PROCEEDINGS OF A WORKSHOP ON
SULPHUR GAS RESEARCH
IN ALBERTA

Edited by

Drake Hocking

David Reiter

Northern Forest Research Centre

Information Report NOR-X-72

December 1973

Canadian Forestry Service

Environment Canada

5320 - 122 Street

Edmonton, Alberta, Canada

T6H 3S5

Foreword

Sulphur dioxide is an air pollutant of world-wide incidence. It is a component of urban air pollution and of emissions from mineral smelters. Generally, other air pollutants accompany sulphur dioxide except where high-sulphur fuels are burned for power generation in remote areas.

In Alberta, urban air pollution is not dominated by sulphur dioxide, nor are large areas affected by mineral smelting operations. The primary sources of sulphur dioxide are sour natural gas processing plants, whose emissions are relatively free from pollutants other than sulphur dioxide. Alberta offers an opportunity to study all aspects of a major air pollutant in isolation from confounding complex mixtures. Also the magnitude of sulphur dioxide emissions poses a particular problem for Alberta. Processing the vast tar sands of northeastern Alberta may introduce emissions on an even larger scale.

This workshop should benefit research programs in industry, consulting firms, and government. Although much research has been and is being conducted, researchers from various disciplines have at times worked in relative isolation. The workshop provided a needed forum for the exchange of data and opinions, and it is hoped that this will be continued in future workshops.

We thank Dr. E.E. Ballantyne, Deputy Minister, Alberta Department of the Environment, Dr. G.T. Silver, Director of the Northern Forest Research Centre; and all participants.

Drake Hocking

S.B. Smith

CONTENTS   <u>Page</u>

Biological Impacts of Sulphur Gases

Monitoring and Regulation

An Overview

PARETIAN ENVIRONMENTAL ANALYSIS

AS APPLIED TO

SULFUR DIOXIDE EMISSIONS IN ALBERTA.*

by

Drake Hocking

Northern Forest Research Centre, Edmonton

1. Introduction

Effective decisions on environmental policy are best reached through systematic mathematical and economical analysis. A non-judgemental criterion for evaluating alternative policies was formulated in the late 19th century by Vilfredo Pareto (1848-1923), an Italian political economist born in Paris. He postulated that any change which harms no one and which makes some people think they are better off is an improvement. This postulate, known in economic theory as the "Pareto criterion" and valuable for its social neutrality, was rarely applied, even in the other theoretical constructs of Pareto and his contemporaries. The idea survived, however, and was taken up in a formal decision analysis system.

Paretian Environmental Analysis, developed by the Harvard Environmental Systems Program, incorporates the interests of the people affected by a decision together with technological and economic data into a set of net benefit functions. Judgements of the analyst are incorporated into the functions by explicitly weighting the net benefits by the estimated political influence of each interest group. Sensitivity of the decision to political influence may readily be tested by solving for different weights.

The analysis admits only those potential decisions that cannot be improved in terms of overall net benefits without making at least one participant worse off. Such decisions are defined as Pareto admissible. The model is logical:

"If an environmental control agency can adjust its policy to the benefit of some interested party, and if no one else is disadvantaged by the change, then the adjustment is likely to be made. Put another way,

no agency is likely to take a measure that purposefully harms one of its constituents if no others stand to gain by it, and a truly interested party is not likely to let itself be disadvantaged by accident or inadvertence." (Schaumburg, unpub.)

In short, you do have to use your judgement. When this is necessary, it is best to make it explicit. The many and diverse elements of complex decisions can be stated concisely in mathematical notation. Systematic analysis reveals informational gaps and provides a way of testing the sensitivity of decisions to error in estimates used to fill these gaps. By programming the functions on a computer, revisions of the decision in the light of new data, can readily be made.

2. Summary of Paretian Environmental Analysis

The basic steps are:

1. Definition of the decision.

   a. the physical system

   b. indices of environmental quality

   c. policy instruments and control measures

   d. constraints

2. Identification of the interested parties.

3. Determination of the technological relations between a potential decision and resulting environmental quality.

   a. relations between the decision and probable emissions

   b. relations between emissions and ambient concentrations

   c. relations between ambient concentrations and environmental quality.

4. Formulation of net benefit functions.

5. Solution for Pareto-admissible decision alternatives.

6. Prediction and prescription.

3. The basic steps applied to SO_2 emissions in Alberta

3.1 Definition of the decision

There are alternative types of control, dispersal, definition, measurement and specification of emissions. It is uncertain in many areas the extent to which emissions influence environmental quality. Any rational decision must first be defined.

