issues:

- pollutants of interest in defining the total pollutant loadings;
- meteorological and climatological parameters of interest;
- time resolution required of the aerometry as specified by the biophysical studies;
- equipment implications and limitations based on the above three factors, recognizing the remoteness of the monitoring sites; and

- implications of logistics of access to remote biophysical sites.

The study team proposed that the workshop focus on the "hybrid option," since this appeared to be the most likely, feasible approach. Table 2 presents details of the hybrid option. In focussing on this option, the workshop attendees were asked to address whether the proposed parameters and methods were necessary and sufficient with respect to:

- temporal resolution;
- spatial resolution;
- precision;
- logistics;
- existing (proven) technological capability; and
- biophysical study strategy.

The last factor, to a certain extent, determines the specifications for the others.

The parameters indicated in Table 2 were selected from a larger set, which is given in Table 3. The selection was influenced by the availability of proven measurement methods for these parameters (Appendix 8.2). These methods were, in turn, influenced by the prospect that AC power would not be available at most of the biophysical sites, but that adequate solar panel/storage battery power supplies might be feasible.

The methods listed in Table 2 are described briefly here as background to the description of the workshop's assessment of the hybrid

Table 2. Hybrid option.

PARAMETER(S)	METHOD	RESOLUTION TEMPORAL	 SPATIAL	COMMENTS
SO_2, NO_2, TSP (trace metals, $SO_4^=$, NO_3^-, NH_4^+)	Filter pack	Monthly	Site-specific	Above-canopy measurements
SO_2, H_2S	Sulphation candles Sulphide strips	Monthly	Site-specific	Above-canopy measurements
SO_2	Passive monitor	Monthly	Site-specific	Above-canopy measurements
O_3	Chemiluminescence	Hourly	Regional	Locate at nearest available site or existing station with AC power.
Dry deposition	Dustfall	Monthly		
Wet deposition (major ions, trace metals)	Sangamo type collector	Monthly	Site-specific	Battery operated, weekly composition, at selected sites only. Summer only. Above-canopy.
Precipitation (rain)		Weekly		Summer only. Above-canopy.
Snow core		Seasonal/ Monthly		
Wind (speed and direction)		Hourly		Above-canopy
Temperature		Hourly		
RH		Hourly		

Table 3. Desirable pollutants to be monitored.

Gases:		
	SO_2, NO_2, HNO_3, O_3, H_2S	
Precipitation:		
	Anions:	$SO_4^{=}$, NO_3^{-}, Cl^{-}, $PO_4^{\equiv}$, HCO_3^{-}
	Cations:	pH, acidity, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, NH_4^{+}; (possibly Al, Fe, Mn, Zn)
Particulate matter:		
	Soluble ions:	$SO_4^{=}$, NO_3^{-}, $PO_4^{\equiv}$, Cl^{-}, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, NH_4^{+} (metal cations unlikely to be detectable)
	Elements:	Al, Cr, Fe, Co, Ni, Cu, Zn, Cd, Pb, Hg, Sn, As, V, Mn, Mg, Ti, Se, S

option. The recommended methods and alternatives are discussed in more detail in Section 4.

The restricted availability of power, together with the relative inaccessibility of the sites and the need to keep costs to a minimum, precluded the installation of a full suite of continuous monitoring instruments. Integrative methods that would determine several parameters simultaneously, therefore, would be required. The sequential filter pack, as used currently in networks such as the Canadian Air and Precipitation Monitoring Network (CAPMoN), the Acidic Precipitation in Ontario Study (APIOS), and in studies carried out by the Kananaskis Centre for Environmental Research, as well as major US studies (see Appendix 8.2), was judged to be the only approach that could be recommended that might operate within the constraints.

Gaseous Compounds

The current capabilities of the filter pack method (with or without a pre-filter denuder to remove certain reactive gases, principally NH_3, from the sampled air stream) comprise the gases SO_2, HNO_3, and NH_3 and any of the ionic or metallic constituents of airborne particulate matter. The sampling configuration must provide sufficient sample to achieve the necesary chemical analysis detection requirements. NO_2 cannot be measured by the filter pack approach at present.

The various versions of the filter pack method are described in the literature (Anlauf et al. 1986). Judgements respecting the applicability of this method to the oil sands region have been based on the results of measurements made at CAPMoN and APIOS sites of similar characteristics to those anticipated for the oil sands, for example, Cree Lake, Saskatchewan (CAPMoN), and Dorset, Ontario (APIOS). The filter pack technique is also the standard, integrative method used at US National Acid Precipitation Assessment Program (NAPAP) National Acid Deposition Program (NADP) sites, in particular, the research site sub-network operated by the US National Oceanic and Atmospheric Administration (NOAA) (Hicks et al. 1986).

Since there was concern that sites may be required to operate without power, the passive sampling options listed in Table 2 were proposed either to complement and supplement the filter pack method, or to replace it. Passive or static methods for SO_2 (lead dioxide sulphation cylinder or plate) and H_2S (zinc acetate impregnated strip) are commonly used in Alberta, as specified in the Air Monitoring Directive (AMD 86-1) published by Alberta Environment. These methods require no source of power. The passive collector for SO_2 described by Orr et al. (1986) is currently used in Ontario at selected sites and can be recommended for consideration for the oil sands program. These techniques are assessed in Section 4.

Dry Deposition

Dry (predominantly, particulate) deposition collected as dustfall is also a passive method suitable for non-powered sites. Dustfall may be collected in a variety of ways, from the dried portion of the combined wet and dry deposition collected in a bulk collector, to the more sophisticated methods of the dry-side bucket collector of a wet-only/dry-only collector, to the dry-only surrogate surface deposition collector used by Oak Ridge National Laboratory (ORNL) in such studies as the Electric Power Research Institute (EPRI)-sponsored Integrated Forest Study (IFS). This collector, which is passive but has a powered lid that closes during precipitation events to expose it only during dry periods, is described in Lindberg and Lovett (1985).

Ozone

Based on the occurrence, at the Sandalta monitoring site, of ozone concentrations approaching or exceeding the 0.08 ppm National Ambient Air Quality Objective (NAAQO), this gas was recommended for inclusion in the monitoring scheme. Neither filter pack nor passive methods are available for O_3; therefore, a continuous monitor at a powered site is required. Since episodes of elevated ozone concentration are expected to be regional in nature (i.e., not directly related to the oil sands plants' plumes), restriction to a single, regionally representative site is not considered to be a drawback.

Wet Deposition

Table 2 indicates that precipitation measurements are recommended to be made with a wet-only collector in summer and with snow cores in winter. If battery/solar panel operation is feasible, the standard CAPMoN (Sangamo) or NADP (Aerochem Metrics) wet-only/dry-only collector is recommended. The dry-only side of the collector could be used for shielding and exposing the dry particulate matter deposition collector (dustfall or ORNL collector).

If, however, the amount of power at the remote biophysical sites is insufficient to power a wet-only/dry-only collector, it may be necessary to use the passive bulk precipitation collector. This device has many limitations, especially for integrative, monthly exposures. These limitations include evaporative losses, contamination, instability of some chemical constituents (notably nitrate and ammonium, with respect to microbiological degradation), and reaction of the condensed-phase constituents with absorbed atmospheric gases, such as NH_3.

Meteorology

Table 2 suggests that only the basic meteorological measurements be made, but the set of parameters need not be so restrictive, since a more complete meteorological package does not add significantly to power demand, capital cost, or data analysis.

Temporal Scale

The recommended time resolution for the components of the hybrid option (Table 2) was based on both logistical considerations and the anticipated requirements of the biophysical program. The difficulty of site access and the likely limited availability of personnel to visit the sites frequently, imply that planned aerometric and biophysical measurements should require attention no more frequently than monthly. More fundamentally, however, it was anticipated that, since the biological studies would presumably focus on long-term, cumulative effects, the important time scales would be annual or seasonal, with the possibility of even longer intervals (see Table 1).

Hourly collection of meteorological data was recommended because such data can be conveniently accumulated and stored on this scale, and any necessary time averages can be generated by post-processing.

Spatial Resolution

With the exception of the proposed regional O_3 measurement, it was recommended that all parameters be measured at each biophysical site. This recommendation is based upon observations that microclimate varies considerably, especially respecting elevation and aspect, in the oil sands region. If unaccounted for, this variability could affect resolution of the air quality characteristics of different plume impingement zones.

The program outlined in Table 2 does not address spatial replication of the aerometric measurements within a biophysical site (e.g., a forest stand). This issue was considered, but the conclusion that below-canopy aerometric measurements would not be feasible, except on a campaign basis in connection with specific biophysical studies, left the question of aerometric spatial replication open. Consequently, the study team recommended that air quality and meteorological measurements be made at a single location above the forest canopy. It is believed that this approach would characterize the exposure of a forest stand adequately. Furthermore, it is argued that a denser set of aerometric measurements would be neither economic nor scientifically supportable, considering the relatively much greater variability inherent in the biological systems' response to their environment.

The feasibility and defensibility of above-canopy, as compared with clearing, measurements of the aerometric parameters was addressed in the workshop and in subsequent deliberations (see Section 5).

2.4 WORKSHOP MODIFICATIONS TO THE RECOMMENDED PROGRAM

The consensus of the first day of the workshop was that, given the desirability of a biophysical program in the region, an aerometric program was also desirable, and probably feasible, if appropriately scaled and designed. Table 1 lists the biological parameters identified during Day 1 as representative of the types of studies that could be undertaken, along with their associated temporal resolution. The focus of the second day's evaluation of the various approaches to an aerometric program was on the hybrid option (Table 2), which appeared to be the most likely model based on the preliminary review.

The major issues identified in discussing the hybrid option (Table 2) were:

- the feasibility of using equipment requiring significant amounts of electrical power, for example, a filter pack sampler, or wet-only/dry-only precipitation sampler;
- the sensitivity of the proposed methods for elemental analysis of airborne particulate matter;
- the relative merits (validity) of sulphation measurements and specific SO_2 measurements by passive methods;
- the advisability of integrated, bulk wet and dry deposition collection, if that were to be the only feasible approach;
- the advisability of a method other than conventional dustfall as a measure of dry, particle deposition;
- the relationship between the probable frequency of site visits, the biological response times of interest and the required time resolution of the aerometric measurements;
- the potential to estimate canopy - pollutant interactions (uptake) from aerometric measurements made only above-canopy;
- the question of how to relate in-stand exposure to external aerometric measurements;

- the feasibility of making (at least some) aerometric measurements in a clearing rather than above-canopy to represent exposure of the forest stand;
- the extent of the aerometric data base that will be required to delineate the pollution gradient;
- the effect(s) of changing composition of the industrial plumes with distance from the source, for example, the different relative depletion rates for gases and particles and for particles in different size classes;
- the importance of meteorological and climatological characterization of each site because of likely between-site differences which may result in measurable biological variation;
- the desirability of making sure the aerometric program is properly designed to accommodate the needs of the biological measurements before implementing a field program;
- the requisite levels of duplication and replication for aerometric measurements, whether above, in, outside, or beneath the canopy;
- implications of the lack of a fully validated regional dispersion and deposition model to aid in site selection;
- site selection criteria respecting the aerometric measurements, plume impingement gradient, and appropriate forest stands;

- consideration in site selection of development plans over the next 25 years;
- the need for more than one background (control) site; and
- the need to plan sites so that the compiled data base could be used in relation to future aquatic and soils monitoring.

Discussion of these points led to minor modifications in the approach proposed in Table 2.

It was agreed that, if the filter pack method (as applied in the standard CAPMoN/APN sampler), or a variant, could be provided with adequate power to operate, the parameters to be determined in the collected material should comprise:

- SO_2;
- airborne particulate matter (APM);
- selected trace metals (in APM); and
- $SO_4^=$, NO_3^-, NH_4^+ (water-soluble ions).

The participants agreed that ozone could be monitored at a powered, regionally representative site. Passive methods for SO_2 and H_2S measurement were recommended. Particular interest was expressed respecting the Ontario Ministry of the Environment's passive SO_2-specific collector for determining SO_2 concentration, rather than sulphation rate (Orr et al. 1986). The applicability and limitations of each of these types of SO_2 collectors are discussed in Section 4.

The consensus of the meeting was that although bulk precipitation is a convenient passive collection method, the composition of the collected sample and the apportionment of the wet and dry components in a monthly sample would be questionable, at best. A wet-only/dry-only collector should be used if feasible, but skepticism was expressed that battery-powered versions of the standard CAPMoN sampler would perform in the remote, harsh environment of the oil sands.

It was recommended that the suite of meteorological and climatological parameters be as complete as possible, including those shown in Table 4. "Upper air data" in Table 4 refers to data at plume height and above, such as temperature profiles, wind, and turbulence, as required by dispersion models. Such models would be used to interpolate and extrapolate monitoring results in space and time and to estimate future pollutant loadings from existing and proposed developments. Collection of total precipitation amount by a tipping bucket and Nipher gauge was supported.

The methods suggested in Table 2 were confirmed as the most appropriate, given the logistical and budgetary constraints.

Reservations were expressed generally about the feasibility of making above-canopy measurements, because of operational problems related to the height of tower/platform that might be required, and because of the known collection inefficiency of precipitation sampling devices in such exposures due to wind shear (Lusis and Vet, pers. comm. 1987). Clearing measurements were recommended, if representative exposures could be determined and fetch considerations could be met (i.e., locally-generated turbulence avoided).

Table 4. Desirable meteorological parameters (workshop).

1.	Precipitation:	rain, snow, snow depth
2.	Temperature:	air, soil
3.	Moisture:	air, relative humidity, soil
4.	Wind:	speed, direction
5.	Radiation:	total, net (regional)
6.	Pressure:	barometric
7.	Upper air data:	(see Appendix 8.2)[a]

[a] Depending upon input data requirements of models: may include wind speed, direction at plume height, mixing height, stability (or turbulence) indicator, etc.

3. AEROMETRIC PARAMETERS

3.1 DESIRABLE AIR QUALITY PARAMETERS

Table 3 presents a list of desirable, candidate pollutants to be monitored. This list was reduced by applying preliminary criteria of necessity, sufficiency, and feasibility to arrive at the recommended list indicated in Table 2. Both lists were addressed by the workshop participants, and a modified short list was produced.

The following sections present the rationale for selecting or excluding parameters and summarize conclusions of the workshop and study team respecting a recommended minimum set of parameters.

3.1.1 Gases

Based on the conclusions of the workshop and subsequent evaluation by the study team, the following are recommended as the target gases, along with their candidate measurement methods:

- SO_2 (CAPMoN/APIOS/NAPAP active filter pack); MOE passive sampler; sulphation plates);
- H_2s (sulphide strips/AMD 86-1);
- O_3 (continuous monitor - AC-powered site).

3.1.1.1 Sulphur dioxide. SO_2 is included not only because it is a major component of emissions and an acid-forming pollutant, but also because it can serve as a surrogate for other gases emitted from the industrial plants in the region. The latter applies to NO_2, for example, which is also emitted from the oil sands plants. Within the study area (radius of about 25 km from the existing plants), chemical transformation and deposition of SO_2 and NO_2 will be indistinguishable, so that relative depletion rates will be similar. That is, receptor measurements of SO_2 will allow estimates of other emitted gases, presuming that the ratios of their emission rates to that of SO_2 are known. In addition, the concentration of SO_2 can be determined with acceptable accuracy and precision at the levels expected in the field. Section 4 provides a detailed assessment of SO_2 measurement methods.

3.1.1.2 Hydrogen sulphide. It is desirable to monitor H_2S because it is emitted by the industrial plants in the region, mainly in low-level fugitive releases. It has been detected by a continuous monitor at Fort McKay, 15 to 20 km from the sources. Since H_2S interferes with the SO_2 determination by the sulphation method, it is desirable to know the concentrations of the two gases simultaneously (and independently), in order to resolve their contributions. The H_2S interference in the sulphation measurement of SO_2 is about 1/3 to 1/2 of the equivalent SO_2 concentration.

3.1.1.3 Ozone. O_3 has been identified as a target gas (see Subsection 2.3) because of its potential effects at existing levels in the region. It is recommended for inclusion in the monitoring program under the assumption that an AC-powered site will be incorporated, so that a continuous monitor could be operated.

The other gases considered, but discarded, included HNO_3, NO_2, and NH_3. These are discussed in the following paragraphs.

Nitric acid vapour (HNO_3) can be easily accommodated by an additional section to the proposed filter pack (nylon filter) - in fact, it is a component of the standard package used in North American networks. Its inclusion, however, is judged to be of a small marginal value, because the concentrations are likely to be very low, and it would add to the complexity (and cost) of the system. For example, HNO_3 concentrations at the Cree Lake, Saskatchewan APN site in 1982/83 ranged from <0.01 $\mu g/m^3$ to 0.6 $\mu g/m^3$, with monthly means of 0.1 to 0.2 $\mu g/m^3$ (equivalent to an upper limit of about 0.3 kg/ha/y nitrate dry deposition).

Nitrogen dioxide (NO_2) cannot be determined by a filter pack method at present, but can be determined at levels down to a few $\mu g/m^3$ over averaging times as short as one day with a passive, diffusional sampler (Cadoff and Hodgeson 1983; Colls 1986), using triethanolamine to trap NO_2. NO_2 levels in the oil sands, however, are known to be very low, based on continuous monitoring by Alberta Environment at the Sandalta site during 1983 to 1986 (Murray 1984; Hansen 1985, 1986). All hourly-averaged NO_2 concentrations were less than 0.05 ppm.

In addition, NO_2 emissions from oil sands plants are only about 15% as much as those of SO_2. Within the proposed study area (ca. 25 km radium from the plants), NO_2 is expected to mimic approximately the behaviour of SO_2 respecting plume depletion. This means that forest stand exposure to NO_2 (not deposition) could be modelled using, for example, the FREDIS model (Alberta Environment's FREquency DIStribution dispersion model). Receptor-level concentrations of NO_2 could be estimated relative to those of SO_2 using the ratio of emission rates.

Ammonia (NH_3) was not identified as one of the gases to be monitored, but it was mentioned in the workshop. It can also be monitored by the standard filter pack method (glass fibre filter impregnated with citric acid). NH_3 levels are expected to be very low, representing background levels, in the absence of application of ammonium-based fertilizers in the region. NH_3 is not associated with industrial emissions in the area. If present, it would be expected to react with acidic gases and particles in the plant plumes, appearing at the impingement zones as ammonium salts.

3.1.2 Particulate Matter

Whether the particulate matter is collected by a filter pack or by dry-only passive deposition methods, monitoring of the following water-soluble ions is recommended because of their potential importance respecting ecosystem acidification:

- sulphate;
- nitrate; and
- ammonium.

The following additional group of ions (Table 3) will normally be detectable in the water extract of the collected particulate matter: calcium, magnesium, sodium, potassium, and chloride. These ions principally represent soil-derived material and are important for determining overall nutrient balance, if that were to be an objective of the biological program. No special sample preparation or handling precautions are necessary to allow samples to be analyzed for these ions, and they could be analyzed on a campaign basis or in the future from archived samples (extracts), if required. Phosphate would also be important in nutrient studies, but like bicarbonate, it is unstable in samples over an extended exposure period. It is recommended, then, that only sulphate, nitrate, and ammonium be considered for inclusion at this stage of design evaluation.

The term "trace metals" as used thus far in the report refers to components of filter pack catch or dry-deposited material and not to the extracts. Only dominant soil-derived metals (Fe, Al, Mn, Zn) would normally be detectable in the latter, if any metal cations could be detected. The elements of interest in dry particles are those associated with the industrial emissions, including:

1. those that may cause cumulative toxic effects;
2. those that may serve as tracers for (cumulative) deposition; or

3. those that may serve as markers of altered biochemical or ecosystem activity.

The metallic elements of interest are shown in Table 5 below, listed in order of their emission rates from Syncrude's main stack (CSC 1984) and flagged by Criteria 1, 2, or 3 above. Comparable data are not available for Suncor, but it is a reasonable assumption based on a comparison of fly ash composition (Barrie 1980; CSC 1984) that the relative metallic elemental composition of emitted particles is similar.

The elements in Table 5 were initially selected based on a review of the literature respecting biological effects studies (see Appendix 8.2). The list also takes into consideration Criteria 1, 2, and 3 above and currently available emission data from the oil sands area (Dabbs 1985). Calculations have been carried out to estimate comparative deposition increments to the soil in the region. These data indicate those elements which should show enhanced concentrations in airborne particulate matter relative to those in soil, hence, those that may serve as tracers in the present study.

Table 5 indicates that S, V, and Ni may be good candidates as tracers of environmental contaminants from the industrial sources present in the region. Barrie (1980) found V from the oil sands plants to be a good tracer of anthropogenic deposition. Case (Dabbs 1985) found that the concentrations of all three of these elements (V, S, Ni) in lichens correlated well with distance from the oil sands emission sources. The order of analytical detection limits for these three elements in

Table 5. Desirable elements in order of particulate emission rate.

Element	Criteria
Iron (Fe)[a]	ND
Aluminum (Al)	3
Vanadium (V)	1, 2
Magnesium (Mg)[a]	3
Titanium (Ti)	(2)
Sulphur (S)[a,b]	1, 2, 3
Manganese (Mn)[a]	3?
Nickel (Ni)	1, 2
Zinc (Zn)[a]	(1)
Lead (Pb)	1, (2)
Chromium (Cr)	1, (2)
Copper (Cu)[a]	(1), (2)
Cadmium (Cd)	1, 2
Cobalt (Co)	1
Selenium (Se)	1, 2
Tin (Sn)	1
Arsenic (As)	1
Mercury (Hg)	1, (2)

[a] Indicates an essential nutrient for trees.

[b] Position in list uncertain; estimated from data other than Dabbs (1985).

Symbols:
1) cumulative toxic effects
2) tracer of accumulation
3) marker of altered biochemcial activity

( ) Indicates marginal qualification.

ND No data.

vegetation on a dry weight basis is V (0.3 ppm); Ni (1 ppm), and S (50 ppm). The only other elements in Table 5 for possible use as tracers, with better analytical sensitivity, are Cd, Se, and Hg; but these would be difficult to detect because of their very low concentrations.

It is not critical which of the elements in Table 5 are monitored initially in particulate matter, since stable archived samples can be analyzed for other parameters at any time in the future. Future research on the composition of the industrial emissions, of filter-collected airborne particulate matter and of vegetation, soils, and other receptor materials may identify highly sensitive tracers of emissions and/or indicators of biochemical alteration. Those might be, for example, rare earth elements (in emissions and airborne particulate matter), or Mo (micronutrient with high analytical sensitivity - 0.03 ppm dry weight basis).

Elements can easily be added to or deleted from the analytical protocols with time and the appearance of new information, as long as the collection methods stay the same.

A question which arose in the workshop, of whether particle size distinction could be accommodated in the program, is difficult to answer. The standard (network) version of the filter pack sampler does not have a specific size discriminating inlet, primarily to avoid loss of reactive gases prior to the filtration stages. The sampler does have selectivity respecting particle size, because it does not necessarily sample isokinetically, but its selectivity is not characterizable. The NOAA/ATDD version of the filter pack which is used in the NAPAP research site equipment has a heated inlet tube (to avoid condensation of moisture in front of the filters) which also acts as a particle selector by impaction and elutriation (Hicks et al. 1986). It was originally believed that the size cutoff would be about 5 µm, which would exclude the larger, soil-derived particles. It now appears, however, that the size fractionation is not very well defined and is likely greater than 10 µm, which would not discriminate against soil-derived material. Tests of the sampler are currently being conducted in a wind tunnel at NOAA, Oak Ridge, TN (Hicks, pers. comm. 1987).

Some of the larger particles, however, will be generated by industrial processes in the region, because of the surface mining nature of both Syncrude's and Suncor's operations. The sand tailings of the processes may also become airborne. This means that some of the larger size fraction particles may be more similar in composition to the industrial emissions than to typical soil-derived material. Without size discrimination in sample collection at receptor sites, the emissions and mining portions of particle deposition cannot be resolved. Such sampling, however, will integrate the overall deposition attributable to the industrial sources, if tracer elements for these sources are analyzed, as discussed below.

Passive elutriators or low-powered Lundgren streaker collectors (which are commercially available) might provide an estimate of particle size, but probably would not collect sufficient sample to permit analysis, under the conditions of low particle loadings such as those that exist in the oil sands. These methods would be expensive and require great care in field use; therefore, they cannot be recommended for use at the biophysical sites because of logistical and cost constraints. Particle sizing could be carried out at a powered site using, for example, a high-volume sampler with size-selective inlet (SSI), or a dichotomous sampler with 2.5 μm and 10 μm fraction cutoffs (the standard NAPS and EPA inhalable/respirable particulate matter sampler). The chemical analysis of the dichotomous sampler filters might permit source apportionment to be carried out by the chemical mass balance approach.

3.1.3 Precipitation

The following discussion refers to the filtered liquid portion of both rain and snowmelt and the refinement of the suggested parameter list.

Of the anions listed as desirable in Table 3, nitrate is not a good candidate if monthly integrated samples are to be collected, because of loss due to microbiological activity and volatilization (in hot weather). Therefore, sulphate (as an indicator of anthropogenic deposition), and chloride (as a soil indicator) should be determined. Chloride, however, may be subject to volatilization losses from acidic samples (as HCl), and may not be detectable regularly (Wiebe et al. 1985). Therefore, chloride may also be deleted from the recommended list.

The cations listed in Table 2, with the exception of NH_4^+, are all characteristics of soil-derived particulate material and therefore will be of little use in evaluating anthropogenic deposition. They would be of interest if nutrient balance or cycling is studied in the biophysical program, since they are major nutrients; otherwise, they are of marginal utility. This is especially so since the precipitation samples do not permit segregation of contributions from particles of various size ranges.

In addition to the filtered liquid portion of a precipitation sample, the insoluble particulate fraction is comprised of particles associated with rainout and washout processes for wet-only samples, and with rainout, washout, and dry deposition processes for bulk samples. Most of the metallic components of anthropogenic original (Table 4) will be in the insoluble fraction (Barrie 1980), so that analysis of this portion of a wet-only or bulk precipitation sample may yield information on anthropogenic deposition. If the filtered particulate portion of precipitation samples were to be analyzed for V, for example, source impact might be estimated, since as discussed above, this element appears to be a good tracer of industrial activity in the region.

3.2 DESIRABLE METEOROLOGICAL AND CLIMATALOGICAL PARAMETERS

Table 6 lists a number of levels of meteorological instrumentation to be considered for ecological research stations (Swift and Roysdale 1985). The list developed in the workshop (Table 4) includes

Table 6. Types of long-term ecological research meteorological stations.

LEVEL	PARAMETERS	INTERVAL	REMARKS
0. Entry	Air temperature Precipitation	Daily	Temporary or satellite station
1. Basic	Air temperature Precipitation Vapour pressure Wind speed	Daily	Minimum standard station, use standard instrumentation
	Wind direction Solar radiation	Daily	Optional for Level 1
2. Research	All of the above	Hourly	Probably use electronic sensors and data logger
3. Supplemental	All of the above plus one or more: Snow depth Wind vector Partial spectrum radiation Soil temperature Water temperature Atmospheric pressure Evaporation Boundary layer fluxes or other variables	As required	Specialized measurement at some sites. May be continuing or short term.

Source: Swift and Roysdale (1985).

most of the highest level (Research plus Supplemental) recommendations. This degree of instrumentation is justified on the basis of the observed variability of meteorological and microclimatological data in the region, as described in Appendix 8.2. It is judged that detailed microclimate characterization of the kind proposed is necessary because of the sensitivity of forest response to climatic factors. These factors are strongly influenced by elevation and aspect, event in the relatively low relief regime of the oil sands region. The modest additional expenditure to achieve these site-specific, detailed data should provide significant benefits in reduced uncertainty in interpreting the biophysical data.

There appears to be little need to discuss these points or Table 4 at greater length, since the more difficult undertaking will be to characterize the pollutant exposure gradient unambiguously. An important consideration, however, will be to locate the meteorological/climatological instrumentation package in consideration of the specific biophysical site characteristics, so that measurements at the site can be assured to be representative.

The issue of the site being representative is addressed in Section 5 respecting site selection criteria. The location of both air quality and meteorological instrumentation should be such that the data are representative of the site as a whole and reproducibly so from site to site.

3.3 SUMMARY OF RECOMMENDED PARAMETERS

The preceding sections have presented an analysis of the aerometric parameters that were identified by the study team and the workshop participants as desirable from the perspective of data requirements for the biophysical monitoring program. This analysis is intended to provide a rationale for the simplest subset of parameters that could be recommended for implementation, pending the more detailed assessment which appears in the next section on instrumentation and methods used to determine these parameters.

The assessment to this stage has led to the recommendation of the following air quality parameters to be considered in the next stage of screening (Section 4):

1. Gases
    - SO_2
    - H_2S
    - O_3
2. Water-extractable ions (in airborne particles)
    - $SO_4^=$
    - NO_3^-
    - NH_4^+
    - Cl^- (optional)
3. Elements in dry particles
    - V
    - S (sulphate)
    - Ni

4. Soluble ions in precipitation

   - $SO_4^=$
   - NO_3^- (optional)
   - NH_4^+ (optional)
   - Cl^- (optional)

5. Elements in filtered particles in precipitation

   - V
   - Ni

4. ASSESSMENT OF INSTRUMENTATION AND METHODS

4.1 AIR QUALITY PARAMETERS

This section discusses the methods recommended for the proposed air quality parameters respecting the following characteristics:

- adequacy of sensitivity/specifications;
- operational (logistical) suitability;
- validity and uncertainty of data produced; and
- general advantages/disadvantages.

4.1.1 Gases

4.1.1.1 Standard analyzers. Three gases: SO_2, O_3, and H_2S, are recommended for monitoring at a powered master site on a continuous basis. A standard continuous analyzer having the necessary sensitivity, however, is only available for ozone. This conclusion is based on a review of the data available from Alberta Environment's Sandalta measurements between 1983 and 1986 (Murray 1984; Hansen 1985, 1986). These data indicated that O_3 concentrations are always above the quantitation limit of the standard chemiluminescence (or ultraviolet absorption) analyzer, which is about 1 ppbv. The tropospheric global background concentration of O_3 is between 10 and 50 ppbv.

The analogous measurements for SO_2 were predominantly at or below the quantitation limit of a standard pulsed fluorescence or flame photometric detector (FPD) instrument, which is about 10 ppb. The levels would be accessible to an enhanced FPD instrument, like that incorporated in the Alberta Environment system for measurement of SO_2 dry deposition gradient (FPD doped with SF_6; Davis and Wright 1985). This enhanced technique is 10 times more sensitive (quantitation limit, 1 ppbv), but would require research-level technical attendance.

The situation for H_2s is expected to be the same as that for SO_2 with respect to continuous monitoring. This expectation is somewhat more tenuous, however, since it was based on reported H_2S exceedances of the 10 ppbv hourly standard at the industry network sites in the region (generally <5 km from the emission sources), and at Fort McKay (ca. 15 to 20 km from the emission sources). In the region of interest, 5 to 25 km from the emission sources, the H_2S concentrations on average will be at or below the operational quantitation limit of standard continuous monitors, that is, about 10 ppb. An enhanced FPD instrument would also allow quantification of H_2S.

4.1.1.2 Filter pack. Unless continuous instrumentation is used that will permit quantification of SO_2 and H_2S at least 90% of the time, there would be little use for the data in this operation. In either case, integrative (e.g., filter pack) methods should also be used at the fully-powered site as back-up to the continuous analyzer and for comparison purposes. This approach would exclude H_2S, since a validated filter pack method for this parameter has not been demonstrated in routine, network use. Such a method for H_2S has been applied in a short-term research study for Syncrude, but its long-term operability is unknown.

The standard integrative filter pack method for SO_2 has a detection limit of about 0.5 $\mu g/m^3$ (0.2 ppbv) and a quantitation limit of 1 $\mu g/m^3$ (0.4 ppbv) at the 90% confidence level when operated over a 28-day cycle. This method, then, is sensitive to global background levels on the proposed operating cycle and is capable of quantifying monthly average SO_2 concentrations throughout the oil sands region. The uncertainty of monthly-mean measurements of SO_2 with the filter pack is about ±30% at the 90% confidence level, at the concentrations that are expected, based on existing data (Anlauf et al. 1986).

4.1.1.3 Passive. The traditional sulphation cylinder and sulphation (Huey) plate as described in Alberta Environment's Air Monitoring Directive (AMD 86-1) are passive collection devices which have been used near the operating plants in the oil sands region for many years. This method must be considered for use in the proposed aerometric monitoring program. The other passive method mentioned in Section 3.1.1 is the diffusion-controlled SO_2 sampler developed by the Ontario Ministry of the Environment (Orr et al. 1986; CSC 1980).

The sulphation methods are treated in detail in another report (Davis and Hunt 1987). The principal interest for the purposes of this report is the sensitivity of the sulphation devices compared with the SO_2 sampler, and the adequacy of either regarding the expected SO_2 levels in the proposed study region. The following discussion focusses on the quantitation limits of these methods.

An analytical detection limit for sulphate in the filtered extract from the exposed sulphation plate of 2 mg/L is quoted for the automated colourimetric methyl thymol blue method (Alberta Environment AMD 86-1 1986). For a 30-day exposure of 50 cm^2 Huey sulphation plates, this is equivalent to 0.01 mg SO_3/day/100 cm^2. The same value applies to a sulphation candle with an area of 100 cm^2 if the extract volume is twice that of the Huey plate. The equivalent SO_2 concentration (assuming a calibration factor of 0.04 ppm SO_2/mg SO_3/ day/100 cm^2) is 0.4 ppb SO_2.