This paper analyses the revision of ambient air quality standards for sulfur dioxide proposed by the Alberta Department of the Environment.

3.1.1 The physical system

Much data defining the present decision are common knowledge in Alberta so the treatment here will be very brief. Owing to the political history of Canada, the province of Alberta is the geographical limit of the decision. Subsidiary decisions will be necessary for each SO_2 emitter currently in operation and for proposed new ones.

Topography and climate, the existing and intended land uses, individual and classes of emitters, and the time horizon (how long the decision will have to be in force) also must be defined. Details of these apply to different successive stages of the analysis. Much of the province is comparatively flat prairie with gentle hills and valleys. Some emitters, however, are situated in severely undulating foothills with complex intersecting valley and ridge systems. The province has short hot summers and long very cold winters. Many areas have extended periods with very light or no wind.

Most emitters are situated in agricultural land with scattered

human residences. Those in the foothills are generally located in forested areas supporting both timber production and recreational uses. Some affect areas of diversified land uses; areas affected by effluents tend to overlap in some cases.

The time horizon for the decision is influenced by any sulfur dioxide emitting process. Although tar sands processing may be likely to dominate total sulfur emissions in the future, for the present these are due almost entirely to sour natural gas processing. The allowable daily production of a gas field is based on a 20-year life. Therefore, 20 years is the effective time horizon for any given area of influence of any one gas plant. Complications may arise from a variety of sources. Most, however, can be handled through modifications to specific requirements: checking how much exposure the area has already had.

3.1.2. Indices of environmental quality

The primary index of environmental quality that is directly relevant to the present decision, is the ambient concentration of sulfur dioxide. A _fluctuating standard_ has merit for serious consideration.

The major source of SO_2 is incinerated tail gas from sulfur recovery. Other sources of SO_2 exist, notably flare stacks. There is very poor knowledge of the details of either combustion or dispersion from flare stacks. This is doubly a problem, as flare stacks are in _continuous_ use at sour gas processing plants where the sulfur content or the volume throughput is small enough to deem a sulfur recovery process unwarranted.

Gas plants have other environmental impacts. Some are covered in other regulatory decisions; some are left to individual complaint and

bargaining; some have been left to legal process. Here, only atmospheric sulfur dioxide will be considered.

3.1.3 Policy instruments and control measures

The Alberta Department of Environment sets standards for ambient air quality, and is the decision body in this analysis. The Energy Resources Conservation Board (ERCB) enforces these standards in the gas processing industry through instruments such as approvals and informational letters. A set of new ambient standards for sulfur dioxide has been proposed by the Department of Environment, specifically for gas plants, and the ERCB has issued "guidelines" for improved sulfur recovery efficiency relating to plant size.

Essentially, ambient air quality standards are the legal basis for regulation of emissions. But the proposed new standards contain, in addition, an effluent or stack concentration standard, to be derived for each plant from dispersion models relating to new ambient standards. This would be a more effective regulatory instrument, being much simpler and cheaper to measure than ambient sulfur dioxide levels. However, it lacks the allowance for adverse weather and temperature inversion effects, so more stringent ambient standards also are proposed.

A novel policy instrument not mentioned in the proposed new standards is a provision for modulating the ambient standard according to probable effects upon receptors. A fuller discussion follows in Section 3, but in short, a higher ambient concentration could be tolerated during winter months when vegetation is less sensitive and gas demand is higher. Short-term modulation of the effluent standard may also be possible with sophisticated monitoring of dispersal conditions and effective predictive models.

Control measures available include reduced quantities and improved dispersion of effluents. Quantities may be reduced by improving efficiency of sulfur recovery or by lowering production rates. Better dispersion may be achieved by increasing the effective stack height.

3.1.4 Constraints

A decision may be limited by legal, technological, economic, or political constraints.

For the current decision, the legislative framework does not limit the regulatory powers of the Department of the Environment and the ERCB. Technological constraints exist at a level of 99.9% recovery of sulfur; combined with a consideration of economics, probably the practical technological constraint is 99.4% recovery. But local economic constraints are minimal because cost increases might be spread over the large volumes exported. Political constraints are very low due primarily to increased public support for measures to improve environmental quality.

In short, the present decision has remarkably broad latitude in all of the legal, technological, economic and political contexts.

3.2   Identification of the interested parties

There are several levels of influence on a decision regarding ambient standards for sulfur dioxide, and there are several ways of classifying interested parties with direct influence. All participants (actors) probably have some interests that are more or less conflicting and that are affected negatively and positively by all degrees or alternatives to a decision. To identify the principle discrete interests, several levels of disaggregation may be attempted. Re-aggregation of interests assumed to be represented in the actions of the principle actors simplifies the model.

In the Alberta sulfur dioxide decision, the interested parties are represented by "lumps" of distinct groups whose real interests are not necessarily congruent. But the interests of groups lumped together do at least converge and are affected in similar ways by the decision.

The major participants, with their interests, are:

a. The Canadian Department of the Environment, through national air quality ambient standards established under the Clean Air Act of 1971.

b. The provincial Alberta Department of Environment, through its Air Pollution Control Branch which sets standards and the ERCB which enforces them.

c. The Alberta government biological management agencies, to establish the best possible standards for their constituents.

d. The general populace, mostly through conservation-minded organizations.

e. Sour gas processing plants, through incurring the major costs of more stringent standards. Although only 42 actually extract elemental sulfur, the other plants have at stake their rates of production.

f. Gas consumers, in the price they pay for their commodity.

g. Provincial government resource development agencies, in exploitation of resources.

3.3 Determination of the technological relations between the decision reached and resulting environmental quality

This phase has three parts: the relations between the decision and the probable actual emissions, the relations between those emissions and ambient concentrations, and the impact of those concentrations upon environmental quality (their effects upon receptors). Any new set of

ambient air quality standards that is more stringent than the previous
standards will probably initiate a round of technological improvements
and/or reduced plant throughflows in efforts to meet those standards. It
is crucial to the decision on standards to consider to what extent the
industry can and will abide by them.

3.3.1 Relations between the decision and probable emissions

Regular violations of ambient air quality standards occur. Many
are caused by probabilistic malfunctions of equipment and stochastic
weather influences. Such violations have been detected by continuous
monitoring stations located some distance from emission sources. Adoption
of emission standards and in-stack monitoring will mean quicker and more
certain detection of violations, permitting more rapid corrective action
by the plant. This aspect of the new proposals will likely lead to fewer
violations of shorter duration; hence closer adherence to the ambient
standards.

3.3.2 Relations between emissions and ground level concentrations

Local topography and weather may lead to ground level concentrations
exceeding ambient standards as frequently as before, despite in-stack
monitoring of emission rates. And flare stacks can lead to very high
concentrations; current regulations permit up to 1.0 ppm for periods up
to 1 hour.

3.3.3 Relations between ambient concentrations and quality

Definition of the quality index, Q, is best done through examination
of the effects of the probable ambient concentrations upon receptors. The
linkage in the case of sulfur dioxide is extremely complex, owing to a wide
range of predispositional and environmental variables.

Levels of SO_2 resulting in measurable adverse effects on human beings are in the order of 0.1 ppm. In Alberta, the areas likely to be subject to the highest concentrations of emissions are mostly uninhabited. Hence the effects are more likely to be noticed first on vegetation. But these effects are impossible to predict because they depend on at least 8 environmental variables (Loman, Blauel and Hocking, 1972, for review).

Most plant species become less susceptible to acute injury during dormancy, which occurs in the winter (op. cit. 1972). Thus it might be possible to build into the standards a provision for modulation according to the current sensitivity of surrounding receptor vegetation. This would be particularly valuable for an industry with seasonally fluctuating volumes like the gas processing plants, since the season of probable lowest receptor sensitivity coincides with the season of highest demand and therefore greatest throughflow and emission rates.

4. Determination of the net benefit functions

The types of benefits that will accrue in many areas are heavily weighted towards those which are difficult to measure:

Benefits:
1. improved human, animal and plant health;

2. reduced material damage (corrosion, etc.);

3. consequent more valuable agricultural and forest harvests;

4. consequent improved recreational opportunities and utilization;

5. vicarious satisfaction of city dwellers knowing that healthy forests are available;

6. reduced risk of long-term land-use degradation; and

7. sale value of sulfur recovered.

Cost data for improved sulfur recovery processes is reasonably accurate, related to percentage recovery and to plant design capacity. Although direct costs of controls increase sharply with efficiency of recovery, the total costs are small and decreasing compared to the overall value of product.

In the Alberta decision, the costs lie in the following:

Costs: 1. purchase, installation and operation of additional Claus units.

2. purchase, installation and operation of tail-gas clean-up units.

3. additional monitoring instruments, if necessary, for ambient quality enforcement.

4. in-stack monitoring instruments (these are already being required by the ERCB).