The precision of the analysis method is dependent on the absolute magnitude of the sulphate concentrations. Sulphate concentrations greater than 10 ppm are required for precision better than 10% (Davis and Hunt 1987). A 10 ppm sulphate concentration corresponds to a sulphation rate of 0.06 mg SO_3/day/100 cm^2 or 4 ppb SO_2.

The limit of quantitation is defined as 10 times the standard deviation of the blank, and the detection limit as 3 times the standard deviation of the blank (American Chemical Society, Committee on Analytical Improvement). For the sulphation method, the quantitation limit would be 10 times the standard deviation for the blank levels in sulphation plates. If the limit of detection for the analytical method alone is 2 mg SO_4/L, the lowest likely value for the limit of quantitation for combined sampling and analysis is of the order of 20 mg/L $SO_4^=$. This corresponds to about 4 ppb SO_2 (assuming a calibration factor of 0.04 ppm/mg SO_3/100 cm^3/day). Given anticipated levels of down to 1 ppb SO_2 at remote sites, the use of the sulphation plates is not feasible for other than relatively high impingement zones.

The Ontario SO_2 sampler is accurate and precise to ±50% at the operational quantitation limit of about 2 $\mu g/m^3$ (0.8 ppbv) for 28-day exposure.

The monthly-mean SO_2 levels are expected to fall in the range of 2.5 to 50 $\mu g/m^3$ (1 to 20 ppbv) in the study area, based on the monitoring results from the Sandalta trailer (Murray 1984; Hansen 1985, 1986) and the CAPMoN site at Cree Lake, Saskatchewan (Wiebe et al. 1985). The Sandalta monthly means (based on continuous monitoring) ranged from 5 to 20 ppbv during 1983 to 1986, and the Cree Lake monthly-mean (filter pack) levels ranged from <0.5 to 1.5 ppbv.

At the quantitation limit of the Ontario passive sampler, the uncertainty of the monthly mean determined by a single device (±50%) should be reduced considerably by exposing multiple devices (say, in triplicate, or at least duplicate) at each site. The annual mean of duplicated monthly-mean values should be precise to within ±25%. This deduction is an educated guess and is not based on analysis of experimental field data (Lusis, pers. comm. 1987). The reported field data (Orr et al. 1986) indicate that the mean sampling rate determined for the Ontario sampler had a relative standard deviation of 31% for mean concentrations greater than 2 $\mu g/m^3$ (0.8 ppbv). This estimate of precision of the mean value is consistent with the estimates given above.

The only passive method for determining SO_2 concentrations, then, that can be recommended for the biophysical sites is the Ontario device (Orr et al. 1986). The sulphation cylinder or plate methods are not sensitive enough to permit quantitation of SO_2 at the concentrations that are expected to be encountered at the low end of the plume impingement gradient or in control areas in the study regions.

It is recommended that the Ontario sampler and the standard sulphate plate (AMD 86-1) be co-located at the fully-powered site or other sites near the high plume impingement zone, so that their performance can be compared.

4.1.2 Particulate Matter - Ions and Trace Elements

The components of interest in airborne particulate matter that were identified in Section 3 are water extractable $SO_4^=$, and acid digestible V and Ni. This is the smallest parameter set that is feasible to quantify the pollutant gradient(s). Extracts and digest liquors are to be archived for future analysis, should other parameters of interest be identified.

4.1.2.1 Vanadium. The analytical sensitivity of V is between 0.001 and 0.01 µg/mL of liquid, depending on the method. Taking the less sensitive of these and assuming that 10 mL of digestion solution is used, the amount necessary to be collected on a filter pack prefilter is 0.1 µg (100 ng). In one month of operation at the recommended sampling rate of 2 L/min (a relatively low rate), about 80 m^3 of air would be sampled. Hence, the lower limit of [V] that could be determined is 100 ng/80 m^3, about 1 ng/m^3. At the greater analytical sensitivity and a sampling rate of 2 L/min, the limiting airborne concentration would be 10 times lower, 0.1 ng/m^3. The concentrations of airborne V expected in the area in this range; that is, vanadium should generally be quantifiable (Barrie 1980).

4.1.2.2 Nickel. The analytical sensitivity for Ni is between 0.01 and 0.03 µg/mL of solution; therefore, by analogy with the above estimation method used for V, the minimum concentration of Ni that could be determined is approximately 1 to 3 ng/m^3.

4.1.2.3 Sulphate. The analytical sensitivity for water-extracted $SO_4^=$ is 0.05 µg/mL of solution. Using similar logic to that applied to V and Ni, the limit of air concentration determination is about 5 ng/m^3. Monthly-mean $SO_4^=$ concentrations are expected to be at least 0.4 µg/m^3 or 400 ng/m^3 (based on Cree Lake results). Given these findings, there would be no difficulty determining particulate $SO_4^=$, even at the low sampling rate suggested (2 L/min).

4.1.3 Precipitation - Rain and Snowmelt

Many of the pollutants, to be monitored in precipitation (Table 3), will not be determinable at most of the biophysical sites because of detection sensitivity and sample instability over the monthly integration times.

Of the anions, $SO_4^=$ is likely to be the only one that will be present in amounts sufficient to quantify at all sites. $SO_4^=$ is also likely to be the only anion sufficiently stable in either wet-only or bulk precipitation samples to produce reliable data.

The soluble cations are all predominantly soil-derived, with the exception of NH_4^+, and so will not yield information about the industrial emissions pollutant gradient. NH_4^+ is sufficiently unstable that its value in monthly samples may be unreliable.

The metals characteristic of industrial emissions will be detected mainly in the insoluble particulate matter in wet-only or bulk precipitation samples and in dry, airborne particulate matter. The elements to be determined, then, will be those discussed in Section 4.1.2, namely, V and Ni, because of their tracer qualities and likely detectability. These elements would be determined in acid digests of filtered particulate material.

4.2 METEOROLOGICAL AND CLIMATOLOGICAL PARAMETERS

A standard, solar panel powered measurement package for remote meteorological/climatological stations is being recommended, so that no difficulties are anticipated, other than those inherent in erecting towers in inaccessible locations. Solar panel/battery-powered meteorological packages are operated at many sites throughout the world, and the technology is well-established, ruggedized, and relatively inexpensive. It is capable of measuring all of the meteorological parameters listed in Table 4, except for the upper air data.

4.3 SAMPLING EQUIPMENT AND POWER SUPPLIES

Three components of the recommended system require electrical power: the meteorological instrument package, the wet-only/dry-only precipitation collector and the filter pack sampler. The latter two merit discussion here; the former is well-established technology.

The standard wet-only collectors that have been used in North American networks are made by Sangamo (CAPMoN) and Aerochem Metrics (APIOS, NADP/NTN). Each of these has been tested in a battery-powered version in Canada without much success (Barrie, Vet, Lusis, Bardwick, Orr, and Stevens, pers. comm. 1986, 1987). The principal cause for failure has been excessive peak power requirements in cold weather operation. Aerochem Metrics have addressed a number of the operational problems, and the advent of long-life lithium batteries has enhanced the feasibility of successful application of this instrument. Aerochem Metrics are producing a 12-V battery-powered version of their collector to Ontario MOE/APIOS specifications that is said to overcome earlier problems (Orr, pers. comm. 1987). The peak power draw of the current version of the Aerochem Metrics collector is 9 W (in the transfer mode: dry-to-wet) and less than 1 W (for the wetness sensor) in the dormant mode.

If the Aerochem Metrics collector were used only for rain collection and not operated during months in which snow or ice melting power was required, the instrument should prove to be reliable in remote operations.

It should be possible to use a channel of the meteorological data logging system to record power supply and system status of all powered equipment, in order to maximize data capture. If the data were transmitted by radio communications, the performance of the system could be monitored regularly and malfunctions identified quickly.

The filter pack system currently being used by Oak Ridge National Laboratory (ORNL) at some remote sites uses a low-powered (2 W), custom-designed Brailsford pump. Another version of this pump has been tested previously by Concord Scientific (CSC 1983) as a candidate for inclusion in a portable, personal monitoring system, so that its performance characteristics have been quantified. At a flow rate of 2 L/min (the recommended flow rate for 28-day sampling) and a pressure drop of 3.7 cm Hg (5 Pa), the continuous power consumption at 12 V was about 1 W. The continuous power demand is well within the capacity of modest solar panel/battery supplies. The supplier to ORNL provides a 30-W solar panel supply for this pump. The power specification should probably be upgraded, to allow for cold and northern solar intensities, to perhaps 100 W. This size of solar panel supply is also feasible in this application with current technology.

Balzer et al. (1987) have recently described an operating system for aerometric monitoring in isolated areas using a 920-W solar panel/ battery system. A 2400-W system is described in Drewes and Legedza (1986).

5. IMPLEMENTATION STRATEGY

Previous sections of this report reviewed the measurement techniques for the aerometric parameters identified by the study team and the workshop as desirable for supporting the long-term biomonitoring of forest stands. Appropriate techniques were selected based on their suitability for use in the oil sands region, bearing in mind the logistical constraints (lack of electrical power, infrequent site visits) and the anticipated low ambient concentrations and hence shallow pollution gradient over the sites. This section describes an implementation strategy for the aerometric program. The section on the overall measurement approach outlines how the measurements should be made and the manner in which the monitoring data should be handled. This section indicates those aspects of the program that may benefit from cooperative efforts with related programs (existing and proposed) conducted in Alberta and elsewhere in North America.

5.1 MEASUREMENT APPROACH

The following aspects are considered in the measurement approach:

1. averaging period;
2. siting - siting criteria, site selection, site specifications;
3. protocols and documentation;
4. data quality assurance and quality control; and
5. data management and reporting.

5.1.1 Averaging Period

The previous sections have provided the rationale for a monitoring program in which monthly averaging of air quality parameters and hourly averaging of meteorological parameters was deemed most suitable. The measurement approach is given in Tables 7 and 8 which summarize the minimum set of parameters to be monitored, the techniques selected, and the time scales of the measurements, for air quality and meteorology, respectively.

The selection of a monthly-averaged sampling period for SO_2 is compatible with the anticipated annual frequency of measurement of most biological parameters. Monthly averaging of the air quality parameters will provide better temporal resolution for the air quality measurements than is necessary for some aspects of the biological measurements. However, the requirement of monthly site visits, for redeployment of air quality samplers, also means higher costs than, say, bi-monthly averaging. The longer averaging period was ruled out in view of the greater likelihood of sample deterioration and the higher risk of low data recovery in the event of sample loss. The availability of monthly averages, however, will allow recovery of seasonally-averaged exposure, if this is desirable for interpretation of the biological observations. Two factors favouring this approach are: (1) the need for resolution at a time scale appropriate to the seasonal distribution of biological activity (particularly physiological activity in leaves); and (2) workshop conclusions respecting the time scale resolution of the interaction between climate and exposure to pollutants.

Table 7. Summary of minimum air quality parameter set to be monitored in the aerometric program.

PARAMETERS	METHOD	TEMPORAL RESOLUTION	COMMENTS
SO_2, TSP[a], $SO_4^=$ V, Ni (up to 18 elements listed in Table 3)	Filter pack	Monthly	At each forest stand (clearing) and at master powered site.
SO_2	MOE passive sampler	Monthly	At each forest stand (clearing) and at master site.
O_3	Continuous	Hourly	Regionally representative master site only.
Dry Deposition[b] Wet Deposition ($SO_4^=$)	Battery-powered. Aerochem Metrics sampler[c]	Monthly	Minimum of summer operation. Winter operation depending on sampler capability.
Snow core	Manual snow core sampler	Monthly	During winter months. Sample integrity to be determined from ambient temperature data.
Precipitation (amount)	Tipping bucket	Event	
Bulk Deposition ($SO_4^=$, up to 18 elements listed in Table 3)	Open bucket	Monthly	Analyses for major ions (except NO_3^- and NH_4^+ and trace metals.

---

[a] Total suspended (airborne) particulate matter.
[b] Dustfall.
[c] Supplemented by ORNL collector on dry side.

Table 8. Summary of minimum meteorological parameter set to be monitored in the aerometric program.

PARAMETERS	METHOD	TEMPORAL RESOLUTION	COMMENTS
Wind (speed and direction)	Anemometer	Hourly	
Temperature	Probes		
Air		Hourly	
Soil		Hourly	
Moisture	Probes		
Air (RH)		Hourly	At each forest stand (clearing).
Soil		Hourly	
Radiation	Pyranometer		
Total		Hourly	At each forest stand (clearing).
Net		Hourly	At regional master site.
Atmospheric Pressure	Barometer		At regional master site.
Upper Air Data	Various	Hourly	Acquire data from nearest upper air station.

The method selected for monitoring SO_2 relies on passive monitors which require monthly visits for retrieving the exposed devices and deploying new ones. In addition, the use of a battery-operated low-volume filter pack sampler for measuring airborne particles (TSP) as well as SO_2, provides desirable redundancy for the SO_2 measurement. The filter pack method will provide samples for the analysis of $SO_4^=$ and the trace metals, as described in Section 4.1.2.

Monthly-averaged (i.e., cumulative) wet and dry deposition sampling using a battery/solar power operated wet and dry sampler is suggested for the collection of rain and dry deposition samples. It is expected that the sampler will not be operable during the colder periods of the year when precipitation is in the form of snow. The rain samples should be analyzed for $SO_4^=$ (high priority) and the major cations (lower priority) as described in Section 4.1.3.

In addition, the collection of monthly bulk samples (i.e., wet plus dry deposition) would be adequate to provide total deposition of heavy metal species and the major ions (Ca^{++}, Na^+, K^+, $SO_4^=$, and probably Cl^-). Only $SO_4^=$ is recommended as essential. The bulk deposition data would require judicious interpretation.

Snow core samples taken monthly during winter, provided there is snow cover, will provide deposition data whose validity should be determined by the temperature history of the snowcore.

Continuous hourly measurements of O_3, SO_2, and H_2S (at a master station), as well as meteorological parameters at each forest stand site are proposed. In the case of the O_3 measurements, it is anticipated that the presence of the oil sands sources would not significantly affect O_3 levels in the region, since O_3 precursor emissions from oil sands plants are expected to be low, and solar actinic radiation is also relatively low. Thus, O_3 measurements taken anywhere within the region of the forest stands would be regionally representative. The location of an O_3 monitor at a convenient site (with AC electrical power) in the study area would therefore suffice. The SO_2 measurements at the master site will provide continuous data for comparison with modelling predictions and to benchmark the two passive collection methods. Standard continuous analyzers for SO_2 and NO_2, each having a quantitation limit of about 10 ppbv (detection limit often quoted as 5 ppbv) would provide a sufficiently complete record of concentrations to validate model predictions in the higher plume impingement regime (short-term means $\geq$10 ppbv). These instruments would not provide a sufficient record to benchmark, routinely, monthly mean concentrations determined by filter pack or passive collectors ($\leq$ 10 ppbv); instruments with a quantitation limit of 1 ppbv would be required for this purpose. H_2S measurements are included at the master site on the presumption that the master site would be an existing station in a network surrounding an existing oil sands plant (see comments in Section 4.1.1 regarding the required instrumentation).

The meteorological parameters listed in Table 7, with the exception of the upper air parameters, are readily measured hourly without significant incremental cost and will provide measurements with a temporal resolution much finer than that of the other aerometric or biological parameters.

5.1.2 Siting

The location of the samplers and ancillary equipment at the forest stand is the most important factor influencing both the scientific validity of the measurements and logistics, and is critical in determining costs.

The choices for locating samplers are above-canopy, within-canopy, or in a nearby clearing. As far as the scientific validity is concerned, the key issue is the collection of a sample that is representative in time and space of the exposure of the forest stand. Above-canopy air samples for SO_2 and TSP taken 1 to 2 m above the mean height of the stand over a 1-month period, should provide representative samples regardless of aerodynamic considerations because of the long sampling period. Other considerations are the fact that tree emissions (of volatile organics and particles) occur in this zone, but it is believed that their presence in the collected sample would not affect the validity of the sample with respect to the parameters of interest.

Above-canopy measurements of wind speed and direction demand that certain aerodynamic requirements be satisfied. Measurement of air temperature, relative humidity, and surface wetness are feasible for above-canopy locations.

In the cases of the air concentration, temperature, and relative humidity measurements, it may be possible to use above-canopy data to estimate concentrations at various heights within the canopy, through the use of dynamic models that are currently under development (Hicks et al. 1986). This may be done in conjunction with detailed field measurements of pollutant-canopy interactions in current research studies, such as those described in Appendix 8.2.

Bulk deposition sampling and precipitation collection for the standard rain gauge and for rain chemistry measurements can in principle be made above-canopy but present difficult logistics for sample collection and deployment. It is also known that precipitation sampler collection efficiency is reduced with increasing height of the samplers above ground (because of wind shear). Above-canopy measurements for bulk deposition and precipitation have, therefore, been ruled out.

For the air concentration and meteorological measurements, the deployment of above-canopy instrumentation is most desirable in principle, but the costs and the logistical aspects in terms of construction and operation are very demanding. The likely range in height of trees in the stand is 12 to 24 m, hence, the tower and platform would have to be 15 to 30 m high. The costs and the logistics of operation (sample retrieval, maintenance) are also demanding. The safety factor in servicing and retrieving samples from an elevated platform under adverse weather conditions has to be considered in the assessment of feasibility of above-canopy measurements.

The collection of deposition and precipitation samples (wet and dry collection, bulk collection, standard rain gauge) in a nearby clearing, which meets the specified siting criteria, is highly desirable for both logistical reasons (sample changing, access) and precipitation sampler collection efficiency. The location of all instrumentation, except for soil moisture and soil temperature, within the clearing is, therefore, the recommended approach. It is recommended that soil temperature and moisture measurements be made within the confines of the canopy at two of the standard depths of 5, 10, 20, 50, 100, 150, and 300 cm, for example, 10 and 50 cm.

A fundamental assumption of this approach (i.e., measurements in clearings) is the expectation that there will be a relationship between the clearing measurements and above-canopy measurements that is at least comparable from site to site. This assumption is independent of details of the pollutant-canopy interaction which determines the relationship between the above-canopy and within-canopy values of the parameters. It should be stressed that the primary purpose of the air concentration measurement is to characterize the concentration gradient over the sites. It is recommended that every effort be made to locate suitable clearings, but it may be difficult to find a clearing within or near each of the forest stands of interest, or impossible to cut one because of forestry regulations.

Within-canopy measurements of air concentration parameters and some meteorological parameters (air temperature, soil moisture and temperature, relative humidity) are feasible for the averaging periods concerned, and will provide representative measures of these parameters at the appropriate sampling location (height or depth). Although there do not appear to be any published data to indicate the intra-stand (as well as the above-stand) variability of monthly deposition samples, it is our opinion that the recommended single measurements (samples) for these parameters will be sufficient, given the financial constraints of the project. If resources permit, one aspect of the study should be to test the hypothesis of a fixed relationship between clearing, above-canopy, and within-canopy measurements by locating multiple samplers at fixed height(s) within the canopy. Such a study would be one component of the campaign studies recommended in the Workshop Document (Appendix 8.2).

5.1.3 Siting Criteria

Siting criteria for the forest stands must address the following aspects:

- permanence of the site for the foreseeable future;
- location along the pollution gradient to allow discrimination of exposures;
- meeting with requirements of the biological measurements, now and in the future; and
- satisfying the requirements for all aerometric instruments.

Since land use in the study area is subject to change as a result of development (through surface mining or related activities), sites must be selected to ensure permanence by being outside areas known to be susceptible to future mining activity. Conversely, if sites are located in areas that are having mining options, formal agreement that would ensure permanence of the site(s) should be sought. It should be noted that natural factors such as forest fires may terminate the existence of sites, but replication of sites is intended in part to accommodate such eventualities.

It must also be emphasized that sites with local, unrepresentative properties must be avoided. For example, sites near, but not necessarily the subject of, mining, forestry, construction (including roads), sulphur stockpiling or waste disposal operations, or near areas that have been recently cleared or burned, can be subject to unrepresentative fugitive emissions of gases or particles.

The second of these criteria is vital for the aerometric and biological measurements. Alberta Environment will select the sites through the concentration estimates provided by the FREDIS model and by site visits. The site visits will ensure that each site has similar topography and forest stand characteristics. However, the location of the sites along the pollution gradient must allow statistically significant discrimination of the concentration measurements between sites to be made.

Based on the estimated precision of the passive measurements for SO_2 (which is the limiting factor, since it has the poorest precision) and on anticipated SO_2 levels (Sections 3.1.1 and 4.1.1), at least three groups of sites are recommended. The stands should be located at sites predicted to have approximately 90, 50, and 25% of the maximum long-term concentration.

Figure 1 shows a hypothetical concentration distribution relating pollutant concentration to distance from a source. A cross-wind distribution could also have been shown. The ratio of concentrations at the maximum and at 25 km has been assumed to be 4:1, based on preliminary predictions of the FREDIS model. The recommended site placements are marked, along with the estimated uncertainty (error bars) in the annual mean SO_2 concentration as determined by passive samplers or filter packs. Error bars are shown for the limit of quantitation of the passive devices, as discussed in Sections 3.1.1 and 4.1.1. These uncertainties are shown as a constant relative error of 25%. In reality, the concentrations near the high end of the distribution would be determined somewhat more precisely, so that the figure represents a conservative estimate of achievable resolution. The figure indicates that the recommended spacing of sites would lead to adequate resolution of the pollutant gradient as long as the high-to-low ratio is greater than 2:1.

A fourth group of sites, the controls, should be implemented in an area or at a distance with as close to zero pollutant exposure as possible. This level might be operationally defined as less than 10% of the predicted (or observed) maximum concentration. This criterion might

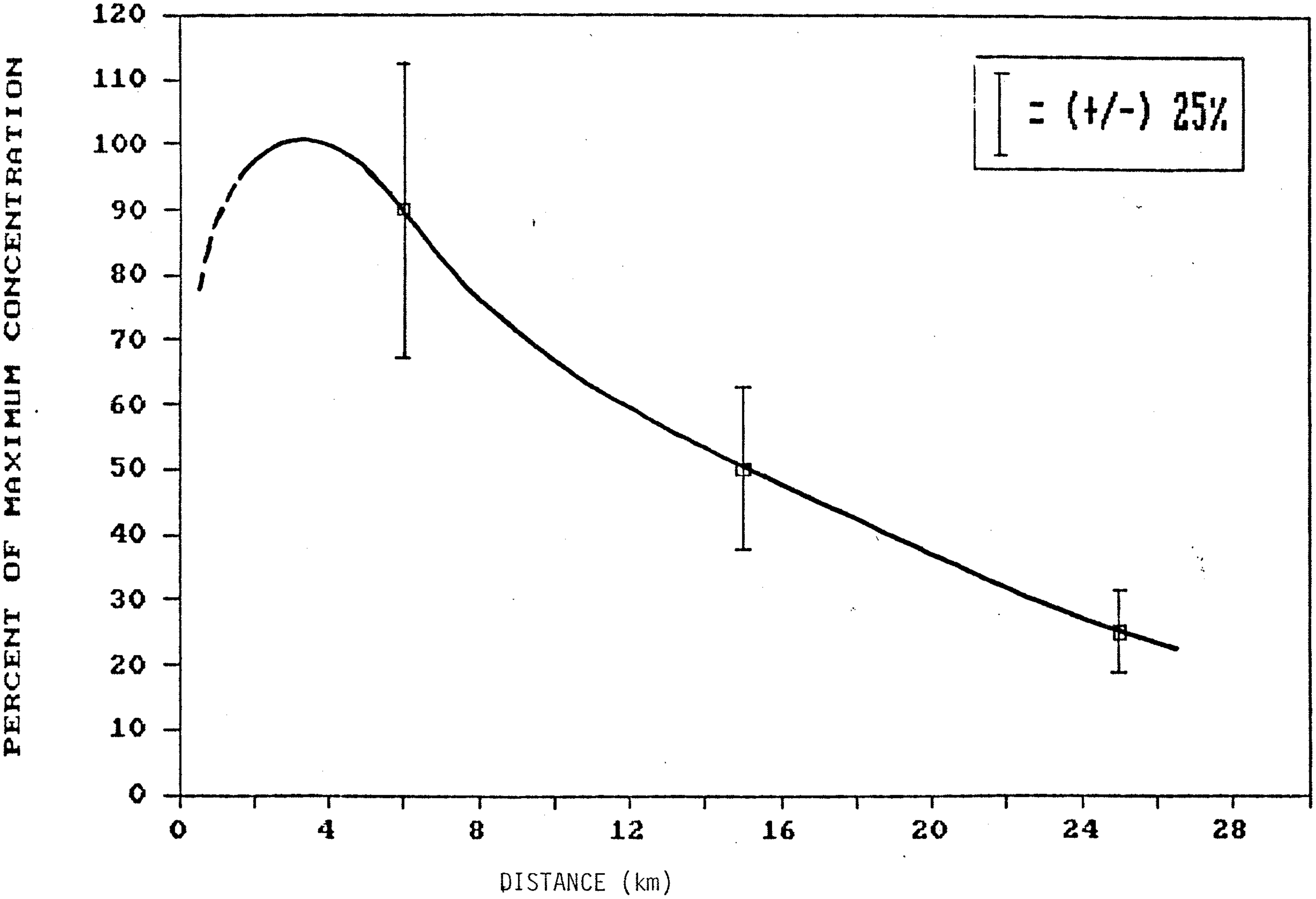

Figure 1. Recommended site locations on a concentration distribution.

require that this group of sites be outside of the 25 km radius area. There may be stands within the 25 km radius area that would meet this zero exposure criterion because of dispersion characteristics of the plumes from the existing plants.

In any case, site selection should take into account the predicted long-term average pollutant concentration field in the region.

Another important aspect of the sites is their distribution among the three exposure levels. The experimental design should optimize the likelihood of resolution of the hypotheses being tested taking into account the number of sites that it is feasible to implement.

Ideally, three stands at each of the four exposures (including the control group) would provide desirable statistics. If only a smaller number of sites is feasible, heavier weighting should be given to the sites with extremes of exposure in order to maximize the detection of effects. It is recommended that at least six sites be implemented - three at each of two exposure zones (high and low). For example, if eight sites are feasible, we recommend that sites with the highest and lowest exposures have three stands each and that the intermediate exposure site have two stands. This example arrangement would complicate (but not invalidate) the statistical analysis because of the unequal weighting.

The additional control sites at the edge of the 25 km radius study area could proceed with observational biomonitoring only (i.e., ARNEWS), assuming zero or background exposure, or with a full or partial aerometric package to demonstrate the actual exposure.

The requirements of the biological measurements are beyond the scope of this report, but the requirements of both programs should be made consistent and compatible from the earliest possible planning stages.

Of importance to the aerometric measurements is the requirement for selecting sites that are likely to have similar microclimates, similar physical and orographic aspects (stands with similar tree heights, species, density of trees and understory coverage, similar elevation, and similar slope aspect).

Siting of the aerometric instruments must ensure representativeness while allowing reasonable logistics. Siting criteria are critical for the wind, precipitation, and deposition instrumentation, as described below. The following site specifications apply to the clearing-based instruments:

1. The clearing should provide unobstructed fetch of at most a 30 to 35 degree elevation angle from the horizontal at the centre of the clearing (about 22 degrees for snow core collection); 10 to 15 degrees is desirable;
2. The ground cover in the clearing should not provide a source of soil-entrained dust; and
3. The site should not be located within 1000 m of roadways with vehicular traffic.

More detailed site specifications are included in the recommended protocols (Appendix 8.4). Details of meteorological siting requirements can be found in Greenland (1986).

Ancillary siting requirements include allowance for precautions to prevent damage to hardware, such as:

1. Waterproof, lockable, metal instrument enclosures bolted onto the tower;
2. Use of armoured cable to minimize vandalism and animal damage;
3. Proper grounding of tower to minimize lightning damage;
4. Use of weatherproof connectors to reduce deterioration rate; and
5. An on-site sign with a contact telephone number, to identify the project.

5.1.4 Protocols and Documentation

The methods selected for measurement of the various aerometric parameters are based on methodologies used in networks in Canada and the US. Since protocols for such measurements exist for the most part, the development of original detailed protocols for the aerometric monitoring program is not necessary, however, existing protocols must be adapted to suit the particular needs of the aerometric program. It is imperative that the adapted protocols be fully documented, compiled, and adopted as the working protocols for the aerometric program. Quality control and quality assurance standards must be specified.

The objective of this section is to provide a list of the protocols and to indicate where modifications are necessary.

Appendix 8.4 contains brief descriptions of each method with a reference to an existing protocol which may be adapted and adopted as the standard operating procedure for the aerometric program.

The following documentation should be provided for the conduct of the aerometric program:

1. Document control
    - Network description (including network objectives)
    - Site selection criteria
    - Site documentation
    - Organizational structure for personnel in the network
2. Quality assurance plan
    - Chain of sample custody
    - Data handling and analysis procedures
    - Field operations
3. Standard operating procedures for each measurement
    - Preventative maintenance requirements
    - Calibration procedures and schedules
    - Instructions for completion of field data sheets
    - Sample transmittal instructions
4. Quality assurance procedures for field operations
    - Technical manual for each instrument
5. Laboratory operations
    - Standard operating procedures for each method

- Quality assurance (QA) and quality control (QC) procedures

Since the overall program is a long-term one, it is inevitable that there will be changes not only in personnel but also in instrumentation, and possibly in protocols and even sites. The maintenance of adequate records of all aspects of the network is essential. A document control system is designed to satisfy this requirement. The document control system such as that described by the US EPA (1984) should be used as the basis for the development of a document control system for this network.

The network description should be formally stated in a brief document describing the background to the establishment of the network and the network objectives. The Alberta Environment (RMD 1986) publication and Section 4 of the Workshop Document may be used as the basis for the document. In the cases of documentation for the site selection criteria, site documentation and the description of the organizational structure and responsibilities for the network, it is recommended that documentation for the aerometric and the biophysical components of the program be combined (Fritschen 1985). Site selection criteria described in the previous section should be combined into the documentation for site selection criteria and amalgamated with the site selection criteria developed for the biophysical measurements. Site documentation must be provided and the format used for the documentation of an APIOS site (Bardswick 1983) should be adopted but extended to include more detail on the following:

- topographical features likely to affect microclimate;
- description of the forest stand; and
- descriptions of the soil characteristics.

It is anticipated that the execution of tasks associated with both the aerometric and biophysical components of the program will be executed by the same personnel, hence it is appropriate that a single document describe the organizational aspects for both components.

The QA and data management aspects are described in more detail in the following sections.

The documentation for field operations summarized in Appendix 8.4 is complete except for items relating to the use of the Ontario passive SO_2 monitor. Documentation for all aspects of the use of these devices will have to be developed. The remaining documentation need only be adapted to reflect the site characteristics and the method of transmission/shipping of samples. This applies to the sample transmission document, the instructions for completion of field data sheets, and QA and QC procedures in the field.

5.1.5 Data Quality Assurance and Quality Control

In order to ensure that the aerometric data collected in the program are of the highest quality, formal QA and QC procedures must be implemented at all stages of the data network operations. The network operations should be based on the adherence to: standard operating procedures as prescribed in a standard operating procedures manual; the conduct of planned field and laboratory audits according to a QA/QC plan; and on prescribed QA procedures for field and laboratory data validation, and assessment operations. The basis for the QA/QC for the network should be a prescribed QA project plan.

5.1.6 Data Management and Reporting

The data will comprise hourly and monthly information and separate record types and structures should be developed for each. In the case of meteorological data, it is recommended that the format used in the Canadian digital archive be adopted. Details of the record structure and format are given in Webb (1986). The hourly O_3, SO_2, and H_2S data should be placed in the same format, but appropriate codes for the designation of the parameter (pollutant) and the designation of units in which data are stored (ppb recommended) should be specified. The data screening and validation, and editing of the raw data are aspects that must not be overlooked. Hourly data from all instruments will be available from a data logger and the following types of screening are required:

- checks for correct station identification, date/time, and parameter codes;
- plausible range for data;
- correct treatment of instrument calibrations;
- examination of outliers; and
- application of the Shewhart test (Box et al. 1978).

The application of these screening procedures will require appropriate checking of field information and the editing, flagging, and/or validation of data.

The monthly data consisting of information on air concentrations for SO_2, TSP, and TSP components ($SO_4^=$ and metals), and precipitation and precipitation components ($SO_4^=$ and metals) also must be stored in a data base. Well-developed data bases for the full range of these data exist only for the APIOS network (OME 1986b), although other networks (CAPMoN) or data bases (ADS, US Acid Deposition System, US EPA 1986) do have adequate data bases and data management procedures for precipitation data. Again, the long-term nature of the project demands that a well designed data base and data management system be implemented.

It must be stressed that such a system must not only include the data values but also appropriate field information for the sample, laboratory information on each component in the sample, and inferred information based on the application of screening methods and the examination of the field and laboratory data. Such a data base, the National Atmospheric Chemistry and Deposition data base (NAtChem), is currently under development for Canadian precipitation and dry deposition data (Vet, pers. comm. 1987) and the system used for that project should be adapted for the monthly aerometric data. NAtChem will adopt the protocols established by the Unified Deposition Database Committee (UDDC) which has set out methods for screening wet deposition data and for the generation of wet deposition statistics. The summary statistics will be similar to those produced in the ADS data summaries for precipitation data. In the case of the air chemistry data, the summaries produced by the APIOS network (OME 1986a) are appropriate and should be considered for use by the Alberta Environment aerometric program. The aerometric program must, therefore, ensure that all appropriate field and laboratory data are entered in the dababase and the network coordinator/data base manager must also include the necessary office comments in the data base.

5.1.7 Data Management Systems

The aerometric data collected in the program will consist of hourly data from the meteorological instruments at each forest stand site, hourly O_3 and SO_2 data from one master site, and monthly-averaged data from each of the forest stands. The volume of data is substantial, and a well-designed data management system must be in place to collect, validate, archive, and report the data, and also to allow for efficient assessment of the data (data analysis).

The data management system must provide the means for the following:

- data capture;
- data validation and screening;
- data editing;
- data reporting; and
- data archiving.

It is useful to place the requirements in the context of the estimated size of the data base. For eight stations, each with hourly measurements of eight meteorological parameters, and one master station with three parameters, there will be 67 parameter-years of data annually. This will generate nearly 600 000 values annually. Assuming that an average of 15 of the 29 desirable parameters associated with the filter pack and passive SO_2 monitoring (Table 7) are measured, the monthly measurements will generate approximately 1440 air quality values (8 stations x 12 months x 15 parameters), and approximately 4800 wet deposition values (8 stations x 12 months x 50 parameters, including flags) each year.

5.2 COORDINATION WITH RELATED PROGRAMS

Both the biological and the aerometric components contain elements that will benefit from cooperative efforts with related programs in Alberta and other areas of North America. Specific areas in which such cooperation may take place, as far as they relate to the aerometric program, are described in this section.

These areas are as follows:

- cooperation with air monitoring networks associated with the oil sands plants;
- cooperation with Canadian Forestry Service (CFS) programs in Albeta and throughout Canada; and

- contact with related agencies conducting similar aerometric programs in association with forest effects studies.

The oil sands plants operate air monitoring networks in the vicinity of their plants, and strong consideration should be given to colocating the master station with one of their stations. In addition, all air monitoring and meteorological data from stations in the area should be requested from the plants and included in the archive. Other areas of cooperation with the plants range from the stated data acquisition and colocation of sites to shared operational aspects (i.e., personnel to retrieve samples, etc.). Specifically, the stations in the region include the following:

- Syncrude: 5 air quality monitoring stations (plus 20 sulphation sites);
- Syncrude: 3 meteorological stations (METNET); and
- Suncor: 5 air quality monitoring stations (plus 20 sulphation sites)

The CFS has been conducting the Acid Rain National Early Warning System (ARNEWS) program throughout Canada, including three sites in Alberta; close collaboration with that program would be of benefit especially to the biological component of the program. Since the ARNEWS program does not include the collection of aerometric data, there will be limited direct impact of ARNEWS on the aerometric program.

Ongoing contact with the following research programs in Canada and the US is strongly recommended:

- Integrated Forest Study (IFS);
- Mountain Cloud Chemistry Program (MCCP)/Chemistry of High Elevation Fog (CHEF);
- Acidic Precipitation in Ontario Study (APIOS); and
- National Forest Response Program (Atmospheric Exposure Cooperatives (US EPA)).

Names and telephone numbers of contacts in these programs may be found in Appendix 8.1.

In view of the long-term nature of the study, it is inevitable that advances in the understanding of the relationships between the stresses on forests and the resulting effects will be made, and may present the need for alternate approaches. Contact with the programs cited above will provide a good source of such information.

6. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are gathered from or are based on the material contained in the report and appendices. An attempt has been made to systematically screen the various options for an aerometric program design, as described in Sections 2 to 5, with the intent of defining a final program. This has been achieved within reasonable limits. There remain choices to be made respecting some components of the monitoring system, and respecting the number of stations to be implemented. These choices depend on a number of factors which cannot be quantified at this time including:

- number and location of acceptable forest stands;
- detailed shape of pollution gradient in the region (as predicted by FREDIS, for example);
- availability of instruments, and instrumentation already installed at, candidate master sites;
- accessibility of sites (significant influence on installation and operating costs);
- feasibility of establishing a clearing for locating monitoring equipment at sites to be selected; and
- number of installations that can be afforded (feedback into statistical design, stand clustering, etc.).

Considering these significant uncertainties, the following conclusions and recommendations relate to the simplest version of each component of the monitoring system that will produce the desired degree of certainty with respect to the pollution gradient to which the forest stands are exposed.

6.1 CONCLUSIONS

The following conclusions can be drawn from the material presented in this report and appendices.

1. An aerometric monitoring network sufficient to support interpretation of biophysical monitoring studies in the Athabasca Oil Sands region is feasible.
2. Monitoring that will adequately characterize the air pollution gradients in the region can be carried out by low-powered DC or passive sampling equipment, or a combination of the two.
3. The total (air) pollution loading need not be measured in order to characterize pollutant exposure of forest stands. The measurement of certain representative gases and constituents of particulate matter and precipitation in conjunction with a regional dispersion model will allow the impact of industrial emissions on accumulation of contaminants in forest vegetation in the region to be determined.
4. Representative or surrogate contaminants that will serve to characterize the pollution concentration field produced by the source emissions from the operating plants are:

- SO_2 (gas);
- $SO_4^=$ (dry particles and precipitation);
- V and Ni (dry particles and precipitation); and
- O_3 (regional).

These substances will characterize the gaseous and particulate stack emissions and the regional or LRTAP contribution to total exposure.

5. Measurement of additional air quality parameters is desirable, since uncertainty in characterization of the concentration (and deposition) field would be reduced; the parameter set listed above is the minimum feasible set. It must be emphasized that this is so only because of the localized nature of the regional (point) sources, their reasonably well characterized emissions, and the existence of a regional dispersion model (FREDIS).
6. The contribution of meteorological and microclimatological variability to the variability of biological response is significant; therefore, detailed monitoring of the following parameters is necessary:
   - wind speed and direction;
   - relative humidity;
   - barometric pressure;
   - air temperature;
   - solar radiation;

- soil temperature; and
- precipitation amount.

7. The monitoring methods identified in this study for the air quality parameters above are sufficiently precise that the pollution gradient(s) over the study region can be resolved, if the annual mean concentration ratio between the highest and lowest impingement zones (biophysical sites) is at least 2:1. This ratio would allow two groups of sites. A ratio of 4:1 would allow three groups of sites. The existing gradient within 25 km of the operating plants (the study area) is the range of 3:1 to 6:1, according to preliminary FREDIS model results.

6.2 RECOMMENDATIONS

The following recommendations are made:

1. Air quality measurements should be made on a monthly-average time scale at each site selected for biophysical monitoring.
2. Meteorological measurements should be made on an hourly-average time scale at each biophysical site.
3. Measurements of both air quality and meteorological parameters should be made in a clearing within or near the forest stand.
4. Each remotely located site should be equipped with the following air quality instrumentation:

- DC-powered CAPMoN filter pack sampler (for SO_2 and TSP);
- Ontario MOE passive SO_2 samplers (at least in duplicate; triplicate preferred);
- Aerochem Metrics wet-only/dry-only precipitation collector (DC-powered);
- Oak Ridge National Laboratory dry-only deposition collector (DC power supplied by Aerochem Metrics supply); and
- AOSERP or APIOS bulk precipitation/deposition collector.

5. Each remotely located site should be equipped with the following instrumentation:
    - wind speed/direction sensors;
    - temperature/relative humidity probe;
    - tipping bucket/Nipher gauge;
    - silicon pyranometer;
    - soil temperature/moisture probes; and
    - data storage system.
6. A master site with access to AC power (probably an existing industrial air monitoring or meteorological station) should be equipped with each of the items in the previous two recommendations, augmented by:
    - continuous O_3 analyzer (UV chemiluminescence or UV absorption) which meets standard NAPS/US EPA specifications (quantitation limit, 1 ppb);

- continuous SO_2 analyzer (enhanced flame photometric detector) with a quantitation limit of 1 ppb (highly desirable, but not essential); and
- standard Alberta AMD 86-1 sulphation (PbO_2) cylinder or plates and sulphide (zinc acetate) strips (in duplicate or triplicate).

7. All instrumentation, methods, and protocols should be based on those already developed and available for established networks or studies. The equipment recommended above meets this criterion.
8. Implementation of the network should be phased, concentrating on establishing a small number of sites in the first year, say, two sites at the extremes of concentration expected in the study area. During the first year, operational details and protocols would be developed and the feasibility of proposed methods and parameters could be evaluated.
9. During the evaluation phase, an augmented set of chemical elements should be analyzed in dry particles and precipitation filtrate to verify the utility of the selection of V and Ni as tracers of industrial emissions. The additional elements would be selected based on Table 5.

10. Samples of soils near the air quality sites should be collected for chemical analysis, so that the influence of soil-derived dust on filter pack TSP and precipitation can be assessed.
11. If financial limitations make it necessary, consideration should be given to the following program reductions, in order of priority:
    - eliminate the AC-powered master site;
    - reduce the number of aerometric monitoring sites (but not the number of biophysical sites); and
    - delete the DC-powered components at the remote sites (i.e., completely passive monitoring).
12. The minimum number of aerometric sites should be six, three at each of two impingement zones (high and low). The number of biophysical sites could be larger if the additional sites are near a site with aerometric monitoring and there are no significant differences in site characteristics.
13. An additional research priority should be to obtain good quality emission data for the existing plants. In particular, characterization of particulate emissions would allow receptor modelling/source apportionment calculations on the filter pack TSP catches (using chemical mass balance methods, for example).

14. Perhaps most important, care should be taken at the early stages of planning the aerometric network to integrate planning for the biophysical studies to follow, including aquatic and soils studies that may be relatively far in the future.

7. REFERENCES

Anlauf, K., H.A. Wiebe, and P. Fellin. 1986. Characterization of several integrative sampling methods for nitric acid, sulphur dioxide, and atmospheric particles. JAPCA 36(6):715-723.

Balzer, W., J. Ettl, K. Reiniger, G. Heinrich, and H. Gusten. 1987. An automatic station for measuring air pollutants in remote areas. Atmospheric Environment 21(1):179-183.

Bardswick, W.S. 1983. APIOS Technical and Operating Manual, APIOS Deposition Monitoring Program. Acidic Precipitation in Ontario Study, Ministry of the Environment. Toronto, Ontario.

Barrie, L.A. 1980. The fate of particulate emissions from an isolated plant in the oil sands area of western Canada. Annals of the New York Academy of Science 338(1980):434-452.

Bondietti, E.A., D.W. Johnson, and S.E. Lindberg. 1985. Project summary, integrated forest study on effects of atmospheric deposition. Prep. for Electric Power Research Institute by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 35 pp. (Available from NTIS, Report No. DE85-015972).

Cadoff, B.C. and J. Hodgeson. 1983. Passive sampler for ambient levels of nitrogen dioxide. Anal. Chem. 55:2083-2085.

Colls, J. 1986. Measurement of nitrogen dioxide profiles by diffusion tubes within a barley canopy. Atmospheric Environment 20(1):239-242.

Concord Scientific Corporation. 1980. Evaluation of modified long-term passive SO_2 ambient air monitors. Report to Ontario Ministry of the Environment. Report No. CSC 99.2-79. 57 pp.

Concord Scientific Corporation. 1983. A report on the development of a personal sampler for SO_2, NO_x, and particulate matter. Report to Health and Welfare Canada. Project No. 957, CSC J224.01. 24 pp.

Concord Scientific Corporation. 1984. A study of metallic emissions from the main stack at Syncrude's Mildred Lake Plant. Syncrude Canada Ltd. Environmental Research Monograph 1984-2.

Dabbs, D.L., ed. 1985. Atmospheric emissions monitoring and vegetation effects in the Athabasca Oil Sands region. Prep. for Syncrude Canada Limited by Dabbs Environmental Services with contributions from Western Research, Concord Scientific Corporation, Hardy Associates (1978) Limited, and CASE Biomanagement. Syncrude Environmental Research Monograph 1985-5. Edmonton, Alberta. 127 pp.

Davis, C.S. and J.E. Hunt. 1987. Evaluation of alternative methods for measuring dry deposition and recommendations for establishing a regional scale dry deposition monitoring network in Alberta. Prepared for Alberta Environment by Concord Scientific Corporation.

Davis, C.S. and R.G. Wright. 1985. Sulfur dioxide deposition velocity by a concentration gradient measurement system. J. Geophys. Res. 90(D1):2091-2095.

Drewes, P. and S. Legedza. 1986. Final status report for the Atikokan Photovoltaic Power Supply. Ontario Hydro Report No. 86200. 12 pp.

Fritschen, L.J. 1985. Characterization of boundary conditions affecting forest environmental phenomena. From the Forest Atmosphere Interaction edited by B.A. Hutchison and R.B. Hicks. D. Reidel Publishing Company. pp. 3-23.

Greenland, D. 1986. Standardized meteorological measurements for long-term ecological research sites. Long-Term Ecological Research Coordinating Committee (LTERCC).

Hansen, M.C. 1985. Summary of air quality observed at the Sandalta Site, April 1984 to March 1985. Prep. for Alberta Environment by Western Research Division of Bow Valley Resource Services Ltd. 60 pp.

Hansen, M.C. 1986. Summary of air quality observed at the Sandalta Site, April 1985 to March 1986. Prepared for Alberta Environment by Western Research Division of Bow Valley Resource Services Ltd. 61 pp.

Hicks, B.B., R.P. Hosker, and J.D. Womack. 1986. Description and Operating Details of the NOAA/ATDD Dry Deposition Inferential Measurement System (DDIMS), National Oceanic and Atmospheric Administration, Atmospheric Turbulence and Diffusion Division. Oak Ridge, TN.

Lindberg, S.E. and G.M. Lovett. 1985. Field measurements of particle dry deposition rates to foliage and inert surfaces in a forest canopy. Environmental Science and Technology 19(3):238.

Murray, W.A. 1984. Background air quality Sandalta trailer, May 1983 to March 1984. Prepared for Alberta Environment by Promet Environmental Group Ltd. 74 pp.

Olson, R.K. 1987. Western Conifers Research Cooperative: 1987 Research Plan. US EPA Environmental Research Laboratory - Corvallis. 80 pp.

OME. 1986a. Annual statistics of concentration and deposition - Daily precipitation and air monitoring network, 1984. Ontario Ministry of the Environment, Air Resources Branch. Toronto.

OME. 1986 b. Data file format description 1984, cumulative/daily ambient air monitoring network. Ontario Ministry of the Environment, Air Resources Branch. Toronto.

Orr, D.B., J.C. Hipfner, W.C. Chan, M.A. Lusis, and J.E. Hunt. 1986. The application of a passive permeation device for the measurement of ambient sulfur dioxide. Accepted for publication in Atmospheric Environment.

Research Management Division. 1986. An acid deposition research program for Alberta Environment 1986/87 to 1990/91. Research Management Division, Alberta Environment. 164 pp.

Swift, L.W. and H.L. Roysdale. 1985. Meteorological data stations at long-term ecological research sites. From the Forest Atmosphere Interaction edited by B.A. Hutchison and R.B. Hicks. D. Reidel Publishing Company. pp. 25-37.

US EPA. 1984. Quality assurance handbook for air pollution measurement systems, Volume I - Principles. United States Environmental Protection Agency, Report EPA-600/9-76-005.

US EPA. 1986. Acid precipitation in North America: 1984 Annual data summary from acid deposition system data base. United States Environmental Protection Agency, Report EPA-600/4-86/003.

Webb. M. 1986. Documentation for the digital archive of Canadian climatological data (surface) identified by element. Atmospheric Environment Service, Canadian Climate Centre, Downsview. 15 pp.

Wiebe, H.A., R.J. Vet, L.A. Barrie and K. Anlauf. 1985. Canadian air and precipitation monitoring network (APN) final data report, December 1982-1983. Atmospheric Environment Service, Downsview. October. 51 pp.

8. APPENDICES

8.1 CONTACT LETTER/LIST OF CONTACTS

November 5, 1986

CSC File: J999

Dear :

RE: Alberta Environment's Proposed Long-Term Monitoring Program for Studies of Effects of Acidic Deposition on Forest Ecosystems in the Oil Sands Region

As discussed by telephone, Concord Scientific Corporation is under contract to the Research Management Division (RMD) of Alberta Environment to design an aerometric program to support studies of cumulative effects of acid-forming and other emissions from oil sands processing plants on terrestrial and aquatic ecosystems.

Concord Scientific is canvassing a number of key researchers and program managers who are known to be associated with monitoring programs in conjunction with recent or on-going studies of the effects of acidic deposition and related phenomena on the long-term viability of forest (or other) ecosystems. The RMD program is intended to address ecosystems generally in the oil sands region of Alberta, but the initial priority is the boreal forest within about 25 km of the two operating oil sands processing plants.

The Terms of Reference for Concord's work are expressed as follows by Alberta Environment:

> "The Contractor will review current and relevant literature on major acid deposition effects research programs and initiate discussions with the principal researchers involved in those programs to determine the ambient air quality, deposition, and climate monitoring requirements pertinent to terrestrial and aquatic effects research. The review will address, for example, the following major points:
>
> (1) atmospheric pollutants and deposition and climate parameters of importance;
>
> (2) equipment required (especially for monitoring low-level emissions at remote sites);
>
> (3) sampling design (number of sampling points, vertical and horizontal distribution of sampling points, sampling frequency, sampling period);

(4) siting criteria;

(5) quality control/quality assurance protocols; and

(6) utilization of models"

The objective of the aerometric program is to quantify and characterize total pollutant loading, deposition, and climate for terrestrial and aquatic receptor sites in the oil sands area. Initially, the monitoring program would run on a 5 to 25 year time-scale. Eventually, it is hoped that the program would extend beyond 25 years (so that changes in soil characteristics, in particular, might be tracked with respect to deposition).

The biophysical and aquatics effects research programs that will accompany the aerometric program will be designed to address the question of whether there are measurable short- or long-term environmental effects due to acidification. The composition of the boreal forest in the region (between approximately 56° and 58°N and 110° and 113°W) is varied, but the initial emphasis will be on pine, spruce, or aspen dominated forested stands in characterized gradients of plume impingement.

The initial stages of the program are being approached as a feasibility study to determine whether a generic aerometric program in conjunction with certain biophysical (or biochemical) observations can be expected to reveal subtle long-term changes, considering the present state-of-the-art in pollution measurement and the variability of the biological systems.

Of critical interest is whether an aerometric program can be mounted at a small number (5 or 6) of remote sites (without normal electrical power), which will provide adequate support to the interpretation of the biological observations.

With this background, we have prepared the attached checklist of points which we propose to discuss with you by telephone. We would ask you to respond only to those that are particularly relevant to your program and for no more than an hour interview. Any written response would, of course, be welcomed. Written material (including reports and other publications), may be sent to us by courier collect (Purolator preferred) at our Toronto office, quoting our reference number, J999. For your information, the Project Officer for RMD is:

Ms. Bonnie Magill
Alberta Environment
Research Management Division
14th floor, Standard Life Centre
10405 Jasper Avenue
Edmonton, Alberta
Canada T5J 2N4
(403) 422-2071

Thank you for agreeing to participate in the study. Dr. Claude Davis, Ms. Donna Stevens, or I from our Toronto office or Mr. Mervyn Davies from our Calgary office will be in touch with you in the near future to arrange a convenient telephone or personal interview time.

Very truly yours,

CONCORD SCIENTIFIC CORPORATION

ROBERT B. CATON, Ph.D.
Vice President and Director
Environmental & Occupational Contaminants

RBC/tmc

CONCORD SCIENTIFIC CORPORATION/ALBERTA ENVIRONMENT
AEROMETRIC PROGRAM FOR EFFECTS STUDIES OF ACIDIC DEPOSITION IN THE BOREAL FOREST

CHECKLIST OF DISCUSSION POINTS FOR CONTACTS

1. Objectives of the respondent's program.
2. Type of forest vegetation for study and reasons.
3. Chemical, biological, and biochemical parameters being monitored (in air, vegetation, soil, water).
4. Measurement techniques (chemical concentrations and wet/dry deposition; meteorology).
5. Siting criteria for vegetation plots and chemical/ meteorological measurements
6. Means of addressing inter- and intra-site variability of biological, chemical, and meteorological parameters.
7. Use of dispersion or deposition models in siting or data interpretation.
8. Temporal resolution (averaging or response times) of aerometric and biological measurements.
9. Specific features relevant to an effects-based aerometric program in the boreal forest in northeastern Alberta.

List of Contacts

Dr. Paul Addison (ARNEWS/CHEF)
Canadian Forestry Service
Research and Technical Services Directorate
351 St. Joseph Blvd.
Hull, Quebec K1A 1Z8
(819) 997-3350

Dr. Len Barrie (AOSERP/CAPMoN/APN)
Atmospheric Environment Service
4905 Dufferin St.
Downsview, Ontario M3H 5T4
(416) 667-4785

Dr. Steve M. Bromberg
U.S. Environmental Protection Agency, MD-75
Research Triangle Park, NC 27711
(919) 541-2919

Dr. Tom Brydges
Atmospheric Environment Service
LRTAP Liaison Office
4905 Dufferin St.
Downsview, Ontario M3H 5T4
(416) 667-4885

Dr. Ellis Cowling
School of Forest Resources
North Carolina State University
Raleigh, NC
27695-8001
(919) 737-2883 or 737-3520

Dr. Jack Durham
Chief, Air Characterization and
    Special Projects Group, MD-57
National Forest Response Program
    Atmospheric Exposure Cooperatives
US Environmental Protection Agency
Research Triangle Park, NC 27711
(919) 541-2183

Mr. Floyd Elder
Environment Canada
National Water Research Insitute
P.O. Box 5050
Burlington, Ontario L7R 4A6
(416) 336-4969

Dr. Bruce Hicks
NOAA/ATDD
P.O. Box E
Oak Ridge, TN 37831
(615) 576-1233

Dr. Allan Legge (AGI/ADRP)
Kananaskis Center for Environmental Research
The University of Calgary
Calgary, Alberta T2N 1N4
(403) 220-5271

Dr. Steve E. Lindberg (IFS)
Environmental Sciences Division
Oak Ridge National Laboratory
Bldg. 1505
P.O. Box X
Oak Ridge, TN 37831

Dr. Sam Linzon (APIOS-Terrestrial)
Ministry of the Environment
Air Resources Branch
880 Bay Street, 3rd Floor
Toronto, Ontario M5S 1Z8
(416) 965-4526

Dr. Maris Lusis (APRIOS-Atmospheric)
Ontario Ministry of the Environment
Air Resources Branch
880 Bay Street, 4th Floor
Toronto, Ontario M5S 1Z8
(416) 965-1634

Dr. Volker Mohnen (MCCP)
Atmospheric Sciences Research Center
State University of New York
100 Fuller Road
Albany, NY 12205
(518) 422-3819

Dr. Richard Olson
Director, Western Conifers Research Cooperative
200 S.W. 35th Street
Corvallis, OR 97333
(503) 757-4696

Dr. Louis F. Pitelka (IFS)
Electric Power Research Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94303
(415) 855-2969

Dr. Allen Torrenueva
Ontario Hydro
Environmental Studies and Assessments Dept.
700 University Avenue
Toronto, Ontario M5G 1X6
(416) 592-6314

Mr. Robert J. Vet (CAPMoN/APN/NAtChem)
Atmospheric Environment Service
4905 Dufferin St.
Downsview, Ontario M3H 5T4
(416) 667-4801

8.2 WORKSHOP DOCUMENT

DISCUSSION DOCUMENT -
WORKSHOP ON

AN AEROMETRIC PROGRAM FOR EFFECTS STUDIES IN THE OIL SANDS REGION

(CSC J999.11)

Prepared for

ALBERTA ENVIRONMENT

by

CONCORD SCIENTIFIC CORPORATION

in conjunction with

DOMINION ECOLOGICAL CONSULTING LTD.
YARRANTON HOLDINGS LTD.
AQUATIC RESOURCE MANAGEMENT LTD.

December 1986

(Revised February 1987)

TABLE OF CONTENTS

1. INTRODUCTION

1.1 BACKGROUND

Based on the results of the Alberta Oil Sands Environmental Research Program (AOSERP), other Alberta-based studies, and on the world literature, Alberta Environment has recognized that research upon which to establish regulatory approaches to planned industrial development in the oil sands region will have to be carried out for an extended period beyond the initial 10-year mandate of AOSERP. Alberta Environment undertook a technical review of atmospheric and terrestrial effects research related to acid-forming emissions in the oil sands area and has reached conclusions respecting objectives for such an extended program (RMD 1986).

Studies to date have demonstrated few measurable biological effects from emissions in the oil sands region, due to the relatively low level of emissions (compared with levels at which observable effects occur) and the inherent ecosystem variability. These factors imply that effects research in the forest ecosystem of the oil sands region must be carried out over a time period of 5 to 25 years in order to permit valid inferences of potential chronic, cumulative impacts.

A category called atmospheric and source studies has been defined within the proposed research program to achieve the models and data necessary to interpret with confidence the potential for emissions from current and future oil sands development on forest ecosystems. One of the research needs in the atmospheric/source studies category is determination of deposition, specifically, quantification of pollutant loading at selected receptor sites.

To address this research need, Alberta Environment initiated a study entitled "Design and Development of an Air Quality, Deposition and Climate Monitoring Program in Support of Terrestrial and Aquatic Effects Research". This workshop is a component of that study, which is being carried out by Concord Scientific Corporation, in conjunction with Dominion Ecological Consulting Ltd., Yarranton Holdings Ltd., and Aquatic Resource Management Ltd.

1.2 STUDY TERMS OF REFERENCE

The study team is, initially, to review the literature on the subject of aerometric monitoring in conjunction with studies of effects of atmospheric deposition of aerosols and precipitation containing acidic (or acidifying) and phytotoxic substances, including metallic substances. In parallel with the literature review, the team is interviewing key researchers and program managers in the field of ecosystem effects studies, concentrating initially on forest (terrestrial) studies, but not ignoring that soils and aquatic receptors are encompassed within the ecosystem approach. The letter and a checklist of discussion points that have been sent to each contact are shown in Appendix 8.1.

Based on this review and the experience of the team members, the major objective of the project is to specify design, protocols, and equipment that would comprise a generic aerometric program sufficient to support as broad a range as feasible of terrestrial and aquatic effects studies that may be implemented.

Since it was apparent that a number of effects study strategies would have to be considered, this workshop was programmed to review a number of possible approaches and recommendations from the study team, with the intention of reaching a consensus on an approach. The consensus approach would then be extended to equipment and protocols.

The workshop is to address both the feasibility of such a generic aerometric program and its design, should feasibility be agreed upon. Feasibility is to be based upon scientific defensibility and adequacy to the requirements of effects studies, in combination with the affordability of the simplest defensible configuration.

The conclusions of the workshop will be incorporated in the team's final report.

1.3 SCOPE OF WORK

The team's priority has been to provide substantiation for a number of approaches that would address various scenarios of effects studies programs, aiming toward a viable aerometric approach. The scope of work has been focussed, in recognition of the time and resources available to the team, on key papers, programs, and researchers, principally in North America and principally since 1980, to maximize the collection of directly applicable information and ideas. The primary objective is to achieve timely design of a practical program that will work for northern Alberta over an extended monitoring period. One of the first principles of monitoring network operation and quality assurance, especially when extended life is anticipated, has been applied deliberately - keep it simple.

2. WORKSHOP OBJECTIVES

The objectives to be achieved at this workshop are twofold:

- To assess the feasibility of carrying out any program to demonstrate environmental impact of atmospheric deposition in the oil sands region; and
- To recommend a course of action for proceeding with the development of a design, pending resolution of the first objective.

2.1 FEASIBILITY OF THE OVERALL PROGRAM

The following sections of this document present:

- Preliminary outline of issues to be addressed;
- Highlights of key points from the literature and program reviews;
- A summary of the study team's approach to the project work program;
- A number of aerometric program design options;
- The study team's recommendations; and
- A bibliography.

The assessment of feasibility will be based on the above information plus the knowledge and experience of the participants and reviewers. The questions to be addressed can be summarized as:

- Can any parameter (or suite of parameters) be monitored to relate atmospheric deposition to uptake by the forest ecosystem on a regional scale in the oil sands area?

- Can the stress factors which may lead to strain in the ecosystem (pollutants, climate, etc.) be identified now, to be incorporated into the monitoring program design?
- Can a scientifically defensible monitoring program be established that will operate effectively in remote areas of the oil sands?

2.2 HOW TO PROCEED

Assuming that one or more of the proposed approaches is determined to be feasible (or can be modified to be), the workshop will address the logistics of proceeding with the development of specifications for the monitoring program and, therefore, of completing the study team's require- ment. In this session, the workshop will address the implications of the requirements of specific (potential) terrestrial and aquatic effects studies for the design of the generic program. The objective is to maximize coverage of effects programs by the simplest, feasible, generic aerometric program. What types of studies can (cannot) be accommodated? The answers to this question may require revisiting the question of feasibility.

2.3 ISSUES TO BE ADDRESSED

The proposed aerometric program is to address as many as possible of the foreseeable approaches to the study of accumulation of pollutants and their effects in terrestrial and aquatic biota, and soils in the oil sands region. In order to anticipate these approaches successfully, it will be necessary to consider a number of fundamental issues. Some of these are outlined below.

2.3.1 Time Resolution of Aerometry Related to Response Time of Effects

The objective of an aerometry program for pollutants is to determine the pollutant dose in a time regime that is appropriate for evaluating the dose-response characteristic of an effect. The dose is not necessarily the simple product of concentration (c) and time (t), as it is often represented, but is a function of concentration, time, and ancillary variables representing modifiers of uptake. That is,

$$D = f(c,\ t,\ x_i),$$

where x_i may represent, for example, probability of leaves being wet when an SO_2 fumigation occurs, or resistance to deposition or uptake at a leaf surface, and so on. The x_i may be functions of D.

If all pollutant concentrations and climatological variables are measured continuously, the appropriate time regimes may be obtained by averaging or integrating routines. The essential meteorological variables can be measured in real time, so that the appropriate averages can generally be calculated.

Existing monitoring methods, however, do not permit continuous measurement of some potentially important gaseous or of any particulate pollutants. Precipitation chemistry cannot be determined continuously, as yet.

Therefore, one must ask what time scale is (a) essential, (b) desirable, or (c) acceptable for each measured variable with respect to the anticipated ecological response. This question is particularly important within the constraints of the oil sands study, because the sites for effects studies will be remote and perhaps without power. Generator power may be both too expensive and polluting. Passive devices have both limited availability for the pollutants of interest and limited time resolution (principally because of sensitivity limitations).

In developing the aerometric program design options (Section 4) and recommendations (Section 5), the study team developed a number of scenarios based on the most likely sets of time response constraints that will be placed on the aerometric data.

2.3.2 Scope of Aerometry

If canopy-pollutant interactions are to be studied, the questions arise whether pollutant concentrations and meteorological variables need to be monitored at several locations vertically and horizontally in an effects study site. Some assumptions about the form of the effects program are necessary to conclude this issue. Several assumptions have been incorporated in the scenarios described in Section 4.

2.3.3 Ancillary Research Needs

The workshop should devote some time to considering atmospheric program research needs that will not be part of an ongoing aerometry monitoring program, but which will likely be essential to an effects research program. Two such examples are climatic measurements for dispersion modelling and the determination of the respective emission source particulate matter chemical signatures for source apportionment analysis of particle catches at receptor sites. The measurement made on the Syncrude stack (CSC 1984) may be sufficient for that source, but comparable data are not available for the Suncor source.

Air quality simulation models and ambient air quality monitoring are two essential interactive components in an air quality management system. The models use mathematical algorithms to simulate transport, dispersion, and transformation processes in the atmosphere. Models are useful in interpolating and extrapolating monitoring results in space and time. For example, models can be used with historical emissions to estimate cumulative loading to date which will be of importance in the evaluation of effects which may have a delayed response time. Similarly, the models can be used with projected emissions to estimate future loadings based on various development scenarios.

The continuing interaction between monitoring and modelling can increase our understanding of important atmospheric processes. Before the models can be used with confidence, it is important to ensure that the input parameters are both reliable and representative. Generally, two types of data are required to drive these models: source and regional climate.

Source Parameters. Source parameters refer to the characteristics defining the emission point and require:

- Identification of all sources of importance in the region which include controlled (stacks) or uncontrolled (fugitive) emissions;
- Release characteristics of each source: point or area, surface or elevated. For point sources, the diameter, exit temperature and velocity will define the rise of the plume. Pollutant release rates are required for all sources; and
- Temporal Variations: All sources can vary with time; they can be continuous or discontinuous, vary on a diurnal or seasonal basis, and may be related to process or meteorology influences.

It is desirable to obtain relevant source data on a near real-time basis rather than go back through plant records to try and recover the appropriate data at the end of the monitoring program.

Regional Climate. The regional climate will determine the behaviour of the plumes after they leave the stack. Key parameters of concern include:

- Wind speed and direction at plume height;
- Lateral and vertical plume spreads; and
- Mixing layer height.

All these parameters can change significantly with space and time, increasing the complexity of collecting a representative database. In many cases, direct observations will not be available and, as a consequence, these parameters will have to be estimated through the use of sub-models.

Wind speed and direction will generally increase with height due to decreased frictional effects. Wind flow will be steered by topographical influence. During stable conditions, the wind within a valley can be completely decoupled from the regional airflow above the valley.

Lateral and vertical plume spreads will have to be estimated from our current understanding of turbulence in the planetary boundary layer. Turbulence can be generated by either thermal or mechanical means. The following will be required to characterize turbulence under convective conditions:

- Surface heat flux;
- Convective velocity scale; and
- Convective mixing layer height.