5. reduced production of sales gas in plants whose allowable throughput is curtailed to meet standards.

6. higher prices of product gas to consumers.

Development of functions:

For each of the gas plants (i) there is associated a particular control method (x_i) with its capital costs $(\Phi_i(x_i))$. Through the federal government, the capital costs may be discounted by an interest rate (in this example, 7.5%) and the amortization period (20 years).

Using these assumptions, the following federal government (f) cost function (C_{f_i}) applies:

$$C_{f_i}(x_i) = .098\ \Phi_i(x_i) + \Theta_i(x_i) \ . \tag{1}$$

The first term would be zero for those plants whose control method
is reduction of the throughput without installation of recovery equipment
In these cases, the second term would represent the annual costs of lost
production (Θ_i).

The annual costs perceived by the gas plant owner (k) would re-
quire different factors a and b allowing for taxation credits on the
control equipment, including rapid depreciation allowances. These may
be represented as follows, for each gas plant i.

$$C_{k_i}(x_i) = a\Phi_i(x_i) + b\Theta_i(x_i) \quad . \tag{2}$$

Summing the costs perceived by the federal government:

$$C_f(X) = \sum_{i=1}^{67} C_{f_i}(x_i) \tag{3}$$

and by the industry:

$$C_I(x) = \sum_{i=1}^{67} C_{k_i}(x_i) \quad . \tag{4}$$

The provincial government probably does not perceive the direct
control costs as its own, because much of the total would remain in the
province through local supplies of equipment and expertise.

For the Alberta situation, the generalized form of the benefit
(B) function for health of living organisms at the resulting environmental
quality (Q') is

$$B(Q') = \sum_{j=1}^{3} b_{o_j} q_j R_{o_j} \tag{5}$$

where (q_j) is the improvement in quality in sector (j) (human habitation, agricultural, or forested zones), (b_{o_j}) is a function of the concentration level prevailing and the particular organism concerned (human, plant, or animal and (R_{o_j}) is the population of organism (o) in sector (j) (for plants, expressed perhaps in acreages). In areas where the soil is sulfur deficient (as in Alberta), some level of emissions (b_{o_j}) above zero will provide positive benefits to plant growth.

The sizes of the benefits perceived by each party are represented by a set of weights (λ). Sensitivity of the decision to differing weights will indicate the importance of the accuracies of these benefit measures.

Together, these generalized cost and benefit functions contain sufficient data to form net benefit (NB) functions for each interested party, as follows:

    a.   For the Canada Department of Environment, the function is derived from (3) and (5):

$$NB_f(x) = \lambda_f B(Q') - C_f(x); \tag{6}$$

    b.   The Alberta Department of Environment (p), together with the Energy Resources Conservation Board, would perceive only benefits:

$$NB_p(x) = \lambda_p B(Q') = \lambda_p \sum_{j=1}^{3} b_{o_j} q_j R_{o_j} \tag{7}$$

    c.   The biological management agencies of the provincial government would also perceive only benefits:

$$NB_{p'}(x) = \lambda_{p'} B(Q') = \lambda_{p'} \sum_{j=1}^{2} b_{o_q j} q_j R_{o_j} \tag{8}$$

where (o) is only plant and animal organisms (excluding direct human health benefits) and (j) is restricted to the agricultural and forested zones.

d. The general populace (g) also perceives only benefits:

$$NB_g(x) = \lambda_g B(Q') = \lambda_g \sum_{j=1}^{3} b_{o_j} q_j R_{o_j} \qquad (9)$$

where the constraints on (o) and (j) in (8) above are
removed.

e. The industry (I) perceives net benefits only as costs; less
the sale value ($) of recovered sulfur:

$$NB_I(x) = \$_s - C_I(x) = \$_s - \sum_{i=1}^{67} C_{k_i} \; (xi) \qquad (10)$$

·where ($_s$) is the overall sale value of recovered sulfur.
For 1973, the value to industry as a whole has been estimated
at thirty million dollars (<u>Oilweek</u>).

f. Gas consumers, when distinguished from their other roles in
the general populace, likewise perceive only costs of in-
creased gas prices.

$$NB_c(x) = dV \qquad (11)$$

where (d) is the price increment and (V) is the total volume
purchased. Because (d) is a direct function of the net costs
of the gas industry (owing to the pricing methods of the
Public Utilities Board), equation (11) becomes

$$NB_c(x) = - \lambda_c C_I(x) \qquad (12)$$

g. Similarly, the provincial government agencies responsible
for development and resource exploitation (p") would perceive
costs to industry in terms of discouragement of new investment
and loss of royalties.

$$NB_{p''}(x) = -\lambda_{p''}C_I(x) \tag{13}$$

where a part of $(\lambda_{p''})$ could be computed from royalty structures.