Under stable conditions where wind-shear-generated turbulence is important, the following are required:

- Friction velocity;
- Surface roughness; and
- Monin-Obukov length.

Under stable conditions, the mixing height will be typically a few hundred metres. Under convective conditions, the mixing height can be up to 2000 m.

2.3.4 Climate Issues

Climatological phenomena can have an impact on aquatic and terrestrial ecosystems. The design of an aerometric program must recognize the importance of climate to allow any data which are collected to be used to the fullest possible extent. Climate can impact either directly or indirectly on these systems and can be related to natural mechanisms as well as to industrial emissions. The following discussion addresses these interactions with the primary focus on terrestrial systems.

Natural mechanisms are defined as those interactions which do not involve the presence of man in general, and industrial emissions in particular. Examples of direct effects of climate-induced stress on forest systems commonly recognized are:

- Drought and flooding;
- Temperature extremes and frost;
- Winter dessication; and
- Mechanical injury (by high winds, snow and ice loading and lightning).

Indirect effects can be less obvious and involve the interaction of climate with other stress factors such as:

- Forest fires;
- Insect pests;
- Diseases; and
- Competitive plant growth.

These direct and indirect effects have always been present and will continue to be present, although some may be reduced through active forest management practices.

With the presence of industry, the interaction of gaseous and particulate emissions with climate can also affect terrestrial systems through the following mechanisms:

- Regional meteorology controlling transport, dispersion, and transformation processes of atmospheric emissions from industry; and
- Microscale meteorology affecting the transfer and removal of airborne emissions from the atmosphere and the airflow in the forest canopy.

Secondary mechanisms involving climate and atmospheric emission interactions include:

- Extreme climate conditions, which can stress the receptor, increasing its sensitivity to injury from air pollutant loadings; and
- Air pollutant loading (as well as other stresses), which can increase the receptor sensitivity to injury from climate extremes.

The complexity of these latter interactions will be difficult to resolve in a field study, but they are important to keep in mind when designing the aerometric and terrestrial components of the program.

Finally, any monitoring program which requires the placement of hardware and the collection of data in the field can require climate data to assess system performance or aid in the data interpretation. Temperature extremes can be used to assess the effectiveness of equipment enclosures. Temperature and pressure measurements can be used to convert actual air sampling flow rates to standard conditions.

3. AEROMETRIC PROGRAMS FOR EFFECTS STUDIES

3.1 LITERATURE AND PROGRAM REVIEW

3.1.1 AOSERP and AG/IADRP

Alberta Environment has been involved in two major integrated environmental effects programs: the Alberta Oil Sands Environmental Research Program (AOSERP) and the Alberta Government/Industry Acid Deposition Research Program (AG/IADRP). The former program has been underway since 1975 in the Athabasca oil sands area and the latter program started in 1983 in southern Alberta.

AOSERP. The Alberta Oil Sands Environmental Research Program (AOSERP) was initiated in 1975 to study environmental effects which could result from the operation of major oil sands developments in the Athabasca Oil Sands region. The program was funded and managed jointly by the Alberta and Federal Governments. In 1980, AOSERP was absorbed by the Research Management Division of Alberta Environment.

The research efforts were focussed on air, land, water, and human systems. Since the beginning of the program the following number of reports have been produced (Pringle 1986):

- AOSERP wide distribution reports (1975 to 1985): 131 reports;
- RMD wide distribution reports (1980 to date): 33 reports;
- Limited distribution reports (1977 to date): 88 reports;
- open file reports (1979 to date): 83 reports; and
- Research Secretariat reports (1975 to 1980): 65 reports.

In all, Research Management Division (RMD) and its affiliations have produced 400 technical and administration reports focussing on environmentally related issues in Alberta.

The initial portion of the AOSERP program (1975 to 1980) focussed on the collection of baseline information which would be used to quantify and characterize existing environmental conditions. Smith (1981) reviewed the research and monitoring activities undertaken during this period and made the following recommendations, as presented in RMD (1986):

1. To characterize and quantify regional and local emission sources to ascertain their relative contribution to environmental acidification;
2. To integrate episodic air quality data with receptor response in order to:
   a. Characterize sensitive environmental ecosystems; and
   b. Develop methodologies to identify and predict short- and long-term effects of acidic or acidifying substances on terrestrial and aquatic ecosystems;
3. To develop a scientific basis and approach to strategies for long-term protection and management; and
4. To coordinate departmental research on acid deposition with other private and public agencies in Alberta and the rest of Western Canada.

During the 1980 to 1985 period, the program concentrated on addressing these recommendations. Considerable effort was focussed on developing a more complete understanding of atmosphere-biosphere interfaces. In 1985, Research Management Division assumed the responsibility for continuing acid deposition related research in the oil sands area (Research Management Division 1986).

Air system research projects undertaken can be categorized as:

- Climatology/meteorology analyses;
- Air quality monitoring program;
- Plume dispersion observations;
- Plume chemistry evaluations;
- Deposition monitoring (wet and snowpack); and
- Modelling projects.

A total of 44 reports which focus on air system research in the AOSERP area have been generated (Research Management Division 1986). In Section 3.2.2 of this document the air quality and climate database as described in some of these reports is presented.

AG/IADRP. The Alberta Government/Industry Acid Deposition Research Program (AG/IADRP) evolved from the work undertaken by the Steering Committee on Acid Gases in the Environment (SCAGE) formed in 1979 by the Alberta Petroleum Industry Government Environmental Committee (APIGEC). In 1981, SCAGE submitted a report recommending a coordinated, interdisciplinary, holistic research plan to assess the impact of acid deposition in Alberta. In 1983, an agreement was signed by the Alberta

Government, the Canadian Petroleum Association (CPA), the Independent Petroleum Association of Canada (IPAC), NOVA An Alberta Corporation, PetroCanada, and Alberta's three main electrical utility companies. This agreement committed $8 million to a seven-year research program (AG/IADRP 1984).

In early 1985, work on the first component of the biophysical research plan commenced. The first phase of the biophysical program is concerned with (AG/IADRP 1985):

- Inventory of sulphur oxide and nitrogen oxide emissions in Alberta;
- Air quality assessments at a background site (Fortress Mountain), and at upwind and downwind sites in the vicinity of point source (Amoco Crossfield gas plant);
- A literature review of the effects of acid deposition on vegetation, soils, surface waters, and ground waters with reference to Alberta conditions; and
- A first-order assessment of the potential impact of acid depositions on the environment in Alberta.

The AG/IADRP program has identified the following compounds to be monitored (Findlay and Primus 1986):

- sulphur compounds: SO_2, H_2S, COS, CS_2;
- nitrogen compounds: NO, NO_2, NO_x, NH_3, HNO_2, HNO_3;
- oxidants: O_3;
- CO_2;

- hydrocarbons;
- coarse and fine particulate;
- stable isotopes, and
- wet deposition (rain).

No literature is available which identifies the details of this air quality monitoring. Presumably concurrent climate conditions are also being monitored. However, no details are available on the specific parameters which are being measured and the methodologies adopted.

3.1.2 Oil Sands Air Quality Database

This section focusses on the identification of air quality data available for the Athabasca oil sands region. Relevant air quality data of potential interest include:

- source and emission parameters;
- continuous ambient air quality observations;
- static sulphation and H_2S observations; and
- snowpack and precipitation chemistry observations.

The object of the following review is not to present a detailed evaluation of these databases but to identify the existence and the source of the databases and to highlight some of the findings. This will provide a background of ambient air quality in the study region.

3.1.2.1 Source and Emission Parameters. The Syncrude Canada Ltd. and the Suncor Inc. oil sands and upgrading facilities are the largest industrial facilities in the study region and are responsible for nearly all the atmospheric emissions in the area. The three primary point sources associated with these plants are the following:

- Syncrude main stack;
- Suncor powerhouse stack; and
- Suncor incinerator stack.

Syncrude and Suncor are required to monitor selected stack parameters such as SO_2 emissions, flue gas exit temperatures, and total flow rates on a continuous basis. In addition, routine manual stack surveys are required to validate the continuous monitoring. All these data can be made available from the Pollution Control Division by the Minister of Environment.

Table 1 lists selected parameters and historical SO_2 and NO_2 emissions associated with the three primary stacks. The Suncor stacks are located within the Athabasca River valley, whereas the base of the Syncrude stack (located above the river valley) is 50 m above the base of the Suncor stacks. Values for stack exit temperatures and velocities have been reported in Walmsley and Bagg (1977) and Dabbs (1985). The SO_2 and NO_2 emissions presented in the table were obtained from Alberta Environment summary documents (Sandhu 1979; Pollution Control Division 1982, 1984). More recent data have not as yet been summarized by Alberta Environment. Dabbs (1985) indicated average annual SO_2 emission rates of 265, 190 and 30 t/d for the Syncrude main, the Suncor powerhouse, and the Suncor incinerator stacks, respectively. Concord

Table 1. Parameters and SO_2 emissions for the three main stacks.

	SYNCRUDE	SUNCOR	
	Main	Powerhouse	Incinerator
Height (m)	183	107	107
Diameter (m)	7.9	5.8	1.2
Temperature (°C)	220	270	540
Velocity (m/s)	24.0	17.0	17.0
SO_2 Emission			
Licensed (t/d)[a]	292	304.8	48.8
Actual 1974 (t/d)[a]	N/O	213.4	37.0
1975	N/O	213.4	24.6
1976	N/O	221.4	25.0
1977	N/O	200.2	20.6
1978	70.0	205.2	16.8
1979	18.8	206.8	20.4
1980	141	231.0	26.8
1981	189	166.0	19.2
NO_2 Emission			
Actual 1976 (t/d)[a]	N/O	N/A	
1977	N/O	43.8	
1978	N/A	15.1	23.6
1979	31.5	12.3	
1980	7.7	14.8	
1981	13.4	12.3	
1982	13.2	11.5	

[a] Values based on 365 days.

Scientific Corporation (1984) conducted a detailed stack sampling program to determine selected metallic element emissions associated with the operation of the Syncrude main stack. The results of this program are summarized in Section 3.2. The total particulate mass emission was found to be 3020 kg/d. Iron was the most abundant metal emission (27 kg/d) and beryllium was the least abundant (0.0005 kg/d).

The above discussions exclude emissions from secondary stacks and from fugitive sources. Secondary stacks service various heater functions required by each plant (e.g., diluent recovery units, steam heaters, hydrotreaters, and H_2 plants). Emissions from these secondary stacks are not routinely monitored and emissions are usually determined from industry-standard emission factors or from manufacturer specification data (if available). Fugitive emissions are those emissions that originate from area sources (or numerous point sources) and are usually unplanned for. Examples include vehicular emissions, wind blown dusts, tailings pond emissions, piping and valve leaks, and storage tank and building vents. These emissions are difficult to quantify and are important in determining air quality in the immediate vicinity of the facilities.

3.1.2.2 Continuous ambient air quality. Continuous air quality data have been collected and summarized by various sources. Table 2 summarizes the continuous monitoring stations which have been in operation in the study region. The Syncrude and the Suncor monitoring

Table 2. Continuous ambient air quality stations in the AOSERP study area.

Station		Period	Parameters
Syncrude	#1	1977 to date	SO_2, H_2S
	#2	1977 to date	SO_2, H_2S
	#3 (Mildred Lake)	1976 to date	SO_2, H_2S
	#4	1977 to date	SO_2, H_2S
	#5	1977 to date	SO_2, H_2S
Suncor Supertest		1976 to date	SO_2, H_2S
	Mannix	1976 to date	SO_2, H_2S
	Ruth Lake	1976 to date	SO_2, H_2S
	Lower Camp	1977 to date	SO_2, H_2S
	Fina	1976 to date	SO_2, H_2S
Alberta Environment			
AOSERP	Birch Mountain	1977 to 1980	SO_2, O_3
	Bitumount Tower	1977 to 1980	SO_2, NO_2, O_3, CO, HC
Research Management Division			
	Sandalta	1983 to 1984	SO_2, NO_2, O_3
Pollution Control Division			
	Fort McMurray	1977 to date	SO_2, NO_2, O_3, CO, HC
	Fort McKay	1981 to 1986	SO_2, H_2S, NO_2

stations are required in the respective Licenses to Operate issued under the Clean Air Act. Alberta Environment has been involved with the collection of data through AOSERP (Birch Mountain and Bitumount Tower), Research Management Division (Sandalta), and Pollution Control Division (Fort McKay and Fort McMurray).

<u>SO_2 Observations</u>. Table 3 summarizes the number of hourly-average SO_2 concentrations observed at the Syncrude and the Suncor stations in 1982 and 1983 which exceeded the Alberta Environment maximum permissible level of 0.17 ppm. In 1982 and 1983, a total of 71 and 143 exceedances were reported, respectively. At the Syncrude #5 station, five hourly concentration values in excess of 0.34 ppm were observed (Dabbs, 1985). Data on values in excess of 0.34 ppm were not available for the Suncor stations.

Strosher (1978, 1981) summarizes air quality in the study area from the Syncrude, Suncor, and AOSERP stations. Table 4 summarizes the number of half-hourly average SO_2 concentrations observed at these stations for the years 1977, 1978, and 1979 which exceeded the Alberta Environment maximum permissible level of 0.20 ppm which was in effect. A total of 27, 90, and 74 exceedances were observed for the years 1977, 1978, and 1979 respectively. The maximum observed concentration for this period was 0.58 ppm as a half-hourly average at Lower Camp in May 1978 (Strosher and Peters 1980).

Table 3. Number of hourly average SO_2 observations in excess of 0.17 ppm.

Station		1982	1983
Syncrude	#1	6	4
	#2	5	3
	#3 (Mildred Lake)	6	19
	#4	11	4
	#5	1	49
Suncor	Supertest	4	9
	Mannix	14	22
	Ruth Lake	2	4
	Lower Camp	6	3
	Fina	16	26
	Total	71	143
	Average/Station	7	14

Source: Dabbs (1985).

Table 4. Number of half-hourly average SO_2 observations in excess of 0.20 ppm.

Station		1977	1978	1979
Syncrude	#1	0	3	3
	#2	0	1	0
	#3 (Mildred Lake)	4	21	1
	#4	1	1	0
	#5	0	6	0
Suncor	Supertest	0	7	6
	Mannix	5	9	15
	Ruth Lake	0	0	9
	Lower Camp	0	8	15
	Fina	17	32	21
AOSERP	Birch Mountain	0	0	0
	Bitumount Tower	0	0	4
	Fort McMurray	0	2	0
	Total	27	90	74
	Average/Station	2	6	5

Source: Strosher (1981).

The Sandalta station observations have been summarized in a series of reports submitted to Gulf Canada Resources (Morrow and Murray 1982) and the Research Management Division (Murray 1984; Hansen 1985, 1986). Three SO_2 exceedances were observed at this station (two in 1981 and one in 1986). Two exceedances were reported at the Fort McKay station in 1984 during the 9-1/2 month monitoring period (Pollution Control Division 1984).

NO_2 Observations. Four of the monitoring stations listed in Table 2 recorded ambient NO_2 concentrations. Table 5 summarizes the maximum hourly average NO_2 concentration observed at each station for each monitoring year. The maximum observed values were less than the Alberta Environment maximum permissible concentration of 0.21 ppm as a 1-hour average.

O_3 Observations. Four of the monitoring stations listed in Table 2 also recorded O_3 concentrations. Table 6 summarizes the maximum hourly average of O_3 concentration observed at each station for each monitoring year. The maximum values in some cases exceed the Alberta Environment maximum permissible concentration of 80 ppb as a 1-hour average. Subsequent analysis of the Birch Mountain and the Bitumount Tower O_3 data indicated average annual concentrations of 37 and 28 ppb respectively (Angle and Sandhu 1986).

3.1.2.3 Static sulphation observations. Total sulphation is measured in the area by Syncrude and Suncor using a network of PbO_2 exposure cylinders or plates. The sulphation network is used as a relatively low-

Table 5. Maximum observed NO_2 concentrations (ppm) observed as a 1-hour average.

Station	1977	1978	1979
Bitumount Tower	0.11	0.06	0.03
Fort McMurray	0.15	0.06	0.14

Source: Strosher (1981).

Station	1981	1983	1984	1985
Sandalta	>0.11	0.02	0.05	0.02

Source: Morrow and Murray (1982); Murray (1984); Hansen (1985, 1986).

Station	1984
Fort McKay	0.04

Source: Pollution Control Division (1984).

Table 6. Maximum observed O_3 concentrations (ppb) observed as a 1-hour average.

Station	1977	1978	1979
Birch Mountain	120	80	75
Bitumount Tower	130	75	75
Fort McMurray	65	80	80

Source: Strosher (1981).

Station	1981	1983	1984	1985
Sandalta	>40	130	80	80

Source: Morrow and Murray (1982); Murray (1984); Hansen (1985, 1986).

cost means to delineate temporal and spatial trends of ambient sulphur compounds. Strosher (1978) found that the summer of 1976 sulphation pattern produced a north-south pattern which was attributed primarily to the presence of the Athabasca River valley and secondarily to the limited east-west spread of the network.

Attempts have been made to relate the sulphation measurements to the dry deposition of sulphur compounds to the vegetation canopy (Dabbs 1985). The analysis of the sulphation network indicates relatively high values in the immediate vicinity of the plants (Dabbs 1985). Low-level fugitive emissions of sulphur compounds were stated as the cause of these high values.

3.1.2.4 Snowpack and precipitation chemistry. The Research Management Division (and AOSERP) have collected rainfall samples and performed subsequent chemical analysis in the study area since 1976 (Olson et al. 1982). The network consisted of 11 to 17 stations, depending on the year, and rainfall event samples were limited to the months of May to September. No data were collected for the years 1983, 1985, and 1986. Concern has been expressed over the quality of the precipitation data in general, especially the earlier years (Davis et al. 1985). The 1984 annual sulphate concentrations in rain samples indicate a peak of 1.2 $mg \bullet L^{-1}$ at Muskeg Mountain and general west-east orientation of the contours. The large scatter in the data and the lack of consistent patterns for other chemical species suggest caution in using the results of the rainfall chemistry program (Davis et al. 1985).

Snow surveys were conducted in the study area for the years 1976, 1978, 1981, 1983, and 1984 (Fanaki 1978; Barrie and Kovalick 1980; and Murray 1981). The annual sulphate concentrations in snow samples indicate a north- south pattern for the years 1976 and 1978. For 1981, the pattern has a northeast-southwest orientation. The maximum observed sulphate concentrations were typically 0.5 $mg \bullet L^{-1}$ of snowmelt.

3.1.3 Oil Sands Climate Data Base

Climate parameters have been monitored in the Athabasca oil sands region by a number of different groups with differing end uses for the data. These groups include air pollution interests (Research Management Division, AOSERP, Syncrude, and Suncor), forest management interests (Alberta Forestry Service), and air transportation interests (Atmospheric Environment Service). The climate data, summarized in Table 7, have not been collected on a continuous basis by all sources.

The Alberta Forestry sites collect daily precipitation and temperature values only during summer months. The Research Management Division MAPS network, tall tower, minisonde releases, and Sandalta trailer have been discontinued. The Atmospheric Environment, Syncrude, and Suncor programs are ongoing.

Longley and Janz (1978) conducted an initial overview of the climate in the study area. This was updated by Rudolph et al. (1984) to

Table 7. Climate data sources.

GROUP	LOCATION (Number)	PARAMETERS[a]
Atmospheric Environment Service	Fort McMurray Airport (1)	U, θ, T, P, RH, Ob, Q
AOSERP/Research	MAPS Network (9)	U, θ, T, P
	Tall Tower (1)	U, θ, T, ΔT, ΔU, $\Delta\theta$
	Minisonde Releases (ca2300)	U, θ, T, ΔT, ΔU, $\Delta\theta$
Research Management	Sandalta (1)	U, θ, T, P, RH, W, S
Alberta Forestry Services		Forestry Lookout (28)
T, P		
Syncrude	Air Quality Trailers (5)	U, θ
	Doppler Wind Sensor (1)	U, θ, ΔU, $\Delta\theta$
	METNET (3)	U, θ, W, T, P, Q
Suncor	Air Quality Trailers (5)	U, θ
	Doppler Wind Sensor (1)	U, θ, ΔU, $\Delta\theta$

[a] Symbols:
U = wind speed
θ = wind direction
ΔT = temperature
P = pressure
ΔT = temperature variation with height
Q = precipitation
RH = relative humidity
W = vertical wind speed
ΔU = wind speed variations with height
$\Delta\theta$ = wind direction variations with height
Ob = observational data

establish temporal and spatial trends from the more recently collected climate data. The following comments on temperature, precipitation, and wind in the area arise primarily from this latter document.

Temperature. The maximum mean annual temperature of 3°C was observed at Mildred Lake. An analysis of the Forestry stations showed that the high elevation stations were about 2°C cooler than the low elevation ones in July. An analysis of the MAPS data show maximum interstation mean daily temperature differences of 6.1, 4.2, 4.6, and 2.0°C for January, April, July, and October, respectively. The average frost-free period ranged from 56 to 156 days, depending on the station location. It is not clear if these differences are due to differing record lengths, local microclimate, or poor quality control.

Precipitation. July precipitation ranged from 60 to 115 mm and is clearly related to station elevation (the largest amounts recorded at the highest elevations). Stations at the highest elevations also recorded precipitation events with the longest durations.

Snowpack accumulation was related to latitude with lower values occurring in the northern parts of the study area. Stations in the valley generally recorded lower values than higher elevation ones. The Birch Mountain station (the highest elevation station) had the lowest snow cover which was attributed to an east-facing slope location. This is in contrast to the Stony Mountain station (with the second highest elevation and located on a west-facing slope) which had the greatest snowcover.

Wind. Spring and autumn, the transition seasons, were the windiest times of the year. Winter has the lowest wind speeds. Mean wind speeds tend to increase with increasing elevation. Wind directions at most stations are affected by terrain features. Those stations located near the Athabasca River valley clearly show the effect of the north-south orientation of the valley. The prevailing winds at Birch Mountain are westerly in the summer and northwesterly in the winter.

3.1.4 Other Studies and Programs

Work outside of Alberta on the effects of acid deposition on forest ecosystems has concentrated on those areas that have shown symptoms of decline or dieback (West Germany, northeastern and southeastern US - Appalachian region), or in areas where impact of long-range transported acidic aerosols is suspected, but has not yet produced demonstratable visible effects (Scandinavia, eastern Canada, British Columbia). Ulrich, one of the most active West German researchers, has summarized the scientific basis for assessing forest ecosystem effects of air pollution in a 1984 paper. An extended quotation from Ulrich (1984) serves as a succinct introduction:

> "The action of a stress factor on a system results in a strain. This strain may be elastic (reversible) or plastic (irreversible). Plastic strain means that the system has permanently changed some of its properties.
>
> Plastic strain can result in invisible (latent) or in visible changes. Visible plastic strain is usually called injury.

This concept helps in realizing possible interactions of various stress factors. If the action of any stress factor results in a plastic strain, this may alter the reaction of the system on the influence of a second stress factor: the range of elastic strain may become smaller, plastic strain may begin at a lower threshold. Table 8 gives an overview about stress and strain in forest ecosystems. The strain is related to ecosystem processes, the physiological reactions of the organisms behind are not considered.

The climate is the driving force for the ecosystem. Its variability causes stress. The variability in the heat climate and in the humidity climate can cause root damages. It is well known that in plants with damaged root systems the elastic strain to almost all stress factors is reduced - such plants are more easily subjected to plastic strain. One should assume that forest ecosystems are well adapted to the stress caused by the mechanical components of the climate (wind, snow cover, ice). If forest damages by wind throw and crown breaking due to snow cover play an increasing role, as it is the case in many areas, this indicates that the elastic strain for these influences has been reduced. The problem is to which other stress factors this decrease in elastic strain can be traced back.

The chemical climate has been drastically changed by air pollution.

. . . From the concept of stress and strain it follows that we would need to know the whole stress situation in order to evaluate the effect of a special stress factor. This knowledge is not available, since we do not know all air pollutants of importance and we do not know the invisible strain which air pollutants and other stress factors are causing in the ecosystem as a whole and in individual organisms. We must expect that the action of many stress factors on a low level of intensity at the same time (e.g., acidity and heavy metals) can limit the elastic strain for any other stress factor so that plastic strain occurs. It is to be expected that the visible plastic strain (injury) follows after a period of invisible plastic strain. If during this period the toxins are accumulating in the ecosystem or in organisms, the visible plastic strain (damage) may occur too late for any recovery. This is partly the case for the forest damages now breaking out in Central Europe.

The present knowledge in this field is very limited. It will probably take more than 20 years of intensive research to arrive at sufficient knowledge about deposition and storage rates of all interesting air pollutants and about their invisible and visible plastic strain in different ecosystems and organisms.

> It would be good to have this knowledge before making decisions. As the situation is, man has to make decisions about air pollution without an unquestionable scientific base. The decisions should then rest on a risk evaluation."

A review by McLaughlin (1985) and responses to it by Prinz et al. (1985), especially Cowling (in Prinz et al. 1985), in the APCA Critical Reviews Program, addresses the current state of knowledge and highlights some of the causes of the difficulty that has been experienced in Alberta, and elsewhere, in developing evidence of cause and effect between atmospheric deposition and forest ecosystem modification, both in the presence and absence of visible injury. As Ulrich points out in the above quotation, the potential strain on forest ecosystems by air pollution requires study, since the accumulation or interaction of stress factors which has led to the present forest dieback in the northern hemisphere is unexplained and may be due, in part, to chronic, low-level or episodic, sub-threshold (for visible injury) chemical exposures.

Most of the reported studies and programs have not taken place in areas subject to strong, or least easily characterizable, pollutant gradients. Their sites are generally located in hilly terrain, at elevation (Torrenueva 1985, and private communication, 1986; McLaughlin 1985; Lindberg et al. 1984), so that gradients are not easily modelled and must be determined by detailed measurements. With the exception of wet deposition, such detailed measurements have not been made, generally. Thus, it is difficult to relate much of the existing information from outside Alberta to the oil sands situation in which emissions from isolated, point sources are impinging on a relatively

Table 8. Stress and strain in forest ecosystems - An overview.

Stress	Causal Relationship	Plastic Strain
Climate		
Heat Climate		
warm	acidification push	root strain
cool	deacidification phase	recovery
Humidity climate		
wet	O_2 deficiency in soil	root damage
dry	water deficiency in soil	root damage
Mechanical climate		
no wind		
storm, snow ice	mechanical stress to roots and canopies	
Chemical Climate		
normal	low nutrient input	
close to sea coast	NaCl salt damage	crown deformance
air pollution	manyfold	leaf injury
	soil	acidification
		bark (cambium) injury
		crown deformance
		root damage
		damage to decomposers: destabilization
Consumers		
Pests		
viruses		diseases
bacteria		
fungi		wood rot
insects		feeding damages
Man		
biomass utilization	diminishing nutrient stocks	complex: destabilization
	changing microlimate	
	diminishing feeding source for decomposers	
Natural falling out of elements of the ecosystem		
death of individuals	e.g. change in microclimate	none in stable ecosystems
deterioration of structural units		

Source: Ulrich (1984).

pristine environment (i.e., one not otherwise impacted by industrial or urban development). Other Canadian studies (British Columbia, Manitoba, Ontario, Quebec) have focussed on major point sources, which currently emit (or, historically, have emitted) a very much larger flux of acidic sulphur gases than the operating oil sands plants. These studies have documented gross visible injury, or recovery from that condition resulting from exposure reductions (dispersion or emission controls). These studies, therefore, have not been considered vital to this review, although, of course, their results offer relevant insights.

Although admitting the importance of dry deposition to total pollutant exposure in forest canopies and ecosystems, very few studies or programs have addressed this issue and fewer still have conducted extended monitoring. The lack of dry deposition measurements (or measurements of the quantities needed to parameterize and calculate dry deposition) is identified by North American researchers (both in the literature and through interviews) as a serious shortcoming of work to date. Only the Oak Ridge National Laboratory/National Oceanic and Atmospheric Administration (ORNL/NOAA) groups (e.g., Bondietti et al. 1985), the Kananaskis group (e.g., Legge 1982), the Ontario Ministry of the Environment (MOE 1985) and the US Environmental Protection Agency (EPA) (e.g., Mohnen 1984) were identified as having made serious attempts to incorporate dry deposition in long-term monitoring programs in support of effects studies (see also NAPAP 1986).

The Western LRTAP Committee (1986) and Alberta Environment (Sandhu 1986) have identified the relatively greater importance of dry deposition, compared with wet deposition, of acidic substances and metals in Alberta. This fact implies that an Alberta program in the oil sands should include such measurements.

Thus, the study group was led to focus on those studies and programs that attempted to carry out integrated monitoring of total loading (concentrations or deposition fluxes) - wet and dry. This focus influenced the priority of contacts (Appendix 8.1) and the collection of literature. The principal relevant studies and programs so identified were:

- Whitecourt Environmental Study Group (West Whitecourt Case Study);
- Acidic Precipitation in Ontario Study (APIOS);
- Canadian Forestry Service (CFS) Calibrated Watershed Studies;
- ORNL/Electric Power Research Institute (EPRI) Integrated Forest Study; and
- US EPA/Environment Canada Mountain Cloud Chemistry Program/Chemistry of High Elevation Fog Program.

Other studies that may provide important input of more limited applicability to the problem at hand are:

- Syncrude Biomonitoring Program (Dabbs 1985);
- US Western Conifers Research Cooperative Studies (Olson 1986); and

- US National Parks Service Wilderness Studies (Fox 1986).

These programs comprise a spectrum of study types from detailed nutrient-cycling/mass balances for entire watersheds to specific source impact monitoring.

The researchers involved in these programs have selected for study ecosystems or specific target receptors for a variety of reasons, and with respect to a variety of criteria. The published Whitecourt studies (Legge et al. 1981, 1982, 1986a,b), for example, were focussed on the impact of sulphur, primarily from a single gas plant, on the pine forest of the boreal plain. EPRI's Integrated Forest Study (Bondietti et al. 1985; Johnson et al. 1986) comprises nine widely separated sites representing many different forest types and climates, across North America including one site in Canada (Turkey Lakes watershed, north-central Ontario).

The principal findings or features of these key programs that contribute to the deliberations of this workshop are summarized below:

West Whitecourt Case Study. The physiology, nutrition, biochemistry, and productivity of lodgepole x Jack pine hybrid trees, and their soils, were studied in stands located along a marked sulphur-gas (monitored as SO_2) gradient with respect to a sour gas sulphur-recovery plant. The first phase of the study covered 1972 to 1976 (Legge et al. 1981, 1982, 1986a), and a follow-up phase covered 1977 to 1985 (Legge and Bogner 1986b). Peak SO_2 concentrations during the two-year (1975 to 1976) intensive measurement program at a single site 1.5 km from the source were greater than 1 ppm (typically < 0.05 ppm). The SO_2 gradient with respect to distance to the vegetation sampling sites was not measured directly. Those sites were at 1.4 to 5.6 km downwind from the source. Wet deposition and particulate matter loadings were not measured, but detailed microclimatology measurements were made.

A major interest in this study is the use of $^{34}S/^{32}S$ ratios in emissions, vegetation, and soils and the use of foliar total S, inorganic S, and organic (or assimilated) S to characterize exposure and ecosystem (trees and soil) modifications due to SO_2. Details of the follow-up work are not yet available, the final report having recently been received by the CPA.

Acidic Precipitation in Ontario Study (APIOS). The variety of research and monitoring studies being carried out in APIOS are summarized in MOE (1985). Of most relevance to the workshop are the deposition monitoring networks in the atmospheric processes program and all of the components of the terrestrial effects studies program. Specifically of interest are:

- deposition monitoring networks (cumulative and daily);
- aquatic effects/limnology studies (calibrated watersheds);
- lichen and moss study;
- soil baseline studies; and
- biogeochemical studies (element cycling).

Interviews with Dr. Maris Lusis (atmospheric) and Mr. Bill Gizyn (biogeochemical) produced the following points of interest.

The objectives of APIOS are similar to those of the Alberta program, in that both are concerned with subtle long-term effects of acidic and metallic deposition. The focus of APIOS, however, is on LRTAP processes, so that the sites are all located away from major point sources. The pollutant loading gradient is with respect to distance away from distant sources (mainly in the US), so that the gradient is relatively flat and monitoring sites are located hundreds of km apart.

The APIOS biogeochemical vegetation studies are sited at four watersheds receiving 30 to 35 kg/ha/y wet $SO_4^=$ (two sites), 20 kg/ha/y and 10 kg/ha/y. Most of the oil sands region would be at the low end of this gradient. The two sites in this group with the highest loadings (Plastic Lake and Harp Lake) are the most intensely studied and are also part of the Calibrated Watershed Study. These sites are within 20 km of the MOE Dorset Research Centre, where intensive continuous and cumulative monitoring is carried out.

The measurements at Plastic and Harp Lakes were carried out as a three-year campaign, intended as a snapshot in time. During this period (1982 to 1985), measurements were made in a variety of forest stands dominated by one or more of the following:

Plastic Lake - white pine/hemlock/red maple/oak

Harp Lake - sugar maple/red maple/beech/yellow birch/poplar.

The measurements comprised:

- throughfall (event);
- stemflow (event);

- soil water;
- groundwater;
- forest stand inventories;
- biomass (complete trees);
- soil profiles;
- forest soil surveys;
- litterfall; and
- litter decomposition.

These were supplemented by wet-only cumulative deposition measurements and by cumulative filter pack sampling for SO_2, NO_x (including HNO_3), and particulate $SO_4^=$ and NO_3^- from the Dorset site. The latter site also provides daily precipitation and acidic gas chemistry, as well as oxidants.