5. Determination of the Pareto-admissible frontier

This stage involves solution of the maximization problem set by summing the set of net benefit functions weighted by a vector $w = (W_1,\ldots,w_7)$ that indicates the political influence of each identified party (k):

$$\text{Maximize} \sum_{k=1}^{7} w_k NB_k(x) \tag{14}$$

subject to

$$Q \leq Q'$$

for each (w).

Completion of the study will involve the fitting of "best-estimate" data to the functions and solving the maximization problem for differing political weights (w) and benefit weights (λ).

6. Prediction and Prescription

Properly, this step should await completion of steps 4 and 5. But some judgements may be made without the quantitative data, aided by the systematic examination of the elements of the decision. The proposed set of new standards is likely to be adopted with little modification. This judgement is based on the array of weights applicable to the participants whose interests lie in more stringent standards.

An ambient standard is desirable for uniformity, but it is hard to enforce. It is logical, therefore, for the ERCB (the enforcement body) to want to apply emission standards to individual gas plants. Emissions are

much easier to measure (and therefore apply standards to) than is en-
vironmental quality, the implied aim of ambient air quality standards.
But this proposed control route is not necessarily the most cost-efficient.
Because of weather, a given emission rate leads to a highly variable SO_2
concentration or _exposure_ at the point of a receptor. Furthermore, the
effects of any given _exposure_ upon _environmental quality_ is also dependent
on the fluctuating sensitivity or tolerance of the receptors. Emission
standards, if constant, must be stringent enough to satisfy the most
probable poor-dispersal conditions and the most probable high sensitivity
of receptors. Sulfur recovery equipment to meet such standards would be
very expensive.

If gas plants were able and willing to modulate SO_2 emissions in
immediate response to ambient air monitors, then continuously stringent
emission standards might not be necessary. In weather conditions giving
good dispersal, higher emission rates might be acceptable. This would be
true even if varying receptor sensitivity were not considered.

If sufficient data were available to describe and monitor the
factors affecting receptor sensitivity, greater emissions might be
acceptable during periods of predictable relatively high tolerance.
Intensive biological monitoring (observation of effects on living organisms)
might be a method of feedback to plant operators for both variables des-
cribed above.

Adequate research to satisfy the uncertainties in the fore-going
alternatives to emission standards will undoubtedly be very expensive. But
it might be more cost-effective in the long run.

Summary and conclusions

In air quality management for natural gas production in Alberta, scarcity and generality of data make many of the factors in net benefit functions impossible to quantify at this time. Specifically, many of the benefits of more stringent SO_2 controls are in areas of diffuse information. Data are weak, for example, on recreational benefits, on health benefits of plants and animals, and on valuations of these.

Furthermore, there is some question as to the cost-effectiveness of the control instruments under development or consideration. In particular, the proposed emission standards (as opposed to ambient standards) seem rather rigid in view of the unpredictable variations in dispersal conditions and the predictable (but as yet unknown) fluctuations in sensitivity of receptors. But allowance for these variables requires the gas processing plants to be able and willing to rapidly modulate emissions in response to physico-chemical and biological monitors.

Solution of net-benefit functions developed for Alberta must follow further research to develop estimates of values presently unknown.

References

Loman, A.A., R.A. Blauel, and D. Hocking. 1972. Sulfur dioxide and forest vegetation. Inf. Rept. NOR-X-49. Northern Forest Research Centre, Edmonton.

Technological Transformation of

Sulphur Gases

POTENTIAL EFFICIENCIES OF THE CONVENTIONAL

CLAUS SULPHUR RECOVERY PROCESS

by

Robin P. Rankine, Rich K. Kerr, Harold G. Paskall

WESTERN RESEARCH & DEVELOPMENT LTD.
Calgary, Alberta

ABSTRACT

The latest advances in Claus process technology are discussed in the light of recent theoretical prediction, together with supporting evidence obtained in the field. Unprecedented efficiency levels can be achieved by conventional Claus sulphur recovery plants employing as few as two catalytic stages. However, to sustain high level efficiencies for extended periods of time, persistent catalyst deactivation problems must be solved.

INTRODUCTION

During the past decade, pollution control agencies in Alberta have imposed increasingly more stringent regulations on the operation of sour gas processing plants in an effort to substantially reduce sulphur dioxide emissions resulting from inefficiency in the sulphur recovery aspect of these operations. In response, a considerable research effort has been devoted, particularly during the past five years, towards a solution of the sulphur dioxide emission problem.

Until recently, the modified Claus process has been universally employed in sour gas processing operations. It would seem natural then that the first research priority would be exploiting this process to its fullest potential. However, by far the greater proportion of the total research effort has been directed towards the development of new processes which are intended to augment the efficiency of the Claus. This emphasis on new processes reflects the widely-held opinion that the potential of the Claus process has been exhausted by existing efficiencies which are generally in the 90-97 percent range. The purpose of this paper is to present, in an informal way, the results of recent theoretical calculations and field scale experiments which together clearly demonstrate the potential of the Claus process to achieve efficiencies well in excess of the above range. It is hoped that these results will encourage interested parties to devote a greater proportion of their research effort towards the solution of certain catalyst problems which continue to reflect on the long-term viability of the Claus process.

THEORETICAL PREDICTIONS

The technique used for thermodynamic equilibrium calculations is that of free energy minimization. It has the distinct computational advantage over equilibrium constant calculations in that no knowledge of reaction mechanisms is required. Several authors (Lees & Ryan 1971, Barry 1972, Boas & Andrae 1971) have used this technique to predict optimum efficiencies for three stage Claus plants in the range 96 to 97 percent. Unfortunately most calculations have been based upon thermodynamic data for sulpur vapour which are dated and in need of revision. Molecular sulphur vapour exists in all forms from S_1 to S_8 (Berkowitz 1965). Based partly upon data from the literature (McBride et al. 1963) and partly upon unpublished data developed by the authors, a multi-phase, multi-component free energy minimization computer program has been developed to predict field and laboratory performance of the Claus process (Rankine 1973).

Since completion of the model last spring, it has been used extensively for theoretical studies of the Claus process. These studies have led to the definition of several criteria for optimum Claus plant performance:

1. Each sulphur condenser should operate at about 260°F., which provides a margin of about 20F° above the freezing point of sulphur.

2. Mist elimination equipment should be utilized in interstage sulphur condensers as well as in the final condenser.

3. Methods of reheat which introduce sulphur compounds into the main gas stream should be avoided. Optimization implies that all sulphur compounds should be introduced as far upstream in the process as possible.

4. The operation of each converter should be adjusted so that the actual and dew point temperatures converge at the converter outlet.

These criteria have not been applied to the design and operation of existing Claus plants.

Practical limitations to these theoretical optimization criteria are:

i) Furnace conversion cannot be predicted thermodynamically. In this example a value of 60 percent was chosen. This is lower than that which is generally observed;

ii) The gas off the first sulphur condenser was assumed to be 330°F;

iii) In considering certain side reactions, which must proceed in the first converter, an outlet temperature of 625°F was chosen. This temperature is well above the sulphur dew point.

Thermodynamic recoveries from a four stage Claus plant processing a rich feed containing 67 percent hydrogen sulphide are:

2 Catalytic Stage Recovery	97.9 percent
3 Catalytic Stage Recovery	99.1 percent
4 Catalytic Stage Recovery	99.4 percent

The optimum yields for lean feed gas are not significantly different.

FIELD EXPERIMENTS

The thermodynamic predictions were tested during July 1973 in a major Claus plant operating in Alberta. This plant employs front-end combustion and four stages of catalytic conversion to process acid gas containing approximately 82 percent hydrogen sulphide. The design capacity of the plant corresponds to an inlet feed rate of equivalent sulphur of approximately 1600 long tons per day. Design features include interstage mist elimination devices and indirect reheat to the final catalytic stage. These features help to suppress the sulphur dew point, thereby enhancing the potential for low temperature converter operation. In addition, the catalytic charge in this plant was completely replaced last May. This provided a test situation in which there should be no kinetic limitations on plant efficiencies and therefore a situation in which thermodynamic predictions should be applicable.

The most pertinent results of field tests are summarized in Table 1. This table includes the distribution of total plant feed to the front-end furnace and to the auxiliary burners, and the actual and theoretical conversion and recovery efficiencies on a cumulative stage by stage basis. Blanks in the table pertain to cases in which either the theoretical calculations do not apply or appropriate measurements could not be taken. The theoretical conversions were based on the actual plant operating conditions, as opposed to the optimum conditions discussed in the preceding section. The theoretical recoveries were based on the actual conversion data together with condenser operating conditions.