The parameters analyzed in the biogeochemical event precipitation samples are:

- volume, pH, Gran acidity, $SO_4^=$, NO_3^-, Cl^-, Ca^{++}, Mg^{++}, K^+, Na^+, NH_4^+, $PO_4^{\equiv}$, Fe, Mn, Al, Zn (latter in filtered samples).

This list is similar to those from other programs that will be described, and the implications of these lists for the selection of pollutants of interest are discussed in Section 3.2. The rationale for selecting the four metals in the above list is that they are the only ones that can be routinely detected in event samples - a point that should be kept in mind.

Orr et al. (1986) have described an experimental passive sampler for SO_2 that is being deployed at selected APIOS sites. Its results agree very well with the filter pack method. There may be an as yet unquantified H_2S interference with this device, but otherwise it is considered by MOE to be validated.

The APIOS-BGC precipitation sampling scheme is of interest. In the first year, about 25 samplers were deployed per watershed, the upper limit allowed by logistical and budget constraints, consistent with QA/QC specifications (MOE 1986). The second year used a replicated scheme, and the third year established a revised plot-oriented scheme based on observations (experience) of unique areas and stands within the forests. A sampling site grid system was set out with random sampler redistribution on the grid between precipitation events, at six plots per watershed.

This procedure was designed to reveal the variability of the quantities and chemistry of the types of precipitation related to canopy effects (throughfall and stemflow) over the three-year snapshot period, seen as a single point in time.

This cycle of experiments is planned to be repeated on a five to ten year schedule. The basic APIOS-C and APIOS-D atmospheric chemistry and deposition networks are planned to continue on their present schedules (MOE 1985).

Canadian Forestry Service Calibrated Watershed and Acid Rain National Early Warning System (ARNEWS). The CFS calibrated watershed ecosystem studies are taking place at Kejimkujik NP, N.S., Acadia Forest, N.B., Montmorency, P.Q., Turkey Lakes, Ont., and in association with the Experimental Lakes Area studies in Ontario. Objectives and parameters monitored are described in Glantz et al. (1986) and LRTAP Liaison Office (1986). The Turkey Lakes site is included in the ORNL/EPRI Integrated Forest Study and will be discussed in that context.

ARNEWS is a long-term observational study of stand characteristics and does not include instrumental monitoring (other than climate parameters).

Integrated Forest Study (IFS) on Effects of Atmospheric Deposition. This study, which is now beginning operation (1985 to 1988), is funded by EPRI and directed by ORNL. Table 9 (from Bondietti et al. 1985) shows the study objectives. The following hypotheses are being tested regarding atmospheric deposition and its effects on elemental cycling processes in forest ecosystems with varying degrees of S, N, and H^+ saturation (critical objective I, Table 9):

Hypothesis I: Dry deposition is a significant component of total atmospheric input of both acidic and nonacidic species to forests, even in remote areas.

Hypothesis II: Along an elevational gradient, high-elevation forests experience higher atmospheric deposition rates than do lower-elevation forests.

Hypothesis III-A Wet and dry deposition of acids cause increased foliar leaching of base cations.

Hypothesis III-B: Ion exchange and weak acid-buffering mechanisms combine to reduce the free acidity of rain as it passes through the deciduous forest canopy, but not in the coniferous canopy.

Hypothesis IV-A: Atmospheric H_2SO_4 inputs will cause equivalent leaching outputs of cations only in S-saturated ecosystems.

Hypothesis IV-B: Atmospheric HNO_3 inputs will cause equivalent leaching outputs of cations only in N-saturated systems.

Hypothesis V: Ecosystem S saturation is governed primarily by geochemical factors, whereas ecosystem N saturation is governed primarily by biological factors.

Hypothesis VI: Hydrogen-ion-saturated ecosystems will retain base cations and release $H^+ + Al^{3+}$, whereas unsaturated ecosystems will retain H^+ and relase base cations.

In addition to these general hypotheses, they have constructed specific hypotheses regarding S-, N-, and H^+-saturation processes individually, which will be tested in manipulative studies:

Table 9. Key, critical, and specific objectives of the forest effects research.

Key Objective: Project short- and long-term effects of atmospheric deposition on nutrient status of various forest ecosystems (including areas experiencing growth decline).

Critical Objective I: Characterize key processes regulating atmospheric deposition and its effects on forest element cycling.

Specific Objectives:

1. Evaluate the effectiveness of different canopy types in neutralizing deposited strong acidity.
2. Determine the relative importance of organic vs inorganic S accumulation in regulating leaching in various forest soils.
3. Determine the replacement efficiency of H^+ for base cations for various forest soils of differing base saturation.
4. Determine the potential for replenishment of exchangeable base cations by soil-weathering processes.
5. Determine the potential for mitigating soil acidification by changing species composition.

Critical Objective II: Determine whether atmospheric deposition could be causing nutritionally mediated changes in forest productivity.

Specific Objectives:

1. Determine total atmospheric deposition to several forest canopies and the relative contribution to total input by major wet and dry deposition processes.
2. Calculate internal vs external (i.e., deposition) H^+ generation and estimate their relative contributions to cation leaching.
3. Determine the effect of acid deposition on foliar nutrient pools and cycling processes in the canopy.
4. Contrast elemental fluxes with soil contents and tree requirements.
5. Based upon the above research results, assess short- and long-term effects of forest nutrient status and productivity, including an assessment of nutritional causes (if any) of growth decline or forest dieback.

Source: Bondietti et al. (1985).

Sulphur Saturation Hypotheses:

S-1 All ecosystems are unsaturated with respect to higher rates of sulphur deposition.

S-2 Incorporation of $SO_4^=$ into soil Fe + Al oxides is an important ecosystem S-retention mechanism, and adsorbed $SO_4^=$ is not released except by additions of more strongly bound anions.

Nitrogen-Saturation Hypotheses:

N-1. Increased atmospheric N additions will eventually cause N saturation in any ecosystem.

N-2. Reduced atmospheric N additions will cause desaturation of currently saturated systems.

Hydrogen-Ion-Saturation Hypothesis:

H-1. Decreases in soil base saturation will not be equivalent to mineral acid inputs because (a) chemical reactions supply exchange sites with base cations, and, (b) in extremely acidic soils, the replacement efficiency of incoming H^+ is limited and leads to increased leaching of H^+ and Al^{+++} instead of base cations.

The 12 sites represent a range of conditions in climate, air quality, soils and vegetation, and loadings of acidic and acidifying substances. The program seeks to integrate monitoring and effects research approaches at all sites. Table 10 summarizes site characteristics. Table 11 summarizes the parameters that will be measured.

Table 10. Sites for EPRI forest-effect studies.

Site	Location	Vegetation	Soils	Climate[a]		Elevation (m)	Deposition Sampling Approach[b]
				-MAT (°C)	MAP (cm)		
Fullerton (FT)[c]	Walker Branch, TN	Mixed deciduous, primarily *Quercus*	Typic Paleudult	14.5	150	300	
Tarklin (TK)[c]	Walker Branch, TN	Mixed deciduous	Typic Fragiudult	14.5	150	300	
Loblolly pine (LP)	Oak Ridge, TN	Loblolly pine	Typic Paleudult	14.5	150	300	W/D
Nolan Divide (SS) and Indian Gap (SB)	Great Smoky Mountain	Spruce fir	Inceptisols	5.3	230	1800	W/D
Douglas fir (D) and Red Alder (RA)	Thompson Forest, WA	Douglas fir and Red Alder (45 years)	Durochrepts	9.8	130	100	W/D
Douglas fir (DY) and Red Alder (AY)	Thompson Forest, WA	Douglas fir and Red Alder (newly planted)	Durochrepts	9.8	130	100	B
Findley Lake (FL)	Findley Lake, WA	Fir-hemlock	Cryandepts	5.4	180	1100	B

Table 10. Continued.

Site	Location	Vegetation	Soils	Climate[a] MAT (°C)	Climate[a] MAP (cm)	Elevation (m)	Deposition Sampling Approach[b]
Mixed Deciduous (CH)	Coweeta, NC	Oak-hickory	Hapludults	12.6	180	700-1000	B
White Pine (CP)	Coweeta, NC	White pine	Hapludults	12.6	180	800-1100	W/D
Whiteface Mountain (WF)	Lake Placid, NY	Spruce-fir	Borofolists, Haplorthods, Inceptisols	4.2	100	1000-1500	W/D
Huntington Forest (HF)	Newcomb, NY	Mixed deciduous	Spodosols	5.4	106	530	W/D
Duke Forest (DL)	Durham, NC	Loblolly pine	Typic Hapludults	15.5	112	215	W/D
Camp Branch (CB)	Falls Creek, TN	Mixed oak	Udults	12.2	145	550	
Turkey Lakes Watershed[d]	Ontario, Canada	Sugar maple birch	Spodosols	4.4	120	350	B

[a] MAT = mean annual temperature; MAP = mean annual precipitation.

[b] B = nonevent collection of bulk deposition and bulk throughfall only; W/D = event collection of wet and dry deposition separately, collection of throughfall and stemflow on an event basis as wetfall-only, collection of suspended particles and gases, event collection of fog, and nonevent bulk deposition and throughfall.

[c] Previously studied site not designated for further study in this project.

[d] Cooperative site funded by the Canadian government.

Source: Bondietti et al. (1985).

Table 11. Draft of standardized data-reporting form for the EPRI forest-effects project.

Ecosystem Content (kg/ha)		Ecosystem Fluxes (kg/ha/y)	
Component	Analyses	Component	Analyses
Overstory Foliage Branch Bole Roots Total	Organic matter, N, P, S SO_4-S, Ca, K, Mg	Atmospheric deposition Bulk, wet-only[a], dry-only[a], and fog[a] or cloud water	H^+, $SO_4^=$, NO_3^-, total N, NH_4^+, Ca^{++}, K^+, Mg^{++}, Na^+, Al^{+++}, Cl^-, HCO_3^-, orthophosphate, total P, organic acids
Understory Total Vegetation	Same as overstory analyses	Atmospheric chemistry Gas concentrations, particle concentrations	SO_2, HNO_3, $SO_4^=$, NO_3^- NH_4^+, Ca^{++}, K^+, Mg^{++}, H^+ Na^+, Cl^-
Litter	Organic matter N, P, S SO_4-S, Ca, K, Mg	Litterfall	Biomass, N, P, K, Ca, Mg S, $SO_4^=$
Soil[b]	Exchangeable Al^{+++}, Ca, K, Mg, Ma, acidity, total N, total S, total C, soluble + adsorbed SO_4-S, extractable P, total P	Throughfall Bulk, wet only[a]	H^+, $SO_4^=$, NO_3^-, total N, NH_4^+, Ca^{++}, K^+, Mg^{++}, Na^+, Al^{+++}, Cl^-, HCO_3^-, orthophosphate
		Stemflow	H^+, $SO_4^=$, NO_3^-, total N, NH_4^+, Ca^{++}, K^+, Mg^{++}, Na^+, Al^{+++}, Cl^-, HCO_3^-, orthophosphate

Table 11. Concluded.

Ecosystem Content (kg/ha)		Ecosystem Fluxes (kg/ha/y)	
Component	Analyses	Component	Analyses
		Leaching	
		Forest floor	H^+, $SO_4^=$, NO_3^-, total N, NH_4^+, Ca^{++}, K^+, Mg^{++}, Na^+, Al^{+++}, Cl^-, HCO_3^-, orthophosphate
		Vegetation increment	
		Overstory	Organic matter, N, S, SO_4-S, Ca, K, Mg, P
		Foliage	
		Branch	
		Bole	
		Roots	
		Total understory	
		Total vegetation	Same as overstory analyses

[a] Only selected samples will be analyzed for organic acids, total N, total P, HCO_3, or Al^{+++}.

[b] To include O_2 where appropriate.

Source: Bondietti et al. (1985)

The IFS aerometric program incorporates extensive wet and dry deposition measurements. Figure 1 depicts the instrumentation at a typical IFS site. Since the objective of the study is to characterize chemical cycling in these forests under varying acidifying stresses, the complete and fully integrated monitoring/effects programs are essential. If the effects hypotheses being tested are a lesser set than the above list, the monitoring program may be modified accordingly. This is the most complete aerometric program identified in the review for any current or planned forest effects study. It is similar to the aerometric approach of the Mountain Cloud Chemistry Program.

Mountain Cloud Chemistry Program/Chemistry of High Elevation Fog. The Canadian CHEF Program is being operated as an integral component of the MCCP and includes four sites in Quebec. The aerometric and effects studies are being directed by the Atmospheric Environment Service (AES) and CFS, respectively. The aerometric protocols are as specified by MCCP, so this discussion will focus on the MCCP program description. Mohnen (1984) describes the two-fold objectives of MCCP:

- To identify the contribution of acidic and non-acidic deposited pollutants to the observed decline in high elevation forests; and
- To develop long-term data that may be used to validate long-range transport and deposition models of source-receptor relationships and to establish trends.

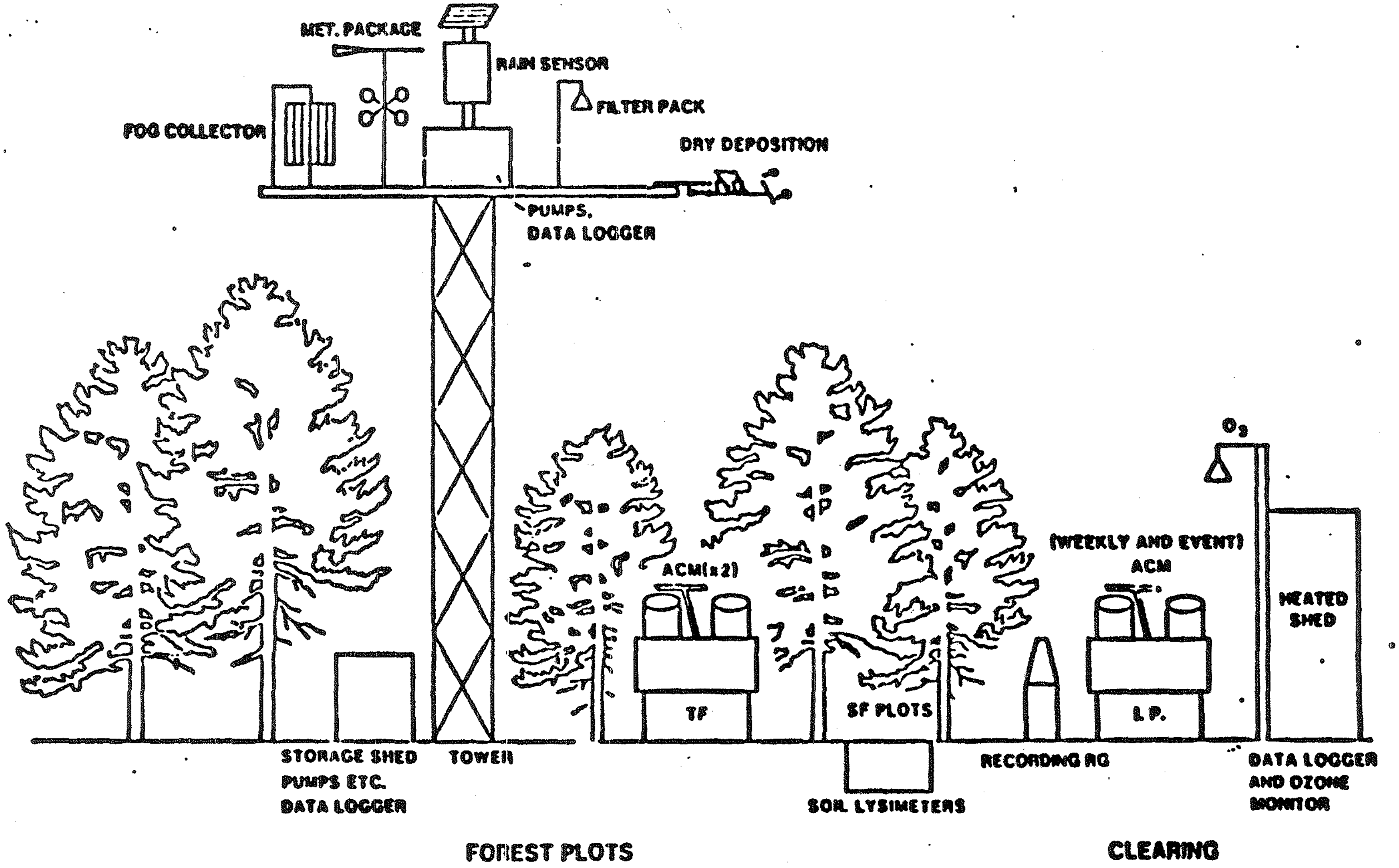

Figure 1. Schematic representation of intensive deposition sampling site (not to scale). Symbols: TF = thoroughfall; I.P. = incident precipitation; ACM = Aerochem Metrics, Inc. sampler; RG = rain gauge; and SF = spruce-fir. Source: Bondietti et al. (1985).

Four major hypotheses to explain the current decline of some forests are cited:

- The acidification - aluminum mobilization hypothesis (Ulrich 1984);
- The general stress hypothesis, in which air pollution in combination with other stress factors has increased the susceptibility to stress such as drought, cloud moisture, nutrient deficiency, and biotic pathogens;
- The magnesium deficiency hypothesis, leading to decreased frost hardiness of, for example, spruce needles; and
- The dry-deposition air - canopy hypothesis, in which gaseous phytotoxicants interact directly with foliage and particles containing acidic and metallic species interact either directly or indirectly to cause damage.

Mohnen (1984) points out that a comprehensive field program should use multiple working hypotheses. MCCP/CHEF uses the above set.

The atmospheric program of MCCP/CHEF is designed to address the potential causes of stress listed in Table 12. The preliminary list of species to be monitored is given in Table 12. Figure 2 indicates the relationship between the hypotheses and observations made by atmospheric scientists and forest scientists.

One of the specific goals of MCCP/CHEF is to characterize the chemical composition of cloud water as it impinges on foliage and to determine quantities deposited on and interactions with foliage. This

Table 12. Potential causes of stress.

Potential Deposition - Induced Stress	Species to be Monitored	Time Scale
1. Al toxicity	H^+ in deposition	Accumulation over year
	H^+ and Al in soil solution (using standard techniques of soil analysis)	Follow seasonal changes
2. Effects on growth regulating hormones and general stress	Aerosol deposition (initially using conc. method but ultimately using actual surfaces for collection) and precipitation for inorganic ions (by I.C.)	Event
	Oxidants (see 4)	Hours
	SO_2	Hours
	Metals (by AA, i.e., Pb, Mn, Fe, Zn, Cd, Mg, Ca, Na, K, Hg, Cu)	Event - weeks
	H^+	Hours
3. Mg deficiency	H^+ wet, aerosol acidity and nitric acid vapor	Event
	Oxidants (see 4)	Hours
4. Oxidant injury	O_3, H_2O_2, PAN	Hours
5. Excess N	N deposition wet (speciation by I.C.) and NH_3, HNO_3, NO_x	Event - seasonal accumulation
	N in soil solution (NH_4^+ and NO_3^- by I.C.)	Event
6. Changes in physiology	Canopy surface - HC, Oxidants, H^+ (wet)	Hours
7. Metal toxicity	Heavy metals (by AA, i.e., Pb, V, Hg)	Accumulation over years
8. Foliar leaching	H^+, $SO_4^=$, NO_3^-, NH_4^+, K^+, Mg^{++}, Ca^{++} in throughfall (by I.C.)	Event

Source: Mohnen (1984).

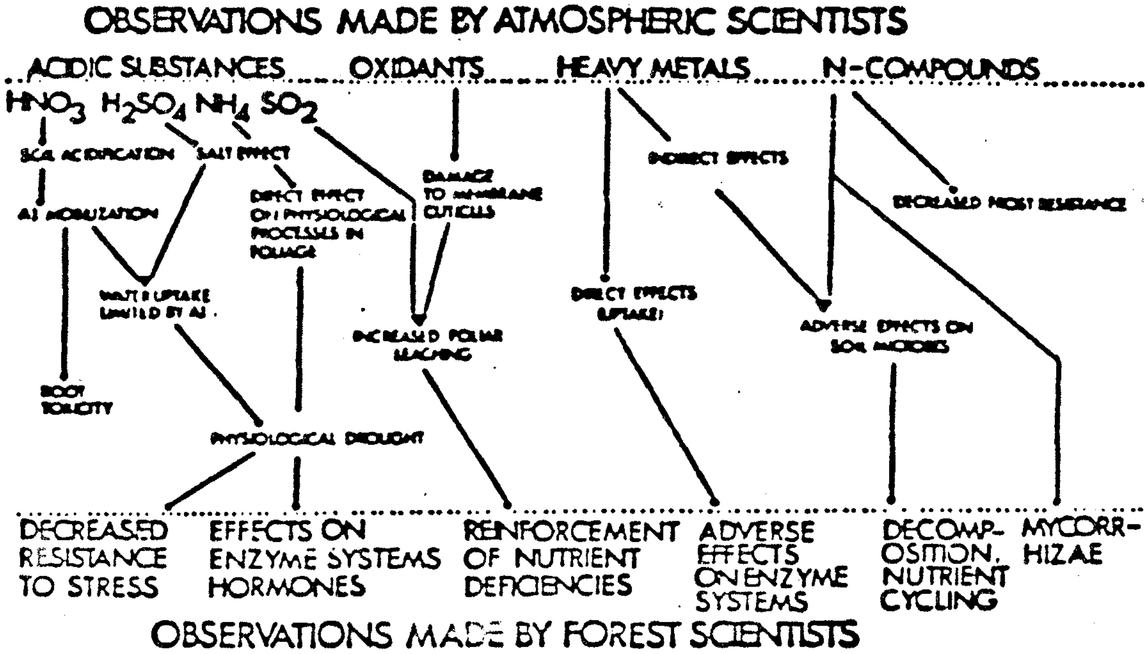

Figure 2. Hypothesized integration of the atmospheric studies with the forest studies.

Source: Mohnen (1984).

aspect, which includes the deposition/formation of rime ice on foliage should be evaluated for its relevance to the oil sands studies.

The MCCP/CHEF atmospheric program, then, consists of:

- Monitoring cloud water for dominant ions, trace metals, and strong oxidants (see Table 12);
- Determining ambient concentrations of O_3, SO_2, NO_x (high priority); H_2O_2, NH_3, HNO_3, and PAN (lower priority); and
- Determining average chemical composition of airborne particulate matter, emphasizing ionic concentration of $SO_4^=$, NO_3^-, H^+, NH_4^+, and heavy metals (see Table 12).

Table 13 lists the meteorological measurements proposed for the MCCP/CHEF research and monitoring stations.

Syncrude Emissions and Biomonitoring Program. The long-term biomonitoring program sponsored by Syncrude (Dabbs 1985) is representative of studies of pollutant accumulation in vascular and non-vascular vegetation that may be considered for the oil sands effects studies. The characterization of metallic emissions from the Syncrude plant (CSC 1984 and Dabbs 1985) can be used as the basis for specifying a list of elements of interest in the heavy metals category.

The observed spatial relation between predicted deposition of certain metals and sulphur uptake by lichens and mosses (as well as deciduous trees - aspen) suggests a means of relating source emissions to

Table 13. Meteorological measurements for the proposed research and monitoring stations.

A. Basic Meteorological Variables

Temperature, wind speed, wind direction, humidity, pressure, precipitation, global radiation, and dewfall.

B. Clouds

		Research Station	Monitoring Station
1.	liquid water content	FFSP, CSIRO	CSIRO
2.	cloud base	laser ceilometer/K-band radar observer reports video camera	observer reports video cameras
3.	cloud droplet spectra	FSSP	

Symbols: FSSP - Forward Scattering Spectrometer Probe
CSIRO - hot wire cloud probe

Source: Mohnen (1984).

impact. Certain lichens also showed reduced growth and other visible symptoms near the oil sands plants.

No ambient monitoring of wet deposition or aerosol was carried out in conjunction with the Syncrude study; the only measurements were emissions tests and the regulatory compliance measurements of SO_2 (continuous and static) and H_2S, near the plants. Lichens take up not only gaseous pollutants, but are also subject to dry particle deposition (and uptake) and to wet deposition. The latter not only carries its own loadings of (dissolved) pollutants, but also acts as a medium for mobilization or removal of material deposited by dry mechanisms in the periods between precipitation events. This complex mechanism is not often addressed in lichen and moss biomonitoring. The net deposition may, of course, be negative, that is, a leaching which depletes certain elements from the vegetation.

Table 14 from Dabbs (1985) lists the elements that have been measured in Syncrude emissions, along with their predicted deposition and accumulation. This list may serve as the basis for a selection of metals of concern in an oil sands monitoring program. For comparison, Table 15, from Air Monitoring Directive AMD-86-1, lists the metals which oil sands plant operators must monitor in emissions.

The timing of the Syncrude biomonitoring studies is also of interest, that is, the periodic re-survey of established sites every 5 to 10 years. This approach is similar in philosophy to the APIOS-BGC studies (q.v.).

Table 14. Elements in Syncrude stack particulate matter.

Element	Terrestrial Abundance ($mg \cdot kg^{-1}$)	SCL Stack Particulate ($mg \cdot kg^{-1}$)
Iron (Fe)	50 000	8 820
Aluminum (Al)	81 300	3 200
Silicon (Si)	277 200	3 070
Calcium (Ca)	36 300	2 450
Sodium (Na)	28 300	1 370
Vanadium (V)	150	920
Magnesium (Mg)	20 900	850
Titanium (Ti)	4 400	780
Manganese (Mn)	1 000	290
Phosphorus (P)	1 180	270
Nickel (Ni)	80	260
Zinc (Zn)	132	130
Lead (Pb)	16	104
Chromium (Cr)	200	98
Copper (Cu)	70	49
Barium (Ba)	250	42
Cadmium (Cd)	0.15	42
Molybdenum (Mo)	15	29
Cobalt (Co)	23	20
Selenium (Se)	0.09	16
Zirconium (Zr)	220	16
Tin (Sn)	40	6.5
Arsenic (As)	5	6.5
Silver (Ag)	0.10	0.6
Mercury (Hg)	0.50	0.6
Berylium (Be)	6	0.2

Source: Dabbs (1985).

Table 15. List of elements to be analyzed from stack particulate samples for the oil sands industry.[a]

Aluminum	Al
Iron	Fe
Vanadium	V
Calcium	Ca
Titanium	Ti
Nickel	Ni
Magnesium	Mg
Molybdenum	Mo
Manganese	Mn
Copper	Cu
Zinc	Zn
Lead	Pb
Chromium	Cr
Cobalt	Co
Sodium	Na
Arsenic	As
Strontium	Sr
Beryllium	Be
Cadmium	Cd
Silver	Ag
Antimony	Sb
Tin	Sn
Tellurium	Te

[a] Mercury and Selenium, because of their volatility, should be analyzed from a bitumen sample.

Source: AMD-86-1 (A-11-2).

3.2 POLLUTANTS OF INTEREST

Table 16 is taken from Concord's proposal to Alberta Environment respecting this project. It lists those pollutants that were thought to be of potential interest, not considering resource constraints. Table 17 summarizes the parameters that are monitored in a number of the programs reviewed, or recommended by researchers in the field. Table 15 lists the heavy metals that are specified to be monitored in emissions from oil sands plants by Alberta Environment (AMD-86-1:A-11-2).

Based on the collective set of pollutants and related parameters shown in Tables 14 and 17, the recommended set of pollutants for the initial phase of an air quality and deposition monitoring network in the oil sands is shown in Table 18.

O_3 has been included in the list of gases because of recent evidence concerning its role in forest effects at levels less than 80 ppb (Duchelle et al. 1982: Wang et al. 1986; Ashmore et al. 1985) and the reported measurements in the region of frequent occurrences of O_3 levels greater than 75 ppb (Table 6). O_3 would have to be determined instrumentally, since no proven integrative or passive method has been found in the literature.

The selection of metals to be determined may depend upon the combination of availability and sensitivity of the analytical methods listed in Table 18. A judicious selection can be made to maximize the coverage within a reasonable analytical budget.

Table 16. Concord's proposed pollutants of interest.

Sulphur oxides and related compounds (sulphates)

Nitrogen oxides and related compounds (nitrates, nitric acid, ammonium salts)

Various ionic, metallic and/or organic species in wet deposition

Photochemical oxidants

Suspended particulate matter

AMD-86-1 metals (same as Table 15)

H_2S

Hydrocarbons

Toxic organics

Table 17. Pollutants of interest - various programs.

Ulrich (1984)	Al, Cr, Fe, Co, Ni, Cu, Zn, Cd, Pb, As, Se, (toxic heavy metals), Mg^{++}, Ca^{++}, NH_4^+, NO_3^-, $SO_4^=$, micronutrients (nutrients)
	SO_2, NO_x, Cl_2 (acid formers)
	HF, Hydrocarbons (gaseous phytotoxins)
	VOC's (oxidant formers)
Cowling (1985, 1986)	C, H, O, N, P, S, K, Ca, Mg, Mn, Fe, Cu, Zn, Mo, B, Cl (essential nutrients)
	Pb, Hg, Cd, Br, F, Zn, Ni, Sn, As, Al (toxic elements)
	H^+, Ca^{++}, Mg^{++}, Na^+, K^+, NH_4^+, $SO_4^=$, NO_3^-, $PO_4^{\equiv}$, HCO_3^-, Cl^- (ions)
Bondietti et al. (1985) (Table 11)	H^+, $SO_4^=$, NO_3^-, total N, NH_4^+, Ca^{++}, K^+, Mg^{++}, Na^+, Al^{+++}, Cl^-, HCO_3^-, $PO_4^{\equiv}$, total P, organic acids
Mohnen (1984) (Table 12)	Pb, V, Hg, Mn, Fe, Zn, Cd, Mg, Ca, Na, K, Cu (metals)
	SO_2, NO_x, HNO_3; O_3, H_2O_2, PAN, NH_3 (gases)
	H^+, $SO_4^=$, NO_3^-, NH_4^+, K^+, Mg^{++}, Ca^{++} (precipitation)
Gizyn (1986)	Gran acidity, $SO_4^=$, NO_3^-, Cl^-, Ca^{++}, Mg^{++}, K^+, Na^+, NH_4^+, $PO_4^=$; Fe^{+++}, Mn^{++}, Al^{+++}, Zn^{++} (precipitation)

Table 18. Recommended pollutants to be monitored.

Gases:

SO_2, NO_2(?), HNO_3, O_3, H_2S(?)

Precipitation (filtered liquid):

Anions: $SO_4^{=}$, NO_3^{-}, Cl^{-}, $PO_4^{\equiv}$(?), HCO_3^{-}(?)

Cations: pH, acidity, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, NH_4^{+}; Al^{+++}, Fe^{+++}, Mn^{++}, Zn^{++}

Particulate Matter:

Soluble ions: $SO_4^{=}$, NO_3^{-}, $PO_4^{\equiv}$(?), Cl^{-}; Ca^{++}, Mg^{++}, Na^{+}, K^{+}, NH_4^{+} (metal cations unlikely to be detectable)

Elements: Al, Cr, Fe, Co, Ni, Cu, Zn, Cd, Pb, Hg, Sn, As, V, Mn, Mg, Ti, Se, S (maximum set feasible by XRF, INAA, IPAA, PIXE, ICP, AA, in a reasonable combination)

Passive samplers for SO_2 and H_2S (TRS) are available. The MOE/Concord sampler (Orr et al. 1986), which appears to be reasonably specific for SO_2 (or acidic S-containing gases), in combination with standard Alberta Environment total sulphation plates or total sulphide strips (AMD-86-1), can probably be used to resolve oxidized sulphur gases from reduced sulphur gases to an acceptable degree.

The time scales on which these parameters would be monitored are addressed according to various assumptions in Section 4, in which design option scenarios are developed.

Specialized measurements of such parameters as foliar S (as defined by Legge and Bogner 1986), stable sulphur isotopes (Legge et al. 1982) or $^{137}Cs/^{210}Pb$ ratio (Schell 1986; Talbot and Andren 1983) may be considered.

^{137}Cs ($t_{1/2}$=30 y) has been produced in the atmosphere mainly by anthropogenic means (nuclear fission). ^{210}Pb ($t_{1/2}$=21 y) is produced by decay of naturally emanating 222 R_n ($t_{1/2}$=3.8 d) from the ^{226}Ra decay series. Both nuclides are bound to atmospheric (fine) particles and are tracers of atmospheric deposition. The amounts of ^{137}Cs and ^{210}Pb deposited depends on tropospheric particle removal processes and scavenging by vegetation (Schell 1986). ^{137}Cs is a tracer of long-range (global) tropospheric deposition and ^{210}Pb a regional tracer of particle deposition.

Specific tracers of oil sands plant emissions may be Ti, V, Ni, Pb, Cd, or Se (see Table 14 and Dabbs 1985), which are enhanced in emissions relative to soil content, at least for Syncrude.

V has been used as a tracer by Barrie (1980) and its accumulation in lichens in the oil sands is correlated with modelled deposition patterns (Dabbs 1985). Choice of a tracer element, or signature group of elements, will depend on the specific biological media or receptors selected for monitoring (lichens, leaves, needles, tree cores, soil, surface water, etc.).

3.3 METEOROLOGICAL PARAMETERS OF INTEREST

Several of the effects studies cited earlier required the acquisition of meteorological data in support of effects studies. The data included both regional-scale climatic data and site-specific or microclimate data.