The most relevant plant operating conditions are summarized in Table II. These include condenser and converter outlet temperatures and the maximum sulphur dew point in each converter. The latter demonstrates how closely each converter was operating to the optimum dew point condition.

DISCUSSION

The field data indicate that theoretical thermodynamic calculation for molecular sulphur vapour and the free energy minimization program accurately predict the behavior of Claus units. Accurate predictions have also been demonstrated in bench scale laboratory studies (unpublished).

Claus sulphur plants can attain recovery efficiencies in the 99+ percent region. These recoveries are sufficiently high to satisfy all present day governmental requirements. However, persistent catalyst problems remain which must be solved to sustain these efficiencies for an extended period of time.

REFERENCES

Barry, C.B. 1972. Reduce Claus Sulphur Emission. Hydrocarbon Processing – April (1972): 102-106.

Berkowitz, J. 1965. Elemental Sulphur. (ed. by B. Meyer) pp 125-159. Interscience.

Boas, A.H. & R.C. Andrae. 1971. Simulate Sulphur Recovery Plants. Hydrocarbon Processing – March (1971): 81-84.

Lees, R.S. & J.J. Ryan. 1971. Computer Design and Simulation of Sulphur Plants. Gas Processing/Can. - July-August (1971): 16-18.

McBride, B.J. et al. 1963. Thermodynamic Properties to 6000°K for 210 Substances Involving the first 18 Elements. NASA Publication SP-3001.

Rankine, R.P. 1973. Temperature Important to Optimized Claus Plant. Gas Processing/Can. March-April (1973): 16-17.

TABLE I

CUMULATIVE PLANT PERFORMANCE*

STAGE	FEED	— CONVERSION —		— RECOVERY —	
		ACTUAL	THEOR.	ACTUAL	THEOR.
Thermal Stage	98.31	66.6	-	-	-
#1 Catalytic Stage	0.48	91.3	90.9	-	89.1
#2 Catalytic Stage	0.43	97.5	97.3	-	95.9
#3 Catalytic Stage ·	0.78	98.9	98.8	98.6	98.6
#4 Catalytic Stage	-	99.3	99.3	99.1	99.1
	100.00	99.3	99.3	99.1	99.1

*All parameters expressed as percentage of total plant feed.

TABLE II

OPERATING TEMPERATURES*

	CONDENSER OUTLET	CONVERTER OUTLET	MAX. CONVERTER DEW POINT
Thermal Stage	375	-	-
#1 Catalytic Stage	350	590	480
#2 Catalytic Stage	330	420	405
#3 Catalytic Stage	280	375	355
#4 Catalytic Stage	255	340	300

*^{0}F

REMOVAL OF SULFUR DIOXIDE FROM WET STACK GASES

OF SOUR GAS PLANTS[1]

by

M.F. Mohtadi and H.B. Dingle

Department of Chemical Engineering
The University of Calgary
Calgary, Alberta

ABSTRACT

Catalytic conversion to elemental sulfur of sulfur dioxide in wet stack gases, using carbon monoxide as the reducing agent, was studied theoretically and experimentally.

Computer models were developed to calculate equilibrium compositions for the reaction system under various conditions using free energy minimization (FEM) and simultaneous chemical equilibrium (SCE).

Experiments were carried out in a reactor designed to simulate the equipment and operating conditions used in industry. Alumina, silica-alumina, copper on alumina, and copper on silica-alumina were used as catalysts. The reaction time was varied from 0.10 to 3.35 seconds. The SO_2 content of the feed gas was kept at 1.0 percent by volume. Water vapor was introduced into the reaction system at concentrations up to 30.0 percent by volume.

The method studied removed up to 90 percent of the SO_2 in the wet stack gas. Side reactions producing carbonyl sulfide and hydrogen sulfide hamper complete conversion of SO_2 in the presence of water vapor.

---

[1]The full text of this paper has been submitted for publication in the Canadian Journal of Chemical Engineering.

Atmospheric Dispersion of

Sulphur Gases

"Short and Medium Range Atmospheric

Diffusion in the Alberta Environment"

by

Richard D. Rowe

Department of Chemical Engineering, University of Calgary

EXTENDED ABSTRACT

Designing industrial stacks in the Foothills region of Alberta is difficult since little is known about the effects of varied topography on the dispersion of plumes. Most sour gas processing plants in the Province are located alongside of the Rocky Mountains, in a so-called "sour gas corridor". In this corridor the ground level concentration of SO_2 emitted from the sulphur recovery plants is strongly influenced by the complicated terrain and by the peculiar meteorological conditions of this region, e.g. frequent temperature inversions and stable Chinook winds.