General Climate. General climate observations are a part of the baseline data needed to support effects research at each site and to allow for intersite comparisons. Long-Term Ecological Research sites established by the US National Science Foundation have defined four levels of meteorological instrumentation as listed in Table 19 (Swift and Roysdale 1985). The Entry level shown in the table relies on manual observations and the Basic level can be dependent on either manual observations or chart records. The Research level would require the use of a data acquisition system and would produce a detailed climatology data set.

Other requirements for meteorological data include vertically resolved, at least up to plume height, temperature, wind, and relative humidity measurements, and cloud cover.

Table 19. Types of long-term ecological research meteorological stations.

Level	Parameters	Interval	Remarks
0. Entry	Air temperature Precipitation	Daily	Temporary or satellite station
1. Basic	Air temperature Precipitation Vapor pressure Wind speed	Daily	Minimum standard station, use standard instrumentation
	Wind direction Solar radiation	Daily	Optional for Level 1
2. Research	All of the above	Hourly	Probably use electronic sensors and data logger
3. Supplemental	All of the above plus one or more: Snow depth Wind vector Partial spectrum radiation Soil temperature Water temperature Atmospheric pressure Evaporation Boundary layer fluxes or other variables	As required	Specialized measurement at some sites. May be continuing or short term.

Source: Swift and Roysdale (1985).

4. PROGRAM DESIGN OPTIONS

4.1 CONCORD'S APPROACH

In developing the aerometric program, the overall ecosystem effects program objectives need to be borne in mind. The successful accomplishment of the aerometric component of the program will be based on the recognition of hypotheses which will guide the design and execution of the work program. The primary purpose of this section is to establish the context of the aerometric program within the overall effects program.

Many of the research programs cited in the previous chapter were based on hypotheses which accepted as factual the existence of forest damage. In some cases, the assessment of the extent of damage was a project objective and in most, the understanding of the role of atmospheric deposition in determining forest structure and function has been a common feature. In cases where damage was observed, the research projects were often formulated in terms of testable hypotheses.

In the case of the AOSERP area, few measurable ecosystem effects directly attributable to atmospheric deposition have been demonstrated. Given the current level of industrial activity in the area and bearing in mind the potential for increased industrial activity in the future, as well as the presence of sensitive receptors (soil and surface waters) in the area, it is appropriate to determine if subtle changes in the forests may occur in the future so that one would be in a position to effect appropriate mitigative measures.

In view of the anticipated low level of stress, it will be essential to enhance the discrimination among pollutant-induced stresses and the climatic, competitional, and biotic pathogen-induced stresses as well as the natural variability in forest systems.

4.1.1 Research Goals

The overall research objectives are:

1. To develop effective techniques for detecting medium- to long-term changes in terrestrial ecosystems in the AOSERP region;
2. To identify any subtle long-term, pollutant-induced stresses in the AOSERP area; and
3. To assess the significance of observed or predicted effects.

4.1.2 Hypotheses

The research program may therefore be directed towards addressing the following hypotheses:

- That stresses/effects on forests as a result of long-term, low-level exposure to air pollutants are detectable; and
- Monitoring aerometric parameters along with biophysical measurements will provide insights into cause and effect relationships.

Hypotheses relating to specific effects or mechanisms for the response of forest ecosystems to atmospheric pollutants and the implied aerometric requirements to support them will be tabulated below.

4.1.3 Research Approach

The research approach will rely on long-term (5 to 25 years) aerometric and biophysical monitoring at sites along a pollutant gradient. The finite and limited resources available dictate that the simplest scientifically defensible program be considered. A wide range of biophysical parameters can be proposed in order to address the overall hypotheses. At this point in time, the biophysical parameters have not been decided, hence it will be necessary to define aerometric monitoring requirements for the widest range of biophysical measurements.

Several of the research programs cited in the previous section included aerometric measurements in support of a wide range of biophysical measurements that were or are being used to address a variety of hypotheses. Tabulated in Table 20 are hypotheses advanced to address pollutant induced stresses, the time scale over which stresses are observed, and the appropriate supportive aerometric measurements.

The workshop attendees are requested to comment on the hypotheses, and make recommendations on the design of the aerometric program that will be supportive of the successful testing of the hypotheses.

Table 20. Summary of forest ecosystem related hypotheses and the suggested aerometric monitoring requirements.

Biophysical Measurements			Aerometric Measurements
Stress Factor	Hypothesis	Time Scale for Observing Effects	Method Temporal Spatial Resolution
CHEMICAL			
Aluminum toxicity	Increased soil acidity leads to increased concentrations of soluble aluminum in soil solution. This leads to accelerated morbidity and/or decreased synthesis of feeder roots.	Annual accumulation	Wet deposition chemistry. Site-specific. Seasonal to annual.
Magnesium deficiency	Acid deposition adds nitrogen but leaches Mg and Ca from needles and from soil. Foliage leaching is accelerated by ozone exposure and frost damage to cuticles and cell membranes.	Annual	Wet deposition chemistry. Site-specific. Ambient ozone hourly. Regional.
Toxic pollutants	Episodic acute exposure (O_3, SO_2) causes injury.	Seasonal to annual	O_3, SO_2. Hourly. Site-specific.
Oxidant injury	Injury to foliar tissue leads to increased leaching of nutrients (Mg especially). Reduced photosynthesis leads to decline in root growth.	Seasonal	Ambient O_3. Hourly. Regional.
Trace metal accumulation	Trace metal deposition may change the availability of some elements to trees and the concentration in trees is altered.	Seasonal (leaves) to annual (stem)	Dry and wet deposition. Monthly. Site-specific.

Table 20. Continued.

Biophysical Measurements		Time Scale for Observing Effects	Aerometric Measurements
Stress Factor	Hypothesis		Method Temporal Spatial Resolution
General air pollution stress	If atmospheric deposition has affected forest production in recent decades, these effects will be detectable in long-term growth records obtainable from measurements on tree rings. Because the above changes will likely result from regional-scale atmospheric loading, they will be systematically associated with regional differences in atmospheric chemistry including acidic precipitation and ozone.	Decades (chemistry)	Wet and dry deposition, ambient SO_2, NO_2. Site-specific. Climate (T, WD, WS, RH). Regional.
Insignificant effects	No currently observable effects. Therefore collect baseline data (species/community studies, tree growth, physiological ecology).	Decades	No aerometric monitoring.
Canopy effects	The acidity of surface water is affected by contact with vegetation which leaches organic acids.	Seasonal	Wet deposition throughfall stemflow chemistry. Event. Site-specific.
Surface waters	Hydrologic patterns affect the composition of surface waters.		Wet deposition chemistry. Event. Site-specific.
Soil alteration	Atmospheric deposition will alter soil composition.	Decades	Wet and dry deposition. Annual. Site-specific.

Table 20. Concluded.

Biophysical Measurements			Aerometric Measurements
Stress Factor	Hypothesis	Time Scale for Observing Effects	Method Temporal Spatial Resolution
Snowmelt effects	Acid pulses during snowmelt contribute most to annual acid and nutrient inputs.	Seasonal	Wet deposition. Snow core. Seasonal. Site-specific.
COMPETITIONAL	Light, water, nutrients, allelochemical factors affect forest ecosystems.	Annual/decades	Meteorological. Regional.
CLIMATIC	Climatic factors (precipitation, frost, wind, temperature, mechanical (wind, snow/ice) affect forest ecosystems.	Annual/decades	Meteorological. Regional.
BIOTIC PATHOGEN	Fungi, insects, bacteria, nematodes, viruses, viroids, mycoplasmas, parasitic seed plants affect forest ecosystems.	Seasonal/annual	No aerometric monitoring.

4.2 DESIGN OPTIONS

In this section, aerometric monitoring scenarios which will address various aspects of the requirements of biophysical monitoring approaches, are presented.

Aerometric measurements are required to establish stress levels caused by atmospheric pollutants or by climatic factors. The information on the stress levels is needed to assist in understanding biophysical observations.

In designing aerometric monitoring options which will characterize the stress levels, the following aspects will be considered:

- temporal resolution;
- spatial resolution;
- precision;
- study strategy:
  - planned activity levels (long-term 20+ years, intensifying as results dictate, snapshop measurements, low level activity with campaign studies, medium and high activity levels with de-escalation as results dictate);
- logistics:
  - lack of mains electrical power, road access; and
- technological capability - the availability of aerometric instrumentation to meet the requirements.

It is essential that the aerometric measurements have temporal resolution that is no longer than the time scale over which biophysical changes occur. In the case of pollutant measurements, the interval over which sampling is integrated will depend on the anticipated concentration level and the sampling rate needed to provide a sample that is large enough to be consistent with the anticipated variability of the parameters monitored. The sample size must ensure that representative and statistically significant measurements are obtained. For parameters expected to be uniform within each site, a single measurement at each site will suffice. In extreme cases, parameters may be reasonably expected to be consistent throughout the region or may be expected to vary within a given site. In the former extreme, a single regional instrument will suffice, while in the latter several measurements at each site would be necessary. For purposes of this discussion, the regional sites are assumed to have mains electrical power, year-round access and amenities for telemetry; other site-specific and within-site stations are expected not to have mains electrical power and limited access.

Common to all design options will be the necessary quality assurance (QA) and quality control (QC) as well as data acquisition and storage activities. The QA and QC, data acquisition, and storage aspects will not be considered in the workshop.

In addition to these features, the intensity with which the biophysical monitoring program is implemented will also dictate the nature of the aerometric program. Implementation strategies considered will include or accommodate:

1. low-level activity escalating based on preliminary results with or without intensive short-term (campaign) studies;
2. consistent activity levels predicated on the need for a very long-term study;
3. initial intense activity with changes in activity levels (e.g., reduced intensity - narrower range of measurements or fewer sites with same level of intensity) as decision points are reached; and
4. the determination of snapshot measurements of the sites at intervals of say five to ten years. The snapshot measurements would of course require intense biophysical monitoring which could be done with or without long-term (e.g., annual) integrated air pollution dose measurements.

In addition to the approaches and strategies for the program, there are logistical considerations which dictate the use of aerometric instrumentation without the mains electrical power since sites are remote of such facilities.

Aerometric instrumentation which can utilize mains electric power is generally adequate to meet all the requirements of effects studies. Notable exceptions are the measurement of dry deposition rates with good precision, accuracy, and temporal resolution, and the measurement of continuous, chemically speciated ambient particulate concentrations. Also, real-time measurement of wet deposition chemistry is not available. One of the tasks of this project is to review available active, and passive, sampling equipment that may utilize battery, solar, or other non-mains operable instrumentation. Emphasis will be placed on identifying suitable power sources to run otherwise fully tested and validated active sampling instrumentation, or the use of passive samplers.

The presentation of this review is premature for this workshop, but a summary of the available passive methods or non-mains operated instrumenta- tion for the pollutants and meteorological parameters of interest is presented in Table 21.

The design options for the aerometric program are described in terms of the time scale (interval) over which aerometric measurements are integrated (short, medium, or long interval) and also in terms of the intensity of the study, namely, intensive (continuous, high intensity), or campaign (periodic, highly intensive measurements). The design options are given below.

1. Short-Interval, Intensive Option. This option assumes that only short-interval (hourly and/or event) responses are appropriate to indicate existing or future effects or strains. It also assumes that the biophysical measurements require detailed within canopy measurements, namely vertically and horizontally resolved air concentration and meteorological measurements, the measurement of event wet deposition, and throughfall and stemflow measurements.

Table 21. Available methods for monitoring at remote sites.

POLLUTANT	METHOD	COMMENTS
SO_2	Filter pack	Battery/solar powered version suitable for AOSERP to be investigated Integration over 24h assumed.
	Passive sampler Diffusion device	Orr et al. (1986) Integration over 28d.
	Passive sampler Sulphation plate	Integration over 30d.
NO_2	Passive sampler Diffusion device	Integration as for SO_2
HNO_3	Filter pack	As for SO_2 above.
H_2S	Passive sampler Sulphide strips	Integration over 30d.
O_3	Continuous (e.g., chemiluminescent)	Assume only regional measurements are required. Use nearest available mains supply.
TSP	Filter pack	Chemical analysis of filter for ions and elements in Table 18.
Wet deposition	Aerochemetrics type sampler	Battery operated version to be investigated. Daily integration. Chemical analysis of ions and elements in Table 18.
METEOROLOGICAL PARAMETERS		
<u>Site Specific</u>		
Precipitation		
rain	rain gauge	
snow	nipher gauge	
snow depth	manual	

Continued . . .

Table 21. Continued.

POLLUTANT	METHOD	COMMENTS
Temperature		
air	thermocouple	
soil	thermocouple	
wet bulb		
Moisture		
air (% RH)		
soil		
Evaporation		
Wind		
Speed	anemometer	
direction	anemometer	
vector		
Radiation		
total		
net		
Barometric pressure		
Regional		Required for regional climate characterization and modelling. Nearest available mains would be suitable.
Upper air		
temperature wind (speed, direction), RH	Balloon tracking or remote sensing (Radar, sodar, lidar)	

In this option, the selection of sites with similar aerodynamic features will be necessary in order to facilitate intersite comparisons. Factors such as elevation, slope and aspect, and canopy height and density will need to be taken into consideration.

The requirements for pollutant monitoring are extreme in that hourly measurements would likely be desired. The shortest time interval for ambient concentration measurements using passive or battery/solar operated active samplers is daily integration using multiday samplers that incorporate a sample changer. In principle, low-volume samplers based on filter pack methods for gases and particles could be used provided suitable power supplies (battery, solar powered, etc.) could be developed. The prospect of the successful development of such power sources suitable for reliable operation in northern Alberta condition is not promising, based on current information.

Meteorological measurements (wind speed and direction, temperatures, relative humidity) with hourly integration of measurements is feasible through the use of solar/battery operated equipment that stores data electronically and transmits data at preselected intervals to a satellite. Concord has installed similar systems in northern Saskatchewan where the system has operated successfully for over one year. The provision of hourly integrated meteorological data is technically feasible and the costs of providing longer interval measurements are not likely to be significantly different.

2. Medium-Interval Option With or Without Campaign Studies. This option assumes that medium-interval (weekly or monthly) site-specific ambient concentration measurements are needed.

This option may be consistent with a planned medium-term (10 to 25 years) study which may yield definitive answers relatively early such that more or less intensive biophysical and/or aerometric monitoring may take place. In this option, it is assumed that above-canopy measurements only will suffice for both concentration and meteorological measurements. The air quality and meteorological measurements would be required to establish seasonal and longer term means.

This option may or may not include campaign and/or shorter-term studies as are appropriate. The campaign studies could for example incorporate within and below canopy measurements (multiple sites per stand), throughfall and stemflow measurements, and shorter interval concentration measurements.

3. Long-Interval, Regional-Scale Monitoring Options. In this option, measurements integrated over long time periods (monthly or longer) are appropriate for the effects studies which could likely be based on a long-term (20 to 25 years) program. The site-specific measurements for particulate concentrations and monthly wet deposition measurements would be sufficient.

Only regional climate monitoring is required for characterizing meteorological conditions at or near plume heights and/or for establishing weather conditions that are representative of the region. Available meteorological data from the region clearly indicate that significant differences in microclimate are likely at different study sites within a 20 km radius of either major source in the study area. Regional climate monitoring options therefore will focus on the choices for characterizing plume level meteorological conditions.

4. Hybrid Option. This option would include above-canopy site-specific measurements consisting of medium and long interval measurements for some pollutants and selected meteorological parameters. In addition, regional-scale measurements of O_3 would be made and existing meteorological measurements would be used to complement the site-specific measurements. Other air quality measurements would include passive samplers for SO_2, H_2S, on monthly sampling intervals, and TSP monthly using low-volume active sampling and dustfall devices.

The meteorological measurements would include a limited number of sites at which hourly meteorological data are obtained. The site selection process would ensure that at least two pairs of sites have features likely to result in similar microclimates. Meteorological data would be acquired by above canopy sensors for wind, temperature, relative humidity with ground-based sensors for soil temperature. Data from these sensors would be stored electronically and radio-telemetered to a satellite periodically. Additional measurements would include snow depth and snow core sampling in winter, battery operated wet deposition collectors in the summer only for collecting rain samples integrated over 28 days.

5. No Aerometric Measurements: Use Existing Climatic Data. One option is not to make any site-specific aerometric measurements. Existing climatic information alone would be used to complement observational or biophysical/biomonitoring studies.

In order to determine the feasibility of including aerometric monitoring in the terrestrial and effects studies, the workshop attendees are requested to:

1. Determine the necessity of aerometric measurements based on their relevance or necessity to some or all biophysical monitoring and also on the logistic feasibility of measurements;
2. Determine if the monitoring scenarios presented are complete; and
3. Select the preferred monitoring scenario(s) for detailed development.

Details of the aerometric monitoring for each of the above options are given in Tables 22 to 24.

Table 22. Short-interval, intensive scenario.

Parameter(s)	Method	Resolution Temporal	 Spatial	Comments
SO_2, NO_2, TSP (trace metals, $SO_4^=$, NO_3^-, NH_4^+)	Filter pack	Daily	Site-specific	Battery operated
O_3	Chemiluminescence	Hourly	Regional	Locate at nearest site with power or existing station
Wet deposition (major ions, trace metals)	Sangamo type collector	Event	Site-specific	Battery operated
Precipitation				
(rain)		Daily		
(snow)		Daily		
Snow core		Seasonal		
Wind (speed and direction)	Anemometer	Hourly		
Temperature		Hourly		
RH		Hourly		
Stemflow		Event		
Throughfall		Event		
Dry deposition	Dustfall	Monthly		

Table 23. Medium-interval, intensive campaign scenario.

Parameter(s)	Method	Resolution		Comments
		Temporal	Spatial	
SO_2, NO_2, TSP (trace metals, $SO_4^=$, NO_3^-, NH_4^+)	Filter pack	Weekly*	Site-specific	
O_3	Chemiluminescence	Hourly	Regional	Locate at nearest available site or existing station with AC power.
Wet deposition (major ions, trace metals)	Sangamo type collector	Weekly*	Site-specific	Battery operated
Precipitation				
(rain)		Weekly*		*Event/daily during campaign studies.
(snow)		Weekly*		
Snow core		Seasonal		
Wind (speed and direction)	Anemometer	Hourly		
Temperature		Hourly		
RH		Hourly		
Stemflow		*		*During short term, e.g. summer studies only.
Throughall		*		
Dry deposition	Dustfall	Monthly		

---

*

Table 24. Long-interval scenario.

Parameter(s)	Method	Resolution Temporal	 Spatial	Comments
SO_2, NO_2, TSP (trace metals, $SO_4^=$, NO_3^-, NH_4^+)	Filter pack	Monthly	Site-specific	
SO_3, H_2S	Sulphation candles	Monthly	Site-specific	
SO_2	Passive monitor	Monthly	Site-specific	
O_3	Chemiluminescence	Hourly	Regional	Locate at nearest available site or existing station with AC Power.
Wet deposition (major ions, trace metals)	Sangamo type collector	Monthly	Site-specific	Battery operated
Precipitation				
(rain)		Weekly		
(snow)		Weekly		
Snow core		Seasonal		
Wind (speed and direction)	Anemometer	Hourly		
Temperature		Hourly		
RH		Hourly		
Dry deposition	Dustfall	Monthly		

Table 25. Hybrid option.

Parameter(s)	Method	Resolution Temporal	 Spatial	Comments
SO_2, TSP (trace metals, $SO_4^=$, NO_3^-, NH_4^+)	Filter pack	Monthly	Site-specific	Above-canopy measurements.
SO_2, H_2S	Sulphation candles Sulphide strips	Monthly	Site-specific	Above-canopy measurements.
SO_2	Passive monitor	Monthly	Site-specific	Above-canopy measurements.
O_3	Chemiluminescence	Hourly	Regional	Locate at nearest available site or existing station with AC power.
Dry deposition	Dustfall	Monthly		
Wet deposition (major ions, trace metals)	Aero-Chemetric type collector	Monthly	Site-specific	Battery operated, weekly composited, at selected sites only. Summer only.
Precipitation (rain amount)		Weekly		Summer only, above-canopy.
Snow core		Seasonal/Monthly		
Wind (speed and direction)		Hourly		Above-canopy
Temperature		Hourly		
RH		Hourly		

5. RECOMMENDATIONS

Of the scenarios or options presented in the previous section, the preferred one from the study team's perspective is the hybrid option (see Table 25). As indicated, this option would comprise above-canopy monitoring of pollutants at each site at which effects studies will be carried out, for those pollutants expected to show a gradient with distance from the industrial sources, and of those meteorological parameters expected to have site-specific characteristics. These would be combined with certain regional (master site) monitoring of pollutants and climatological parameters that are not expected to have strong gradient characteristics (e.g., oxidants, mixing height). The proposed suite of pollutants and parameters is intended to support the range of effects studies that seem most likely, from lichen accumulation to aquatic bioconcentration or bioaccumulation. The specific effects studies will dictate ancillary continuing or campaign monitoring activities (e.g., throughfall and stemflow collections).

The time scales of the recommended option would accommodate all but detailed event- or episode-scaled effects studies.

The preferred option is a compromise, selected on the basis of logistics and availability of resources, as well as on considerations of practicality of maintaining quality control over an extended network operational lifetime. From the latter perspective, even the recommended compromise may be optimistic.

The option of observational or biomonitoring studies only (i.e., no aerometry) should be considered by the workshop, but the consensus of those effects researchers canvassed prior to the workshop is that knowledge of the pollutant dosage obtained in parallel with observation biophysical monitoring is desirable.

Cost has not yet been applied as a criterion in selecting the preferred option. Available funding may limit the scope of this option (parameters monitored, number of sites instrumented, etc.), or may dictate another option, for example, the long time interval option (Table 23). The latter would be more limited in the types of effects studies which would be supported, while still providing acceptable support for many types of effects studies. The details of cost estimates for the activities of the options have not been presented, but rough estimates will be available for discussion in the latter stages of the workshop. It is recommended that cost play a minor role in the workshop participant's assessment of feasibility and that this evaluation be left primarily to the post-workshop activities of the study team, who will attempt to specify the simplest version of the option that the workshop has deemed to be the best scientifically-defensible compromise.

6. REFERENCES AND BIBLIOGRAPHY

Acid Deposition Research Program. 1984. Researching acid deposition: workshop proposals. Prep. for Alberta Government/Industry Acid Deposition Research Program. Calgary, Alberta. 59 pp.

AG/IADRP. 1984. First Annual Report, January 1, 1983 to March 31, 1984. 9 pp.

AG/IADRP. 1985. Second Annual Report. April 1, 1984 to March 31, 1985. Prep. for Alberta Government/Industry Acid Deposition Research Program. Calgary, Alberta. 12 pp.

Angle, R.P. and H.S. Sandhu. 1986. Rural ozone concentrations in Alberta, Canada. Atmos. Environ. 20:1221-1228.

Ashmore, M., N. Bell, and J. Rutter. 1985. The role of ozone in forest damage in West Germany. Ambio 13(2): 81.

Baes, C.F. and S.B. McLaughlin. 1986. Multielemental analysis of tree rings: a survey of coniferous trees in the Great Smoky Mountains National Park. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 154 pp. (Available from NTIS, Report No. DE86-006750.)

Barrie, L.A. 1980. The fate of particulate emissions from an isolated power plant in the oil sands area of western Canada. Annals of the New York Academy of Science 338(1980):434-452.

Bennett, D.A., R.L. Goble, and R.A. Linthurst. 1985. Acidic deposition phenomenon and its effects: critical assessment document. Prep. for Clark University, Worcester, Massachusetts and North Carolina State University at Raleigh by Environmental Protection Agency. Washington, D.C. 182 pp. (Available from NTIS, Report No. PB85-233393.)

Bogle, M.A. and R.R. Turner. 1983. Lead in vegetation, forest floor material, and soils of the spruce-fir zone, Great Smoky Mountains National Park. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 14 pp. (Available from NTIS, Report No. DE84-012353.)

Bondietti, E.A., D.W. Johnson, and S.E. Lindberg. 1985. Project summary, integrated forest study on effects of atmospheric deposition. Prep. for Electric Power Research Institute by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 35 pp. (Available from NTIS, Report No. DE85-015972.)

Box, G.E., W.G. Hunter, and J.S. Hunter. 1978. Statistics for experimenters: An introduction to design, data analysis, and model building. J. Wiley and Sons, Toronto. 653 pp.

Cercasov, V. 1985. Investigation of the atmospheric particulates deposited on leaves using instrumental neutron activation analysis. Atmospheric Environment 19(4):681-683.

Concord Scientific Corporation. 1984. A Study of Metallic Emissions from the Main Stack at Syncrude's Mildred Lake Plant. Syncrude Canada Ltd. Environmental Research Monograph 1984-2.

Cowling, E.B. 1986. Dry deposition information needs for studies of the effects of regionally dispersed airborne chemicals on forests and other terrestrial ecosystems. In: Proceedings of the NAPAP Workshop on Dry Deposition, Draft Report. 1986. Harpers Ferry, West Virginia; 1986 March 25-27.

Dabbs, D.L., ed. 1985. Atmospheric emissions monitoring and vegetation effects in the Athabasca Oil Sands region. Prep. for Syncrude Canada Limited by Dabbs Environmental Services with contributions from Western Research, Concord Scientific Corporation, Hardy Associates (1978) Limited, and CASE Biomanagement. Edmonton, Alberta. 127 pp.

Davidson, C.I., W.D. Goold, T.P. Mathison, and G.B. Wiersma. 1984. Airborne trace elements in Great Smoky Mountains, Olympic, and Glacier National Parks. Environmental Science and Technology 19(1):27-35.

Davis, C.S., P. Fellin, D. Stevens, S. Todd, and K. Heidorn. 1985. Evaluation, analysis, and assessment of snowpack and precipitation data from a monitoring network in the AOSERP study area. Prep. for Alberta Environment by Concord Scientific Corporation. RMD Report 86/36. 341 pp.

Duchelle, S.F., J.M. Skelly, and B.I. Chevone. 1982. Oxidant effects on forest tree growth in the Appalachian mountains. Water, Air, and Soil Pollution 18(1/3):363-373.

Erkinjuntti, R., M. Gerlander, A. Hautojarvi, P. Hari, K. Kaisla, H.-S. Katainen, S. Kellomaki, T. Raunemaa, and T. Tuomi. 1982. The effects on forest of air pollution from energy production: application of the PIXE method to elemental analysis of pine needles from the years 1959-1979. Canadian Journal of Forest Research 12(2): 384.

Evans, G., P. Finkelstein, B. Martin, N. Possiel, and M. Graves. 1983. Ozone measurements from a network of remote sites. Journal of the Air Pollution Control Association 33(4):291-296.

Fernandez, I.J. 1983. Acidic deposition and its effects on forest productivity - a review of the present state of knowledge, research activities, and information needs - second progress report. NCASI Technical Bulletin 392. New York: National Council of the Paper Industry for Air and Stream Improvement, Inc. 164 pp.

Findlay, R.L. and C. Primus. 1986. The Alberta Acid Deposition Research Program (ADRP) Overview and Status. Presented at the 2nd Symposium and Workshop on Acid Forming Emissions in Alberta and Their Ecological Effects. 1986 May 13-15. Calgary, Alberta. pp. 37-44.

Fisher, R.F. 1978. Climatic Habitat of Canadian Forest Trees. Handbook on Agricultural and Forest Meteorology edited by R.A. Treidle, Atmospheric Environment Services. pp. 35-63.

Foster, N.W. 1983. Acid precipitation and soil solution chemistry within a maple-birch forest in Canada. Forest Ecology Management 12: 215-231.

Foster, N.W. and J.A. Nicolson. 1982. Acid precipitation and vegetation interaction in the Turkey Lake forest watershed. Prep. for Environment Canada by the Great Lakes Forest Research Centre. Sault Ste. Marie. 2 pp.

Francis, A.J., D. Olsen, and R. Bernatsky. 1981. Microbial activity in acid and acidified forest soils. Prep. for US Department of Energy by Brookhaven National Laboratory. Upton, New York. 31 pp. (Available from NTIS, Report No. DE81-030149.)

Fritschen, L.J. 1985. Characterization of Boundary Conditions Affecting Forest Environmental Phenomena. From the Forest Atmosphere Interaction edited by B.A. Hutchison and R.B. Hicks, D. Reidel Publishing Company. pp. 3-23.

Gibson, J.H., and R.A. Linthurst. 1985. Effects of acidic precipitation on the North American continent. Prep. for Corvallis Environmental Research Laboratory by Colorado State University. Fort Collins, Colorado. 22 pp. (Available from NTIS, Report No. PB85-239382.)

Glantz, C.S., M.Y. Ballinger, and E.G. Chapman. 1986. An inventory of current environmental monitoring projects in the U.S.-Canadian transboundary region. Prep. for the US Environmental Protection Agency by Pacific Northwest Laboratory, Battelle Memorial Institute. Richland, Washington. 290 pp.

Hakkarinen C. and M.A. Allan. 1986. Forest health and acidic deposition: a synthesis report. Prep. for the Electric Power Research Institute. Palo Alto, California. EPRI Report No. EA-4813-SR.

Hall, D.J. and R.A. Waters. 1986. An improved readily available dustfall gauge. Atmospheric Environment 20(1):219-222.

Hall, R.J. and G.E. Likens. 1985. Experimental acidification of a stream tributary to Hubbard Brook. Prep. for Environmental Research Laboratory, Duluth, Minnesota by Cornell University. Ithaca, New York. 9 pp. (Available from NTIS, Report No. PB85-222792.)

Hansen, M.C. 1985. Summary of air quality observed at the Sandalta site, April 1984 to March 1985. Prep. for Alberta Environment by Western Research Division of Bow Valley Resource Services Ltd. 60 pp.

Hansen, M.C. 1986. Summary of air quality observed at the Sandalta site, April 1985 to March 1986. Prep. for Alberta Environment by Western Research Division of Bow Valley Resource Services Ltd. 61 pp.

Healey, J. 1986. Mountain cloud chemistry project site operator's manual. Prep. by the Management Center of the Mountain Cloud Chemistry Project, W.S. Fleming and Associates, Inc. Albany, New York. 33 pp.

Heit, M., Y. Tan, C. Klusek, and J.C. Burke. 1981. Anthropogenic trace elements and polycyclic aromatic hydrocarbon levels in sediment cores from two lakes in the Adirondack Acid Lake region. Water, Air, and Soil Pollution 15(4):441.

Hicks, B.B. 1985. Application of forest-canopy-atmosphere turbulent exchange information. In: Hutchison, B.A., and B.B. Hicks, eds. 1985. The forest-atmosphere interaction. Boston: D. Reidel Publishing Company. pp. 631-644.

Hicks, B.B. 1986. Notes on dry deposition program development. Communication to M. Lusis, Ontario Ministry of the Environment: 1986 October 08.

Hicks, B.B., R.P. Hosker, and J.D. Womack. 1986. Description and operating details of the NOAA/ATDD dry deposition inferential measurement system (DDIMS). National Oceanic and Atmospheric Administration, Atmospheric Turbulence and Diffusion Division. Oak Ridge, Tennessee, November.

Hidy, G.M. and J.R. Young. 1986. Acid deposition and the west: a scientific assessment. Environment Research and Technology Document No. P-D572-503. 187 pp.

Hileman, B. 1983. Acid fog. Environmental Science and Technology 17(3): 117A-120A.

Hosker, R.P., Jr. and S.E. Lindberg. 1979. Review: atmospheric deposition and plant assimilation of gases and particles. Atmospheric Environment 16(5):889-910.

Hosker, R.P., K.S. Rao, and B.B. Hicks. 1984. Preliminary estimates of airborne pollutant fluxes to the Camp Branch and Cross Creek watersheds. Prep. for U.S. Department of Energy by National Oceanic and Atmospheric Administration. Oak Ridge, Tennessee. 104 pp. (Available from NTIS, Report No. DE85-016914.)

Hosker, R.P., K.S. Rao, and B.B. Hicks. 1984. Preliminary estimates of airborne pollutant fluxes to the Camp Branch and Cross Creek watersheds. NOAA Technical Report ERL ARL-131. 97 pp. (Available from NTIS, Report No. PB85-161982.)

Hutchison, B.A. and B.B. Hicks, eds. 1985. The forest-atmosphere interaction. Boston: D. Reidel Publishing Company. 684 pp.

Irving, P.M. 1983. Acidic deposition effects on vegetation: A review and analysis of methodology. Prep. for US Department of Energy by Argonne National Laboratory, Argonne, Illinois. 37 pp. (Available from NTIS, Report No. DE84-004014.)

Jacobsen, J.S. 1983. Ecological effects of acid rain. Journal of the Air Pollution Control Association 33(11):1031-1054.

Jaeger, L. 1985. Estimations of surface roughness and displacement heights above a growing pine forest from wind profile measurements over a period of 10 years. From The Forest Atmosphere Interaction edited by B.A. Hutchison and R.B. Hicks, D. Reidel Publishing Company. pp. 71-90.

James, B.R. and S.J. Riha. 1984. Soluble aluminum in acidified organic horizons of forest soils. Canadian Journal of Soil Science 64(1984): 637-646.

Johnson, D.W. 1983. Acid rain and forest productivity. In: Green, A.E.S. and W.H. Smith, eds. 1983. Acid deposition causes and effects. A state assessment model. Proceedings of a workshop. 1983 March 23-24; University of Florida, Gainsville, Fla. pp. 37-52.

Johnson, D.W. 1985. Changes in soil acidity due to natural processes and acid deposition. Proceedings of the NATO ARW conference on effects of acidic deposition on forests, wetlands, and agricultural ecosystems. 1985 May 12; Toronto, Ontario. 22 pp. (Available from NTIS, Report No. DE85-012103.)

Johnson, D.W., H. Van miegroet, D.W. Cole, and D.D. Richter. 1983. Contributions of acid deposition and natural processes to cation leaching from forest soils: A review. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 20 pp. (Available from NTIS, Report No. DE83-014027.)

Johnson, D.W., S.E. Lindberg, E.A. Bondietti, and L.F. Pitelka. 1986. The integrated forest study on effects of atmospheric deposition. Oak Ridge National Laboratory, Environmental Sciences Division. (Available from NTIS, Report No. DE86-005022.)

Jones, H.C., F.P. Weatherford, J.C. Noggle, and C. McDuffie, Jr. 1986. Air pollution measurement and effects research: A perspective on agriculture and forests. In: Proceedings of the NAPAP Workshop on Dry Deposition, Draft Report. 1986. Harpers Ferry, West Virginia: 1986 March 25-27.

Kaemal, J.C. 1986. Flux and profile measurements from towers in the boundary layer. From Probing the Atmospheric Boundary Layer edited by D.H. Lenschow, American Meteorological Society. pp. 19-28.

Kelly, J.M. 1984. Litterfall sulfur and nitrogen inputs as influenced by power plant proximity. Water, air, and Soil Pollution 27(2): 143-152.

Krouse, H.R., A.H. Legge, and H.M. Brown. 1984. Sulphur gas emissions in the boreal forest: The West Whitecourt case study V: Stable Sulphur Isotopes. Water, Air and Soil Pollution 22(1984): 321-347.

Krupa, S., R.N. Kickert, and M. Nosal. 1986. An analysis of numerical models of air pollutant exposure and vegetation response. In: Proceedings of the Second Symposium and Workshop on Acid Forming Emissions in Alberta and Their Ecological Effects. 1986 May 13-15; Calgary, Alberta.

Labine, C. 1986. Environmental monitoring considerations of integrating new technology to forestry. Presented at Forest Climate '86 Symposium/Workshop on Climate Applications in Forest Renewal and Forest Reproductions. 1986 November 17-20. Orillia, Ontario.

Lam, D.C.L., A.G. Bobba, D.S. Jeffries, and J.M.R. Kelso. 1986. Relationships of spatial gradients of primary production, buffering capacity, and hydrology in Turkey Lakes watershed. In: Isom, B.G., S.D. Dennis, and J.M. Bates, eds. 1986. Impact of acid rain and deposition on aquatic biological systems. Philadelphia: American Society for Testing and Materials. 114 pp.

Lannefors, H.O. and B.L.B. Wiman. 1985. Aerosol characteristics in a mature coniferous forest - methodology, composition, sources and spatial concentration variations. Atmospheric Environment 19(2):349.

Lee, J.J., and D.E. Weber. 1978. The effect of simulated acid rain on seedling emergence and growth of eleven woody species. Forest Science 3(25):393-398.

Legge, A.H. 1982. Sulphur gas emissions in the Boreal Forest: the West Whitecourt case study; II: research plan and background. Water, Air, and Soil Pollution 17(1982):379-398.

Legge, A.H. and J.C. Bogner. 1986. Foliar sulphur: a measure of the state of forest ecosystems under air pollution stress. Proceedings of the Seventh World Clean Air Congress. 1986; Sydney, Australia; Volume II: 118-125.

Legge, A.H., D.R. Jaques, G.W. Harvey, H.R. Krouse, H.M. Brown, E.C. Rhodes, M. Nosal, H.U. Schellhase, J. Mayo, A.P. Hartgerink, P.F. Lester, R.G. Amundson, and R.B. Walker. 1981. Sulphur gas emissions in the Boreal Forest: the West Whitecourt case study; I: executive summary. Water, Air, and Soil Pollution 15(1981): 77-85.

Lester, P.F., E.C. Rhodes, and A.H. Legge. 1986. Sulphur gas emissions in the Boreal Forest: the West Whitecourt case study; IV: air quality and the meteorological environment. Water, Air, and Soil Pollution 27(1986):85-108.

Lindberg, S.E. 1986. Collection and analysis of trace metals in continental precipitation at forested sites in the southeastern United States. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 16 pp. (Available from NTIS, Report No. DE86-008540.)

Lindberg, S.E. and R.C. Harriss. 1981. The role of atmospheric deposition in an eastern US deciduous forest. Water, Air, and Soil Pollution 16(1981):13-31.

Lindberg, S.E., and G.M. Lovett. 1982. Application of surrogate surface and leaf extraction methods to estimation of dry deposition to plant canopies. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 10 pp. (Available from NTIS, Report No. DE83-003435.)

Lindberg, S.E., R.C. Harriss, and R.R. Turner. 1982. Atmospheric deposition of metals to forest vegetation. Science 215:1609-1611.

Lindberg, S.E. and G.M. Lovett. 1985. Field measurements of particle dry deposition rates to foliage and inert surfaces in a forest canopy. Environmental Science and Technology 19(3):238.

Lindberg, S.E., S.B. McLaughlin, and D.W. Johnson. 1984. An overview of research at Oak Ridge National Laboratory on effects of atmospheric pollution on forest systems. Prep. for the German/American Exchange on Forest Decline. Oak Ridge, Tennessee. 54 pp. (Available from NTIS, Report No. DE85-017580.)

Lindberg, S.E., D.S. Shriner and W.A. Hoffman Jr. 1981. The interaction of wet and dry deposition with the forest canopy. Prep. for the Office of Health and Environmental Research, US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 32 pp.

Lindberg, S.E., R.R. Turner, and G.M. Lovett. 1982. Processes of atmospheric deposition of metals and acids to forests. Prep. for Electric Power Research Institute and US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 14 pp. (Available from NTIS, Report No. DE82-017442.)

Lindberg, S.E., R.R. Turner, D.S. Shriner, and D.D. Huff. 1981. Atmospheric deposition of heavy metals and their interaction with acid precipita- tion in a North American deciduous forest. Prepared for the Office of Health and Environmental Research, US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 4 pp. (Available from NTIS, Report No. CONF-810963-1.)

Lindberg, S.E., R.R. Turner, and G.M. Lovett. 1982. Processes of atmospheric deposition of metals and acids to forests. Prep. for Electric Power Research Institute and US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 14 pp. (Available from NTIS, Report No. DE82-017442.)

Lindberg, S.E., G.M. Lovett, E.A. Bondietti, and C.I. Davidson. 1984. Recent field studies of dry deposition to surfaces in plant canopies. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 20 pp. (Available from NTIS, Report No. DE85-001281.)

Lindberg, S.E., G.M. Lovett, D.D. Richter, and D.W. Johnson. 1986. Atmospheric deposition and canopy interactions of major ions in a forest. Science 231(1986): 141-145.

Lovett, G.M. 1983. Pollutant deposition in mountainous terrain. Prep. for the Electric Power Research Institute and the Office of Health and Environmental Research, US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 16 pp. (Available from NTIS, Report No. DE84-012350.)

Lovett, G.M., and W.A. Reiners. 1982. Cloud water: an important vector of atmospheric deposition. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 9 pp. (Available from NTIS, Report No. DE83-004646.)

LRTAP Liaison Office. 1986. Canadian research catalog on LRTAP and acid rain. Environment Canada, Atmospheric Environment Service, Downsview. 180 pp.

Mahendrappa, M.K. 1986. Abilities of organic horizons under some eastern Canadian forest stands to alter the acidity of rainwater. Canadian Jornal of Forest Research 16: 18-22.

Marmorek, D.R., D.P. Bernard, M.L. Jones, C.S. Davis, N.W. Reid, A.R. Fradkin, and R.B. Caton. 1986. Target loadings for acidic deposition in western Canada: A synthesis of existing information. Prep. for the Western Target Loading Planning Group and the National Research Council Associate Committee on Scientific Criteria for Environmental Quality by ESSA Environmental and Social Systems Analysts Ltd. and Concord Scientific Corporation. Vancouver, British Columbia. 201 pp.

McLaughlin, S.B. 1985. Effects of air pollution on forests; a critical review. Journal of the Air Pollution Control Association 35(5): 512-534.

McLaughlin, S.B., D.C. West, and T.J. Blasing. 1984. Measuring effects of air pollution stress on forest productivity: perspectives, problems, and approaches. Tappi Journal 67(1):74.

McLaughlin, S.B., T.J. Blasing, L.K. Mann, and D.N. Duvick. 1983. Effects of acid rain and gaseous pollutants on forest productivity: A regional scale approach. Journal of the Air Pollution Control Association 33(11):1042-1048.

McLaughlin, S.B., C.F. Baes III, G.E. Taylor, R.F. Walker, L.L. Sigal, R.K. McConathy, and R.J. Norby. 1984. Interactive effects of acid rain and gaseous air pollutants on natural terrestrial vegetation. Prepared for US Environmental Protection Agency by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 14 pp. (Available from NTIS, Report No. DE85-005255.)

Miller, P.R., O.C. Taylor, and R.G. Wilhour. 1982. Oxidant air pollution effects on a western coniferous forest ecosystems. Prep. for Corvallis Environmental Research Laboratory by Pacific Southwest Forest and Range Experiment Station. Riverside, California. 12 pp. (Available from NTIS, Report No. PB83-189308.)

Mohnen, V.A. 1984. Atmospheric deposition to mountain forest systems: workshop proceedings April 1984. Prep. for National Science Foundation by State University of New York at Albany. Albany, New York. 63 pp. (Available from NTIS, Report No. PB84-246412.)

Mohnen, V.A, J. Healey, and R. Bradow. 1985. Mountain cloud chemistry quality assurance project plan: cloud-precipitation deposition monitoring. Prep. by the Management Center of the Mountain Cloud Chemistry Project, W.S. Fleming and Associates, Inc. Albany, New York. 51 pp.

Morrow, M. and W.A. Murray. 1982. Climatological and Air Quality Report for Gulf Sandalta 1981-1982. Prep. for Gulf Canada Resources Inc. by Promet Environmental Group Ltd. 70 pp.

Murphy, C.E. Jr. and R. Lorenz. 1985. Analysis of forest environmental measurements to estimate parameters of microclimate and air pollution deposition velocity models. In: Hutchison, B.A. and B.B. Hicks, eds. 1985. The forest-atmosphere interaction. Boston: D. Reidel Publishing Company. pp. 383-393.

Murray, W.A. 1981. The 1981 snowpack survey on the AOSERP study area. Prep. for the Alberta Oil Sands Environmental Research Program by Promet Environmental Group Ltd. AOSERP Report 125. 137 pp.

Murray, W.A. 1984. Background Air Quality Sandalta Trailer, May 1983 to March 1984. Prep. for Alberta Environment by Promet Environmental Group Ltd. 74 pp.

Muylwyk, R. 1982. Solar Cells Power Monitors in Remote and Cold. Pollution Engineering, August. pp. 32-33.

National Resource Ecology Laboratory. 1985. NADP/NTN annual data summary. Precipitation chemistry in the United States, 1983. Prep. for the National Atmospheric Deposition Program, US Geological Survey. Fort Collins, Colorado.

National Swedish Environment Protection Board. 1983. Ecological effects of acid deposition. Report and background papers 1982. Proceedings of the Stockholm conference on the acidification of the environment. 1982 June 21; Stockholm, Sweden. 320 pp. (Available from NTIS, Report No. DE85-750164.)

Neary, A., ed. 1986. Procedures manual, terrestrial effects. Acidic Precipitation in Ontario Study. Prep. for the Ontario Ministry of the Environment by the Technical Subcommittee of the Terrestrial Effects Working Group. Toronto, Ontario. 95 pp.

Nosal, M. 1983. Atmosphere-biosphere interface: probability analysis and an experimental design for studies of air pollutant-induced plant response. Prep. for Alberta Environment by Statistical Research Laboratory, University of Calgary. Edmonton, Alberta. RMD Report 83/25. 98 pp.

Olson, R., B. Thomson, H. Bertram, and R. Peters. 1982. Athabasca Oil Sands Precipitation Chemistry Studies 1976-79 and 1981. Prep. for Alberta Environment by Alberta Environment and Alberta Environmental Centre. AOSERP Report 129. 59 pp.

Orr, D.B., J.C. Hipfner, W.C. Chan, M.A. Lusis, and J.E. Hunt. 1986. The application of a passive permeation device for the measurement of ambient sulfur dioxide. Accepted for publication in Atmospheric Environment.

Overrein, L.N., H.M. Seip, and A. Tollan. 1980. Acid precipitation - effects on forest and fish. Final report of the SNSF-project 1972-1980, prepared for the Norwegian Council for Scientific and Industrial Research, the Agricultural Research Council of Norway, and the Norwegian Ministry of the Environment. Oslo, Norway. 175 pp.

Peake, D., M.A. MacLean, P.F. Lester, and H.S. Sandhu. 1986. Secondary air pollutants (peroxyacetyl nitrate, nitric acid, particulate nitrate, and ozone) in Alberta, Canada. Proceedings of the Seventh World Clean Air Congress. Sydney, Australia. Volume III; 226-233.

Perttu, K. 1985. Data acquisition for forest environmental measurements in Sweden. In: Hutchison, B.A., and B.B. Hicks, eds. 1985. The forest-atmosphere interaction. Boston: D. Reidel Publishing Company. pp. 105-115.

Peters, R.R. and H.S. Sandhu. 1980. Nitrogen oxides emissions for Alberta, 1976-1979. Prep. by Alberta Environment, Research Management Division. 12 pp.

Phipps, R.L. and L.J. Puckett. 1984. Historical perspective on tree growth patterns: tree-ring analysis evidence for the effects of acid deposition on trees. Proceedings of the US-Canadian Forest Responses to Acidic Deposition Conference. 1984 March; Orono, Maine. p. 73.

Pollution Control Division. 1982. Industrial sulphur emissions for Alberta, 1977-1981. Alberta Environment. 32 pp.

Pollution Control Division. 1984. Nitrogen oxides emissions for Alberta 1978-1982. Alberta Environment. 21 pp.

Pringle, J., ed. 1986. Research Management Division, Alberta Environment: Publications Catalogue. Alberta Environment RMD 86/34. 92 pp.

Prinz, B. 1985. Effects of air pollution on forests: critical review discussion papers. Journal of the Air Pollution Control Association 35(9): 913-924.

Proceedings of the NAPAP Workshop on Dry Deposition, Draft Report. 1986. Harpers Ferry, West Virginia. 1986 March 25-27.

Research Management Division. 1986. An Acid Deposition Research Program for Alberta Environment 1986/87 to 1990/91. Research Management Division, Alberta Environment. 164 pp.

Rudolph, E. and G. Halbwachs. 1983. The bioindicator-monitoring network "Inn-Salzach-Area" - a border crossing network. European Journal of Forest Pathology 13(5/6):334-343.

Rudolph, R.C., M.M. Oleskiw and R.A. Stuart. 1984. Climatological analyses of recent data from the Athabasca Oil Sands area. Prepared for the Alberta Oil Sands Environmental Research Program by Intera Environmental Consultants Ltd. AOSERP Report 130. 199 pp.

Sandhu, H.S. 1979. Industrial sulphur emissions for Alberta, 1974-1978. Alberta Environment. 21 pp.

Schell, W.R. 1986. Deposited atmospheric chemicals. Environmental Science and Technology 20(9):847-853.

Schwiesow, R.L. 1986. A Comparative Overview of Active Remote-Sensing Techniques. From Probing the Atmospheric Boundary Layer edited by D.H. Lenschow, American Meteorological Society. pp. 19-28.

Shriner, D.S., C.R. Richmond, and S.E. Lindberg. 1980. Atmospheric sulfur deposition: environmental impact and health effects. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc. 568 pp.

Simpson, J.R., M.O. Smith, R.D. Stevenson, and L.J. Fritschen. 1985. An approach to microcomputer based data acquisition and control for forest environmental measurements. In: Hutchison, B.A. and B.B. Hicks, eds. 1985. The forest-atmosphere interaction. Boston: D. Reidel Publishing Company. pp. 117-132.

Smith, S.B. 1981. Alberta Oil Sands Environmental Research Program, 1975-1980: Summary report. Prep. for the Alberta Oil Sands Environmental Research Program by S.B. Smith Environmental Consultants Limited. AOSERP Report 118. 170 pp.

Steinnes, E. and H.W. Nuernberg, eds. 1983. Monitoring of trace element deposition by means of mosses. Zeitschrift Analytische Chemie 317(3/4).

Strosher, M.M. 1978. Ambient air quality in the AOSERP study area, 1977. Prep. for Alberta Oil Sands Environmental Research Program by Alberta Department of the Environment, Pollution Control Division. AOSERP Report 30. 74 pp.

Strosher, M.M. 1981. Background air quality in the AOSERP study area, March 1977 to March 1980. Prep. for Alberta Environment by Pollution Control Division, Alberta Environment. AOSERP Report 173. 84 pp.

Strosher, M.M. and R.R. Peters. 1980. Meteorological factors affecting ambient SO_2 concentrations near an oil sands extraction plant. Prepared for Alberta Oil Sands Environmental Research Program by Alberta Environment, Pollution Control Division and AOSERP. AOSERP Report 106. 87 pp.

Swift, L.W. and H.L. Roysdale. 1985. Meteorological Data Stations at Long-term Ecological Research Sites. From the Forest Atmosphere Interaction edited by B.A. Hutchison and R.B. Hicks: D. Reidel Publishing Company. pp. 25-37.

Talbot, R.W. and A.W. Andren. 1983. Relationships between Pb and Pb-210 in aerosol and precipitation at a remote site in northern Wisconsin. J. Geophys. Res. 9:474-496.

Taylor, G.E. and R.J. Norby. 1984. Significance of elevated levels of ozone on natural ecosystems of North America. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 25 pp. (Available from NTIS, Report No. DE86-002185.)

Technical Committee for the Long-Range Transport of Atmospheric Pollutants in Western and Northern Canada. 1986. Western and Northern Canada acid deposition/LRTAP activities, annual report 1985. Prep. for Alberta Environment. Edmonton, Alberta. 26 pp.

Tomlinson, G.H. III. 1983. Air pollutants and forest decline. Environmental Science and Technology 17(6):246A-256A.

Torrenueva, A.L. 1985. Effects of acid deposition on forest. Phase I: critical assessment of the scientific literature. Prep. for the Canadian Electrical Association by Ontario Hydro Environmental Studies and Assessments Department. Toronto, Ontario. 175 pp.

Turner, R.R., M.A. Bogle, and C.F. Baes. 1985. Survey of lead in vegetation, forest floor, and soils of the Great Smoky Mountains National Park. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 117 pp. (Available from NTIS, Report No. DE85-018119.)

Turner, R.R., S.E. Lindberg, and J.M. Coe. 1985. Comparative analysis of trace metal accumulation in forest ecosystems. Prep. for the US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 3 pp. (Available from NTIS, Report No. DE85-013988.)

Turner, R.S., D.W. Johnson, J.N. Elwood, W. Van Winkle, and R.B. Clapp. 1986. Factors affecting the long-term response of surface waters to acidic deposition: state-of-the-science. Prep. for US Department of Energy by Oak Ridge National Laboratory. Oak Ridge, Tennessee. 271 pp. (Available from NTIS, Report No. DE86-010006.)

Ulrich, B. 1984. Effects of air pollution on forest ecosystems and waters: the principles demonstrated at a case study in central Europe. Atmospheric Environment 18(3):621-628.

Vandenberg, J.J. and K.R. Knoerr. 1985. Comparison of surrogate surface techniques for estimation of sulfate dry deposition. Atmospheric Environment 19(4):627.

Wang, D., F.H. Bormann, and D.F. Karnosky. 1986. Regional tree growth reductions due to ambient ozone: evidence from field experiments. Environmental Science and Technology 20(11):1122-1125.

Wiebe, H.A., R.J. Vet, L.A. Barrie and K. Anlauf. 1985. Canadian Air and Precipitation Monitoring Network (APN) Final Data Report, December 1982-1983, Atmospheric Environment Service, Downsview, Ontario. 51 pp.

Woodman, J.N. and E.B. Cowling. 1987. Airborne Chemicals and Forest Health. Environ. Sci. Technol. 21(2):120-126.

8.3 WORKSHOP ATTENDEES

Mr. Randy Angle - Alberta Environment, Pollution Control Division
Mr. Earle Baddaloo - Alberta Environment, Research Management Division
Mr. Neil Barnes - Forestry, Lands and Wildlife; Forest Land Use Branch
Ms. Esmeralda Cabral - Alberta Environment, Research Management Division
Dr. Robert Caton - Concord Scientific Corporation
Dr. Roy A. Crowther - Aquatic Resources Management
Mr. Mervyn Davies - Concord Scientific Corporation
Dr. Claude Davis - Concord Scientific Corporation
Mr. Sven Djurfors - Syncrude Canada Ltd.
Dr. Yan Lau - Alberta Environment, Pollution Control Division
Dr. Allan Legge - Kananaskis Centre for Environmental Research, University of Calgary
Dr. Maris Lusis - Ontario Ministry of the Environment
Ms. Bonnie Magill - Alberta Environment, Research Management Division
Mr. Doug Maynard - Canadian Forest Service
Mr. Dave McCoy - Canterra Energy
Mr. Robert Myrick - Alberta Environment, Research Management Division
Dr. Craig Palmer - Alberta Environment, Earth Sciences Division
Mr. Chris Powter - Alberta Environment, Research Management Division
Dr. Percy Sims - Alberta Environment, Research Management Division
Dr. Glen Singleton - Alberta Environment, Research Management Division
Dr. Larry Turchenek - Alberta Research Council
Dr. Ron Wallace - Dominion Ecological Consulting Ltd.
Dr. Tony Yarranton - Yarranton Holdings Ltd.

8.4 METHODS AND PROTOCOLS

A. Passive SO_2 Sampler
B. Bulk Precipitation Sampler
C. Snow Core Sampling
D. Filter Pack Method
E. Wet-Only Precipitation Sampler (Aerochem Metrics)
F. Dry-Only Deposition Collector (ORNL)
G. Analytical Method - Sulphate Analysis by Automated Ion Chromatography Method B

8.4A. PASSIVE SO_2 SAMPLER

1. Description

The passive SO_2 sampler consists of a wafer-type holder (37 mm) with an impregnated Whatman 41 cellulose filter placed between two polycarbonate Nuclepore 8 μm pore membranes. The Whatman 41 filters are impregnated with a potassium carbonate (25% w/v)/glycerol (10% v/v) solution. The wafer filter holder is placed in a shelter (inverted plastic plant holder) and exposed for a predetermined time period (typically 28 days).

2. Filter Preparation Procedure

The teflon and nylon filters used in the sampling network can be obtained commercially from Membrana Corporation. The cellulose (W-41) filters are impregnated with a potassium carbonate/glycerol solution. All filters are stored in a desiccator in their original packages or containers when not in use.

Solution Preparation

1. Wash the roller, tray, volumetric flask, and glass sheets thoroughly using ethanol and rinse with deionized distilled water. Dry this equipment using Kimwipes.
2. Add into a 1-L volumetric flask approximately 300 mL of deionized distilled water. Dissolve 250 g of potassium carbonate (K_2CO_3) into the deionized distilled water.
3. Add 100 mL glycerol to this solution. Bring the total volume of the solution up to 1000 mL with deionized distilled water.

4. Thoroughly mix the 1-L solution to dissolve the K_2CO_3 completely.

Filter Impregnation

1. Pour a sufficient amount of the solution into the clean tray to cover a filter sheet. Using clean polyethylene gloves and clean forceps soak the 8" x 10" Whatman 41 filter sheets in the solution (soak individually).
2. Place the soaked filter sheets onto the clean glass sheets. Any excessive solution is then removed by using a hand-held roller.
3. Place the sheets into a drying oven for approximately 30 minutes at 60°C.

Filter cutting

1. After the filter sheets have been dried, place a non-impregnated sheet on the top and bottom of a stack of five impregnated sheets. These sheets are then placed on a plastic cutting board.
2. A 40-mm cutting die cleaned with ethanol and deionized water is placed onto the drill chuck. The sheets are cut, discarding the top and bottom non-impregnated cut filters. The impregnated cut filters are then placed into new Whirlpak bags. Each bag is given a batch number. Filters are stored in a desiccator to avoid contamination.

Source: APIOS Technical and Operating Manual, Section 4.3.2.1.1.

3. Filter Extraction

Whatman 41 filters are extracted in a beaker in an automatic shaker with 50 mL of 0.05% (v/v) hydrogen peroxide. This is followed by a 15 minute shaking in 25 mL hydrogen peroxide which is made up to 100 mL with hydrogen peroxide.

4. Analysis for $SO_4^=$

As outlined in the Ontario Ministry of the Environment Handbook of Analytical Methods for Environmental Samples (Page SH13-SH21). The method is reproduced in its entirety in Appendix 8.4G.

5. QA/QC

Quality assurance/quality control procedures to include:

- colocate passive samplers;
- field blanks;
- blank filters from each batch of filters prepared; and
- laboratory QA/QC as outlined in analytical method.

REFERENCES TO METHOD

Bardswick, W.S. 1983. Technical and Operating Manual, APIOS Deposition Monitoring Program. Report by Ontario Ministry of the Environment, Air Resources Branch. Toronto, Ontario.

Concord Scientific Corporation. 1980. Evaluation of Modified Long-Term Passive SO_2 Ambient Air Monitors. Report by Concord Scientific Corporation and United Technology and Science. Toronto, Ontario.

Ontario Ministry of the Environment. 1983. Handbook of Analytical Methods for Environmental Samples. Report by Ontario Ministry of the Environment, Laboratory Services and Applied Research Branch. Rexdale, Ontario.

Orr, D., M. Lusis, J. Hipfner, W. Chan, and J.E. Hunt. 1986. The Application of a Passive Permeation Device for the Measurement of Ambient Sulfur Dioxide, accepted for publication by Atmospheric Environment.

8.4B. BULK PRECIPITATION SAMPLER

1. Description

Sampler consists of a 100-L polyethylene container (commonly used as a domestic refuse receptacle) with polyethylene bag inserts.

2. Sample Collection and Handling Procedures

Remove the bungy cord from the sample bucket being careful not to lift it over the sample bag (to avoid contamination falling from the cord into the sample bag).

Remove the sample bag as follows:

- Gently push the portion of the bag which is outside the bucket up over the top of the bucket about 1 inch.
- Grasp the portion of the bag above the bucket between the thumb and forefinger of each hand and lift the sample bag out.
- Holding the top of the bag with one hand, use the other hand to squeeze the bag just under the fold (approximately 1 inch down from the point where the bag folded over the edge of the bucket).
- Gently squeeze any excess air out of the bag and then tie the bag where it was squeezed with a cable tie.
- Place the sample bag upright into the supplies box.

Deployment of New Sample Bags.

- Put on a clean pair of disposable plastic gloves. Grasp a clean bag near the top and separate the two halves. Do not place fingers further than 3 inches into the bag at any time.

- Placing thumbs inside the bag and fingers outside, shake the bag in the air until it has expanded fully.
- Leave a small amount of air in the bag and squeeze near the top so that the bag is half full of air.
- Push the bag into the bucket until it hits the bottom (Note: this is necessary to keep the bag partially inflated in order to displace the air in the bucket).
- Slide the fold over the top of the bucket so that 3 to 4 inches of the bag extend down the outside of the bucket.
- Put on a clean glove being careful not to touch the fingers of the gloves. (Note: it is very important to use a new glove because the next step requires the hand to touch the inside of the bag where precipitation will collect.)
- Reach into the bag at the rim of the bucket and flatten the bag against the top of the inside wall. Do not shove your hand all the way into the bag, insert it only to the depth of the glove.
- Secure the bag to the outside of the bucket using the bungy cord supplied. The bungy cord should be attached approximately 2 inches down from the top of the bucket just under the second ridge around the bucket.

Decanting Procedures

Samples should be decanted in a clean work area to avoid possible contamination.

- Bring the sample indoors and place upright on a clean level surface. If the precipitation sample is frozen, allow the sample to melt.
- Swirl the bag to liberate any particles that may have adhered to the walls of the bag.
- Take the lid off from one of the polystyrene sample bottles and place the lid upside down being careful not to touch the inside of the lid. Check the bottle for any flaws, cracks, or visible contamination. If the integrity of the bottle is doubted, discard it and use another one. Clean one bottom corner of the bag with distilled water and a Kimwipe. Wipe dry with a Kimwipe. Clean the scissors with distilled water and a Kimwipe. Wipe the scissors dry with a Kimwipe. (Note: clean both blades in the open position).
- Elevate the cleaned corner of the bag and cut off the corner using the scissors. Lower the corner and carefully pour the sample into the sample bottle.
- Label the bottle with the station name, number, and collection date using labels provided. Store the sample in a refrigerator.

Source: APIOS Technical and Operating Manual Sections 4.3.1.1.1, 4.3.1.1.3 and 4.3.1.1.4.

3. <u>Sample Analysis</u>

Precipitation sample to be filtered through a 0.45 μm membrane filter. Filtrate to be analyzed for $SO_4^=$ (by IC) as outlined in the Handbook of Analytical Methods for Environmental Samples (Page SH13-SH21). The method is reproduced in its entirety in Appendix 8.4G.

4. <u>QA/QC</u>

Quality assurance/quality control procedures to include:

- colocate sampler;
- split or duplicate samples;
- field blanks;
- blank bags; and
- analytical QA/QC as outlined in analytical method.

8.4C. SNOW CORE SAMPLING

As outlined in the attached reference.

SNOWPACK: RECOMMENDED METHODS FOR SAMPLING AND SITE SELECTION.

WORK GROUP

D.K. Sandberg, B.C. Ministry of Environment and Parks, Vancouver, B.C.
Co-ordinator.

N.R. McQuaker, B.C. Ministry of Environment and Parks, Vancouver, B.C.

R.J. Vet, Environment Canada, Downsview, Ontario

H.A. Weibe, Environment Canada, Downsview, Ontario.

TABLE OF CONTENTS

I. INTRODUCTION

This report has been prepared under the auspices of the Quality Assurance Sub-Group reporting to the Federal-Provincial Research and Monitoring Coordinating Committee (RMCC) for the Long Range Transport of Atmospheric Pollutants. The objective of this report is to recommend methods for monitoring snowpack chemistry with particular reference to methods for site selection and sampling. Specific terms of reference include the following:

1. To review procedures for monitoring snowpack chemistry on a regional/national basis;
2. To explore in detail current approaches to siting criteria and to recommend siting criteria suitable for monitoring snowpack;
3. To explore in detail current approaches to sampling and to recommend appropriate procedures; and
4. To identify Quality Assurance requirements for snowpack monitoring.

The various recommendations appearing in this report are made with the realization that they will be reviewed on an on-going basis and undoubtedly revised as further experience is obtained.

This report provides guidelines for the execution of snowpack sampling programs so as to assure the production of valid data. Various programs may moderate or change some of the guidelines to meet logistical or specialized needs of the program involved.

II. SITE SELECTION

Sites are chosen with the objective of monitoring snowpack chemistry on a regional spatial scale at a specific time. A regional scale will usually define a rural or remote area of reasonably homogeneous geography and may extend from tens to hundreds of kilometres. Snowpack data of this scale provide information on the larger scale processes of pollutant transport, transformation and deposition as they relate to precipitation chemistry as well as wet and dry deposition.

The selection of the number of sampling sites in a large geographical area will require consideration of an adequate representation of non-homogenous topography, snow depth and snowpack chemistry.

The sampling site itself must be chosen at a location representative of the region, preferably in representative topography that is somewhat sheltered from effects of wind.

1. Within 50 km of the site there will be no anthropogenic emission sources which could affect precipitation chemistry. Sources greater than 50 km from the site are considered to exert a regional influence.
2. Within 1.0 km of the site, there will be no local sources of contamination, such as:
   - i. Air, water, or surface transportation (especially roads).
   - ii. Surface sources such as sewage treatment lagoons.
   - iii. Furnaces, incinerators, or combustion sources.
   - iv. Any residential, commercial, or industrial activities.

3. Wherever possible, the sampling site shall be located at a distance of 2.5 times the height of any object protruding above ground level. An optimal site would be the centre of a clearing, completely surrounded by trees where the radius of the clearing is 2.5 times the tree height. The snowpack should be observed to be free of debris from surrounding objects (ie. trees).
4. The site shall be located in such a way that extreme local meteorological conditions such as high winds, leeward/windward effects, etc. are minimized.
5. The sampling site should be free of any evidence of drifting or wind scouring of the snowpack.
6. Whenever possible, the site should be located at a terrestrial location. If sites are selected over frozen bodies of surface water, care should be taken to avoid:
    a. non-representative snow depth due to wind scouring
    b. lack of access during freeze up and thaw
    c. unsuitability of lake sites in temperate areas (e.g., coastal)
    d. inability to define snowpack layers from ice layers at the interface level

III. SITE DOCUMENTATION

Site documentation describing the site must be available and should include the following:

1. Latitude and Longitude or Universal Transverse Mercator Co-ordinates of site;
2. Elevation of site above sea level;
3. Physical characteristics of the site including distance from obstructions, heights of obstructions, ground type (if determined) and topography of the site and region;
4. Distance of site from emission sources (stationary and mobile);
5. Site photographs to consist of five photos: one site in each of the cardinal directions looking out from site and one close-up of the site. An aerial photograph should be included when available;
6. Geographic delineation of region represented by the site.

Additional site documentation may include:

1. Appropriate topographic map;
2. Information on normal meteorological conditions expected;
3. Means of site access.

IV. SAMPLING PROCEDURES

A. Sampling Time

In selecting sampling times, consideration must be given to periods of freezing and thawing during the accumulation period of the snowpack as snowpack composition changes significantly when thawing occurs. Documentation must be included of the sampling times and snowpack conditions which the sample is chosen to represent. Acceptable choices of sampling times include:

1. Collection of an identifiable column of snowpack which has been deposited during a defined period when melt has not occurred, (once or more per year). These samples will quantitatively represent wet and dry deposition over the accumulation period of the snowpack.
2. Collection of a complete profile with segregation of strata that were not subject to melt and strata that were subject to melt into separate samples.
3. Collection of a "snowpack composite" designed to represent in one sample the snowpack chemistry up to that time. These samples will not quantitatively represent the true deposition to that time if melts had occurred.

B. Sampling Equipment

1. Snow Sampler

Acceptable techniques for sampling snowpack include:

Core Sampling - inserting a hollow tube (snowcorer) into the snowpack to a desired depth and removing a snow 'core'.

Pit Sampling - exposing a profile of the snowpack by digging a pit followed by the removal of undisturbed snow from the snowpack profile using a scoop.

The required characteristics of the sampling device (tube or scoop) are as follows:

1. Able to allow removal of a representative sample of a snowpack, i.e., a representative column of snow from the desired portion of the snowpack profile.
2. Able to remove a column of snow of a known sampling diameter and depth and (if required) able to allow segregation of melted and non-melted layers in the entire column.
3. Able to remove a column of snow which, after melting, will provide a liquid volume sufficient for the required chemical analyses.
4. Able to minimize disruption of any stratified layers within the column of snow.
5. Composed of material proven to minimize or avoid contamination of the sample through absorption or desorption effects.

6. Able to be used at very low temperatures and in adverse weather conditions such as high wind.
7. Able to be operated in a simple manner so as to avoid complicated or time-consuming field procedures.
8. Able to be transported to site with little effort and without being contaminated in transit (lightweight/compact).
9. Able to accommodate variable snow depths up to an expected maximum.

2. <u>Sample Bags/Bottles</u>

After removal from the snowpack, snow samples should be transferred from the corer/scoop to plastic sample bags, using contamination-free procedures. If a snowcorer is used for sampling, exclude any debris at the base of the core from the sample. Pre-cleaned plastic bottles are used to contain the melted snow samples following melt. These plastic bags and bottles should have the following characteristics:

1. High resistance to cracking and puncture under cold temperature conditions.
2. Good sealability.
3. Proven cleanliness and inertness (i.e., no contamination, adsorption or desorption effects on the samples).

Bags and bottles should be thoroughly tested for contamination, adsorption or desorption effects before the onset of the sampling program.

Plastic bags should be made of food-grade, low density polyethylene. For durability under cold temperatures and to eliminate gas diffusion into samples, a laminated bag consisting of an inner layer of polyethylene and an outer layer of nylon should be used, when available. When snowpack samples for metals analysis are collected, bags may require pre-conditioning (below).

Bottles used to contain snowpack samples should be new low-density polyethylene and demonstratively free of absorption/desorption effects. Bottles used for snowpack samples where metals analysis is required must be pre-conditioned as follows:

a. soaking of bottles for 24 hours in 1% v/v HNO_3.
b. multiple deionized water rinses.
c. soaking in deionized water for at least 8 hours.

C. Collection Procedure

1. During sampling, great care must be taken to avoid contamination of the snowpack sample. The following procedures should be followed:
    a. A site should be approached from a downwind direction and sampling should be carried out facing the wind.

b. No vehicle should approach the site within 200 m; helicopters should approach no closer than 200 m or at a point where rotor downwash does not disturb the site.

c. Implements (shovels, etc.) other than the sampling device should not contact the snow to be sampled.

d. Contact with the sample must be avoided (i.e., hands, clothing); clean, plastic gloves should be used throughout the sampling process. The wearing of disposable coveralls is recommended.

e. Equilibrate the corer/scoop to the snow temperature. Precondition the corer/scoop by inserting it into the same depth of snow several times prior to sampling.

2. Whenever possible, three discrete samples from a site should be obtained for chemical analysis. Where analysis is to be carried out for chemical species with high intra-site variability (e.g., metals), additional samples should be taken.

   Multiple samples from a single site are required to provide estimates of intra-site variability.

   Multiple samples should be taken at as many sites as possible.

3. Discrete samples in separate containers must be used for samples collected for metals analyses; splitting of samples for major ion and metals analyses should be avoided.

4. Plastic bags used for transport of the collected snow sample should be heat-sealed in the field or as soon as possible thereafter.
5. Measurements of snowpack depth and notes on the physical structure of the snowpack should be made following sampling.
6. The snow should be stored (frozen) in the bag until delivery to the laboratory; where this is not possible, the sample may be melted in a clean environment, transferred to a pre-weighed sample bottle, using contamination-free procedures, and immediately transported to the laboratory (i.e., within 72 hours).

D. Laboratory Procedures

1. Samples received in plastic bags from the field should be melted (preferably at 4°C) and quantitatively transferred to sample bottles.
2. Sample volume should be determined by weighing the sample and preweighed bottle or sampling bag.
3. Filtering of the sample may be required prior to analysis. The type of filters used must be demonstrably free of absorption/desorption effects. The following alternatives are recommended:

a. Major Ion Analysis

- No filtering - direct analysis of the bulk sample is possible where insoluble materials are minimal and can be demonstrated to not contribute to soluble parameters tested.
- Filtering through a 0.45 µm membrane filter or equivalent - interfering insoluble materials may be removed from soluble portion; filter may be preserved for specialized analyses (e.g., total P, TKN).

b. Metals Analysis

- Separately collected sample should be used. Sample should be filtered on arrival at lab using a 0.45 µm membrane filter (or equivalent).
- Filter should be retained for digestion and subsequent insoluble metals analyses; soluble portion should be preserved below pH 1.5 with HNO_3 for subsequent soluble metals analysis.

4. Sample analysis should follow established precipitation procedures. The following priority major ion parameters should be determined within 24 hours of sample arrival at the laboratory; pH, acidity, alkalinity, ammonium and nitrate. Alternately, samples must be maintained at 4°C if analysis cannot be done within 24 hours.

5. Samples should be stored at 4°C until all analyses are completed.

V. SAMPLE HISTORY

Sample history provides information for a particular sample and is used to provide relevant information for the data base as well as information used to make quality control decisions. It is recommended that sample history be documented in the form of a report which includes the following:

1. Site identification.
2. Sampler identification.
3. General description of sampling device and collection procedures.
4. Depth of snowpack (total).
5. General snowpack conditions (comments).
6. Snowpack profile description (for example, depth of crystal and melt layers; estimate of density and size of snow crystals).
7. Climatological data for snowfall period (if available - optional).
8. Identification of snowfall period represented by sample (if available - optional).
9. Portion of snowpack sampled (upper/lower depths).
10. Sampling time and date.

11. Date(s) of melt/transfer (if applicable).
12. Transit period - dates shipped/received.
13. Diameter of sampling tube/scoop. Depth of sample collected in mm water equiv. calculated from sample volume and diameter of sampling device.
14. Observed foreign materials in sample (comments).

The following information shall be entered into the data base: site identification, date of sampling, site description, collection procedures, sampling device, time in transit, observed foreign material, and analytical results. If the sample remained at room temperature for a period exceeding 72 hours, all analytical results entered into the data base for that particular sample should be flagged.

VI. QUALITY ASSURANCE PROCEDURES FOR SNOWPACK SAMPLES

In addition to established Quality Assurance Procedures for Network Monitoring and for Lab Analysis, the following procedures must be followed for snowpack sampling.

1. During a sampling program, a number of 'field blanks' must be taken. The sampling and lab procedures should be applied to randomly selected bags and bottles using deionized water in place of snow. The 'field blanks' should follow the samples through all steps. Field blank data should be included in the data set for all snowpack samples.

2. Bags and bottles used in sampling snowpack should be tested on a batch basis prior to sampling to ensure that contamination or adsorption/desorption effects are not present. Bag and bottle blank data should be included in the data set for all snowpack samples.
3. All sampling devices which will contact the snow samples should be pre-tested for adsorption/desorption effects on the samples. The devices should be pre-cleaned and bagged in the laboratory.

8.4D. FILTER PACK METHOD (low-volume Oak Ridge pump)

1. Description

Low-volume air sampler (2 to 3 Lpm) is used to collect gaseous and particulate pollutant by drawing air at a flow of 2.0 Lpm through a two-stage, 47 mm filter pack. The filter packs are sheltered on a support pole above the ground. A 2 µm teflon pre-filter (for the collection of particulates) is in the first stage and two impregnated Whatman 41 filters (for the absorption of SO_2) are in the second stage.

2. Filter Preparation Procedure

The teflon filters can be obtained commercially from Membrana Corporation. The cellulose (W-41) filters are impregnated with a potassium carbonate/glycerol solution. All filters are stored in a desiccator in their original packages or containers when not in use.

Solution Preparation.

1. Wash the roller, tray, volumetric flask, and glass sheets thoroughly using ethanol and rinsing with deionized distilled water. Dry this equipment using Kimwipes.
2. Add into a 1-L volumetric flask approximately 300 mL of deionized distilled water. Dissolve 250 g of potassium carbonate (K_2CO_3) into the deionized distilled water.
3. Add 100 mL of glycerol to this solution. Bring the total volume of the solution up to 1000 mL with deionized distilled water.
4. Thoroughly mix the 1-L solution to dissolve the K_2CO_3 completely.

Filter Impregnation

1. Pour a sufficient amount of the solution into the clean tray to cover a filter sheet. Using clean polyethylene gloves and clean forceps soak the 8" x 10" Whatman 41 filter sheets in the solution (soak individually).
2. Place the soaked filter sheets onto the clean glass sheets. Any excessive solution is then removed by using a hand-held roller.
3. Place the sheets into a drying oven for approximately 30 minutes at 60°C.

Filter Cutting

1. After the filter sheets have been dried, place a non-impregnated sheet on the top and bottom of a stack of five impregnated sheets. These sheets are then placed on a plastic cutting board.
2. A 50 mm cutting die cleaned with ethanol and deionized water is placed onto the drill chuck. The sheets are cut, discarding the top and bottom non-impregnated cut filters. The impregnated cut filters are then placed into new Whirlpak bags. Each bag is given a batch number.

Source: APIOS Technical and Operating Manual, Section 4.3.2.1.1.

3. Sample Handling Procedures

Loading of Filter Packs

Filter packs must be washed after every sampling period. The following washing procedures are to be followed prior to loading the packs:

- Disassemble all filter packs and place the parts and 2 pairs of tweezers in a sink full of warm water and laboratory detergent.
- Put on a clean pair of disposable polyethylene gloves and scrub all parts with a soft brush. All gaskets and filter screens need to be thoroughly cleaned.
- Using clean gloves thoroughly rinse the parts with tap water. Follow with two rinses of deionized distilled water.
- Set aside the parts to dry on a clean tray. To speed up drying, the parts can be placed in a drying oven at 60°C for 30 minutes. If left to air-dry, the washed parts should be covered with Kimwipes to prevent possible contamination.
- When dry, the filter packs should be re-assembled using clean disposable gloves and stored in clean bags (Ziploc or Whirlpak) or used immediately to load filters.

The filter handling area in the field office should be a clean work area. Smoking nearby should not be allowed while handling filters. The following procedures are to be followed for loading filter packs.

- Pour 50 mL of ethanol into a clean 250 mL beaker. Insert a clean pair of tweezers into the beaker.
- Layout clean Kimwipes over the filter loading area and disassemble the filter packs placing the top collar and each stage upside down over the Kimwipes.
- Open the Whirlpak bag containing the W-41 filters and remove the protective covers from the box containing teflon filters. (Teflon container might be marked Zelfluor.)
- Wipe the tweezers dry with a Kimwipe.
- Place a teflon filter into the top collar of all the packs. Since the top collar and stages are placed upside down, the filters must be placed into the filter pack upside down. This requires the teflon filters to be placed into the top collars dull side up. (The smooth shiny side is the collection surface.)
- Rinse the tweezers in the ethanol beaker and wipe dry with Kimwipes.
- Insert the first stage of the pack into the top collar containing the filters. Visually check to ensure the top O-ring has not failed or shifted.
- Rinse the tweezers in the ethanol beaker and wipe dry with Kimwipes.

- Remove two impregnated W-41 filters from the bag and place them into the bottom of the first stage of every pack. Ensure these filters are properly seated inside the O-rings by gently tapping the edges of the filter.
- Carefully insert the second stage downward into the first stage to complete the loading of the pack.
- Place the filter packs into a new Zip-loc bag.

Note: It is very important to label the packs so that no confusion exists when loading and unloading packs on the tower. The baseplates on the sampling boom are to be labelled to prevent any errors during the deployment of new packs.

Unloading of Filter Packs.

The following procedures are to be used for unloading filter packs.

- Pour 50 mL of ethanol into two clean 250 mL beakers. Place a pair of clean tweezers into each beaker. One beaker and a pair of tweezers are used for handling impregnated filters only. The second beaker and pair of tweezers are to be used for handling the teflon and nylon filters. Lay clean Kimwipes over the filter unloading areas.
- For each filter pack, three Whirlpak bags should be labelled Teflon and W-41.

- Using disposable plastic gloves and tweezers, carefully remove the top collar and pick up the teflon filter by the edge, being careful not to touch the darkened exposed area.
- Using tweezers fold the exposed filter onto itself into quarters and place it into the corresponding Whirlpak bag forcing out any excess air before closing.
- Repeat Step 4 to unload the nylon filter.
- Remove the second stage from the first stage of the filter pack.
- Using the ethanol solution reserved for impregnated filters, remove the tweezers and pick up the two W-41 filters by the edge and fold into quarters. Place the folded W-41 filters into the corresponding Whirlpak bag forcing out any excess air before closing.

Source: APIOS Technical and Operating Manual, Sections 4.3.2.1.2 and 4.3.2.1.4.

4. Filter Extraction

Whatman 41 filters are extracted in a beaker in an automatic shaker with 50 mL of 0.05% (v/v) hydrogen peroxide. This is followed by a 15 minute shaking in 25 mL hydrogen peroxide which is made up to 100 mL with hydrogen peroxide.

5. Sample Analysis

Analysis of W41 for $SO_4^=$ (by IC) as outlined in the Handbook of Analytical Methods for Environmental Samples (Page SH13-SH21). The method is reproduced in its entirety in Appendix 8.4G.

Particulate Matter (PM) is determined by weight (on Teflon filter) using an analytical balance.)

6. QA/QC

Quality assurance/quality control procedures to include:

- colocated samplers;
- field blanks and handling blanks;
- routine instrument calibrations;
- routine service and maintenance;
- blank filters from each batch prepared; and
- laboratory QA/QC as outlined in analytical method.

8.4E WET-ONLY PRECIPITATION SAMPLER (Aerochem Metrics)

1. Description

Aerochem Metrics wet-only sampler with polyethylene/nylon laminated bags inserted into polyethylene buckets.

2. Sample Collection and Handling Procedures

Removal of Collected Samples

- Touch the sensor with a wet finger to activate the hood.
- When the hood has completely rested on the dry side, turn the instrument off.
- Remove the bungy cord from the sample bucket being careful not to lift it over the sample bag (to avoid contamination falling from the cord into the sample bag).
- Remove the sample bag as follows:
  - Gently push the portion of the bag which is outside the bucket up over the top of the bucket about 1 inch.
  - Grasp the portion of the bag above the bucket between the thumb and forefinger of each hand and lift the sample bag out.
  - Holding the top of the bag with one hand, use the other hand to squeeze the bag just under the fold (approximately 1 inch down from the point where the bag folded over the edge of the bucket).

- Gently squeeze any excess air out of the bag and then tie the bag where it was squeezed with a cable tie.
- Place the sample bag upright into the supplies box.

Instrument Cleaning

After the sample bag is removed, wash the underside of hood with Kimwipe wetted with ethanol (in squirt bottle). Then rinse with a Kimwipe wetted with distilled deionized water and wipe dry with a Kimwipe.

Also, once per week using a Kimwipe wetted with ethanol, clean the sensor grid.

Deployment of New Sample Bags

- Put on a clean pair of disposable plastic gloves. Grasp a clean bag near the top and separate the two halves. Do not place fingers further than 3 inches into the bag at any time.
- Placing thumbs inside the bag and fingers outside, shake the bag in the air until it has expanded fully.
- Leave a small amount of air in the bag and squeeze near the top so that the bag is half full of air.
- Push the bag into the bucket until it hits the bottom (Note: this is necessary to keep the bag partially inflated in order to displace the air in the bucket).
- Slide the fold over the top of the bucket so that 3 to 4 inches of the bag extend down the outside of the bucket.
- Put on a clean glove being careful not to touch the fingers of the gloves. (Note: It is very important to use a new

glove because the next step requires the hand to touch the inside of the bag where precipitation will collect.)

- Reach into the bag at the rim of the bucket and flatten the bag against the top of the inside wall. Do not shove your hand all the way into the bag; insert it only to the depth of the glove.
- Secure the bag to the outside of the bucket using the bungy cord supplied. The bungy cord should be attached approximately 2 inches down from the top of the bucket just under the second ridge around the bucket.
- Turn the power back on. The hood should return to cover the wet bucket with a tight seal.

Decanting Procedures

Samples should be decanted in a clean work area to avoid possible contamination.

- Bring the sample indoors and place upright on a clean level surface. If the precipitation sample is frozen, allow the sample to melt.
- Swirl the bag to liberate any particles that may have adhered to the walls of the bag.
- Take the lid off from one of the polystyrene sample bottles and place the lid upside down, being careful not to touch the inside of the lid. Check the bottle for any flaws, cracks, or visible contamination. If the integrity of the

bottle is doubted, discard it and use another one. Clean one bottom corner of the bag with distilled water and a Kimwipe. Wipe dry with a Kimwipe. Clean the scissors with distilled water and a Kimwipe. Wipe the scissors dry with a Kimwipe. (Note: Clean both blades in the open position.)

- Elevate the cleaned corner of the bag and cut off the corner using the scissors. Lower the corner and carefully pour the sample into the sample bottle.
- Label the bottle with the station name, number, and collection date using labels provided. Store the sample in the refrigerator.

Instrument Checks

The instruments installed at every event precipitation sampling site should be checked during every visit to the site. The following checks are to be carried out to determine if the instrument or gauge is operating properly.

Aerochem Metrics Precipitation Collector

- The precipitation collector should be kept level at all times. Place a level over the north-south and east-west axes on the wet side bucket to ensure that the collection surface is level. Use a clean polyethylene bag to cover the sample to avoid contaminant prior to placing the level on the bucket.

- Activate the sampler using a wet finger. The hood should move to cover the dry bucket. After a few seconds, the hood should return to cover the wet bucket. Check to see that the hood gasket forms a tight seal over the wet bucket.
- Verify that the collector is functioning properly by testing the electrical operation and heater circuit with the Aerochem Metrics test kit. Attach the test plug to the cannon plugs of the sensor and motor box to verify that 0.6 to 0.7 A of current flows through the heater when the collector is activated.
- The hood gasket and sensor head should be checked for cleanliness and the electrical wiring and ground fault breaker tested every visit to the site.

3. Sample Analysis

As outlined in the Ontario Ministry of the Environment Handbook of Analytical Methods for Environmental Samples (pages SH13-SH21). Method is reproduced in its entirety in Appendix 8.4G.

4. QA/QC

Quality assurance/quality control procedures to include:

- colocate samplers;
- field blanks;
- blank bags;
- duplicate or split samples;
- analytical QA/QC as outlined in analytical method;

- routine instrument calibrations; and
- routine service and maintenance.

8.4F. DRY-ONLY DEPOSITION COLLECTOR

1. Description

The deposition plates consist of a petri plate 9.4 cm lid with a 1.3 cm rim. The electronically operated rain shield (30 x 18 cm) is 4 cm above the deposition plate in the "closed" (rain-protected) position. In the open position the shortest distance between the deposition plates and the cover is 50 cm. The sampler utilizes as a wet sensor a heated resistance grid.

REFERENCE

Lindberg, S.E. and G.M. Lovett (1985). "Field Measurements of Particle Dry Deposition Rates to Foliage and Inert Surfaces in a Forest Canopy". Environmental Science and Technology 19(3): 238-244.

8.4G SULPHATE - AUTOMATED ION CHROMATOGRAPHY METHOD B

SUMMARY

Matrix.	This method is routinely used for sulphate determinations on precipitation samples, some surface waters, and some air particulate samples.
Substance determined	Sulphate ion, $SO_4^=$
Interpretation of results	Results are reported as mg/L sulphate
Principle of	Via ion chromatography (HPLC), sulphate is separated from other anions in samples using a column packed with ion exchange resin and an eluent composed of a mixture of sodium bicarbonate and sodium carbonate. Sulphate is converted to the acid form by ion exchange and its concentration is determined from the conductivity of the sulphuric acid produced. Manually drawn calibration curves are used.
Time required	Time required for analysis depends upon eluent composition for analysis concentration and flow rate as well as the size of the separator column. With the experimental conditions specified for this procedure about 8 min. per sample are required.
Range of Application	a. 0.05 to 5.00 mg/L b. 0.05 to 10.0 mg/L
Standard deviation	Between run standard deviations are 0.034 in the 0.06 to 2.0 mg/L range; 0.078 in the 2.0 to 5.0 mg/L range and 0.167 in the 5.0 to 10.0 mg/L range based on duplicate samples.
Accuracy	Control is maintained by 2 independently prepared quality control standards (QC-A and QC-B) at 80 and 20% of range such that (A + B) and (A - B) do not vary by more than 0.14 mg/L (3 standard deviations) from their long-term means.
Detection criteria	0.056 mg/L
Inteferences and shortcomings	Oxalate at concentrations of 50 mg/L can interfere with the measurement of sulphate.

1. Introduction

Sulphate is the major anion in precipitation samples and consequently, this method was designed primarily for sulphate determination; however, it is also routinely used for the simultaneous measurement of chloride and nitrate.

Using a modified Donex ion chromatograph system 10, anions are separated in a separator column by reaction with an ion exchange resin and an eluent. The anions are then converted to their acid form in a suppressor column (e.g., sulphate to sulphuric acid). The sodium carbonate-bicarbonate eluent becomes carbonic acid. A conductivity metre measures the conductivity of each anionic species against the carbonic acid eluent background. A precolumn is used to trap foreign matter thereby extending the life of the separator column. In order to accommodate automation, modifications are made allowing automatic sample injection.

2. Interferences and Shortcomings

Each anionic species on the ion chromatograph is identified by its retention time: the time between sample injection and optimum peak height development. If the retention times of two anions are similar and one ion is present in considerably higher concentrations than the other, the broader and higher peak formed by this high concentration will overlap the peak of the lesser ion. Consequently, the capacity to determine an anion at low concentrations depends upon the concentrations of other ions having similar retention times. Oxalate peaks overlap sulphate peaks at oxalate concentrations of 50 mg/L.

Interferences may also be caused by the presence of ions which form strong complexes with the anions measured, or cause the anions to precipitate when mixed with the alkaline buffer. The latter is unlikely due to the low ionic strength of precipitation samples.

3. Apparatus

3.1 Dionex ion Chromatographic System 10 including following:

3.1.1 anion precolumn, 3 x 150 mm; anion separator column (analytical), 3 x 250 mm; anion suppressor column, 6 x 250 mm

3.1.2 sample loop. 0.30 mL volume, tubing coiled

3.1.3 #1 pump - eluent delivery at 40% flow
#2 pump - regenerant delivery at 60% flow

3.1.4 regeneration time (normal cycle: 10 min. regeneration followed by 30 min. rinse with distilled, deionized water)

NOTE: All reagants and standards are prepared with distilled, deionized water and volumetric, class A pipettes and flasks. All glassware must be washed with 4% HCl and thoroughly rinsed with distilled, then distilled, deionized water, before use.

4.11 Super Stock Standard Solutions (300 mg/L Cl; 400 mg/L NO_3 as N; 2000 mg/L SO_4)

This is a combined stock solution prepared by weighing 0.4946 g sodium chloride, 2.8872 potassium nitrate and 2.9572 g sodium sulphate on an analytical balance weighing to 4 decimal places. Combine reagants in a volumetric flask and make to 1 L with distilled, deionized water.

4.12 Intermediate Stock Standard Solutions (30 mg/L Cl; 40 mg/L NO_3 as N and 200 mg/L SO_4)

Pipette 100 mL super stock standard solution and dilute to 1 L in a volumetric flask.

4.13 Working Standards

Working standards are prepared according to the following table, using distilled, deionized water.

% Range	Conc. mg/L			Volume Intermediate Stock Solution
	SO_4	Cl	NO_3-N	
10	1.00	0.15	0.20	5 ml/L
20	2.00	0.30	0.40	10 ml/L
40	4.00	0.60	0.80	20 ml/L *
60	6.00	0.90	1.20	30 ml/L
80	8.00	1.20	1.60	40 ml/L
100	10.00	1.50	2.00	50 ml/L

* The 40% standard is also used as an in-run sensitivity check and is therefore prepared in 2-L volumes (40 mL/2L)

4.14 Quality Control Super Stock Solution

This is prepared exactly as for the calibration super stock standard solution (reagant 4.11); however, a different supply of chemicals is used.

4.15 Quality Control Intermediate Stock Solution

Pipette 100 mL quality control super stock solution into a 1-L volumetric flask and dilute to the mark.

4.16 Quality Control Working Standards

An 80% (QC-A) and 20% (QC-B) standard are prepared by diluting 80 mL and 20 mL of quality control intermediate stock solution respectively, each to 2 L. New standards should be run simultaneously with old standards at least once.

4.17 Eluent Stock Solution

Combine 25 g sodium carbonate and 25 g sodium bicarbonate in a 1-L volumetric flask and dilute to the mark.

Pen 2 = low analytical range, full-scale equivalent to 5 μS/cm

Calibration: Blank plus 6 mixed standards, 10, 20, 40, 60, 80, 100% full scale. Calibration curve based on peak height.

Calibration range: Pen 1(1V) = SO_4: 0.05 to 10.00 mg/L; NO_3-N: 0.01 to 2.00 mg/L; Cl: 0.01 to 1.50 mg/L.

Pen 2(0.5V) = SO_4: 0.05 - 5.00 mg/L; NO_3-N: 0.01 -1.00 mg/L; Cl: 0.01 - 1.20 mg/L

5.2 Machine Set-Up

5.2.1 With power and air supply conditions set (see Dionex Operation Manual) and appropriate reagents in reservoirs, select ELUENT (.004M $NaHCO_3$/.0024 Na_2CO_3) and allow to run through suppressor column at 80% flow (≃370 mL/h) for 15 to 30 min., to stabilize column.

NOTE: It is assumed that suppressor column is freshly regenerated at beginning of run (Section 5.5) and that all reagant lines are air free (i.e., pump has been primed for all reagents - see Dionex Manual for procedure) ensuring that no air is introduced into the system.

5.2.2 While stabilizing column, set up recorder using the Dionex Ion Chromatograph conductivity metre by setting meter to zero mode and with both pens of recorder at 1 V, zero the pens.

5.2.3 Set mode switch to CAL and adjust both pens to full scale (i.e., 100 chart lines) using SPAN adjustment on underside of recorder.

5.2.4 Recheck ZERO and CAL, then select LIN mode and 10 μmho scale. Set pump flow to 40% (≈180 mL/h) and put all columns on line. Offset conductance to zero and bring each pen up to five chart lines with the zero adjust on the recorder to accommodate any drift in signal. Change pen 2 to .5V.

NOTE: If flow is higher, the pressure will be greater than 500 psi and may cause columns to explode or leak.

5.2.5 Turn on pump with sample probe in wash.

5.2.6 Program the Supergrator with suitable program: PGM 1 for the 500 mm column and PGM 2 for the 250 mm column.

NOTE: Refer to Supergrator 3 Operating Manual (8.4) for program explanation.

As long as the instrument is not switched off, the program is retained in the memory and may be called up each day or edited as desired.

5.2.7 They system set-up should correspond to Figure 3.

Peak heights of samples are read as percent concentration, converted to mg/L, with a correction for sensitivity changes during the run.

6. Precision and Accuracy

Based on duplicate samples, standard deviations for sulphate measurements are 0.034 in the 0.06 to 2.0 mg/L range; 0.078 in the 2.0 to 5.0 mg/L range and 0.167 in the 5.0 to 10.0 mg/L range.

This method is applicable to a variety of anions and the standard deviations are as follows:

Chloride	0.017	0.03 to 1.20 mg/L range
Nitrate	0.020	0.03 to 0.20 mg/L range
	0.012	0.20 to 0.50 mg/L range
	0.016	0.50 to 1.00 mg/L range

Accuracy is controlled by two indpendently prepared standards (QC-A and QC-B) at 80% and 20% of range (8.0 mg/L and 2.0 mg/L) such that (A+ B) and (A - B) do not vary by more than 0.14 mg/L (3 standard deviations) from the long-term mean of (A - B).

7. Bibliography

Crowther, J. and J. McBride. 1978. Analysis of Precipitation Samples by Ion Chromatography. Part 1 - Determination of Anions. Ontario Ministry of the Environment, Laboratory Services Branch, Toronto, Ontario.

Dionex Ion Chromatographs 10, 14, 16. Operation and Maintenance. Dionex Corporation, Sunnyvale, California.

McBride, J., K. Clarke, J. Crowther, O. Lindow, and M.W. Rawlings. 1979. Automation of Anion Chromatographic System. Ontario Ministry of the Environment, Laboratory Services Branch, Toronto, Ontario.

Supergrator 3 Operating Manual ROM 326, Columbia Scientific Industries.

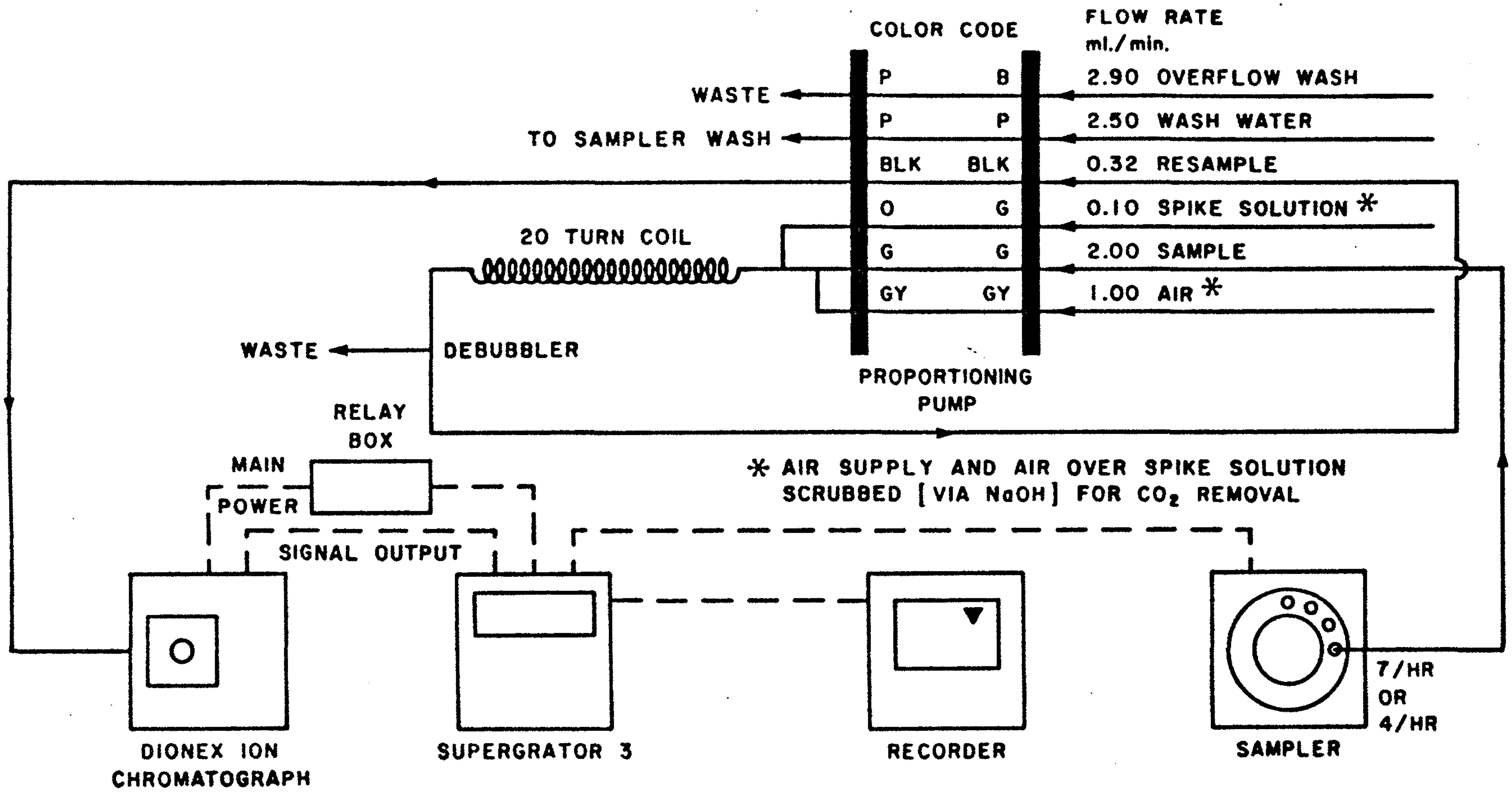

Figure. Automated ion chromatograph system (anions).