A number of projects concerned with the short-range behavior of plumes from gas plants are reviewed.

Previous investigations include:

(i) Photographic observations of plume rise from gas plant stacks.

Sulphur plant plumes have stack exit temperatures in excess of 1000°F and are only visible at low ambient temperatures, below about 7°F, due to a change in phase of the water vapor (1). The effluent from the Ram River sulphur plant stack was successfully marked during field trials

this summer (1973) by two techniques: incomplete combustion of hydraulic fluid and Army smoke pots yielding respectively dense black and white plumes. (ii) Case studies of incidences of high ground level SO_2 concentration, as recorded by continuous monitors, in the vicinity of a gas plant.

This investigation (2) tested the applicability of existing correlations for estimating the ground level concentration of SO_2 discharged from sulphur recovery plant stacks and ascertained the meteorological conditions which cause pollution episodes. High ground level concentrations are usually attributable to a non-uniform atmospheric state, such as inversion break-up or plume trapping. Inversion break-ups, which are associated with high pressure systems, clear skies and low winds, are not unusual in Alberta and may be regarded as part of the normal variation in the meteorological conditions of the province. (iii) The passage of a plume across a complicated terrain.

A helicopter-borne fast response SO_2 monitor was used to investigate the diffusion of a sulphur plant plume across a long ridge close to the plant (3). The plume path was approximately normal to the spine of the ridge and the topography was almost ideally two-dimensional. The potential flow streamline across the terrain was shown to be a conservative approximation to the lowest plume centreline data with rise removed. The following simple stack design method was recommended: the effective stack height is the sum of the height of the potential flow streamline above the terrain (rather than the physical stack height) plus plume rise; the ground level SO_2 concentration should then be calculated, in the usual manner, using Pasquill's standard deviations.

Leahey (4) has recently studied the diffusion characteristics of air flow over a river bank with a bivane. He recommends the alternative simple stack design method in which air flows parallel to the terrain. Pasquill's standard deviations are changed to agree with the bivane measurements.

Future investigations include:

(i) Atmospheric turbulent dispersion of stack plumes in complicated terrain.

Investigate the behavior of sulphur plant plumes flowing across distinct topographical features. Effluent marking techniques have been developed and time-lapse photogrammetry will be used to record the visible plume passage. Atmospheric boundary layer velocity profiles will be simultaneously determined using a novel smoke-line technique; a smoke rocket is projected vertically leaving an initially straight smoke-line, the deformation of the smoke-line as a function of time yields the velocity profile and the locations of regions with recirculating flow. The velocity profile will also be determined with the conventional optical-balloon-sonde technique. A radio transmitting temperature probe attached to the balloon will be used to measure the lapse rate.

(ii) Flare stack design.

To improve our understanding of the behavior of flames in cross-winds for the safe and economic design of flare stacks. The velocity field of model flares in a wind-tunnel with a laser anemometer will be investigated. The flame temperature will not present a problem since

this form of anemometry has already been used (5) at higher temperatures (about 10,000°C). Using laser anemometry for remote measurement of wind velocities has been discussed; it may be possible to probe real flares.

The requirement to study medium range diffusion (10 - 100 km range) to determine, for example, the summation effects of the group of gas plants located in the sour gas corridor, is outlined.

Finally, a rational strategy for the control of SO_2 emission from sulphur recovery plants in Alberta is proposed (6). This strategy takes into account the divergent views of industry, government and environmental groups. It advocates a comprehensive study of the fate of SO_2 in the atmosphere and a flexible attitude towards regulations which control SO_2 emission.

Acknowledgements

References

(1) Havlena, J., Kumar, V. and Rowe, R.D., "The Visibility and Rise of Sulphur Recovery Plant Plumes", Air Pollution Control Association Meeting, Seattle, November (1973).

(2) Mohtadi, M.F. and Rowe, R.D., "Sulphur Recovery Plant Plumes", Gas Processing/Canada, May-June, 16-20 (1973).

(3) Rowe, R.D., "The Dispersion of Plumes from the Jumping Pound Gas
     Plant", Western Research and Development Consultant Report to
     Shell Canada Limited, February (1973).

(4) Leahey, D., "A Study of Air Flow Over a River Bank", submitted to
     Atmospheric Environment.

(5) Rowe, R.D. and Sambrook, R.M., "Laser Doppler Anemometry of Electric
     Arcs" Opto-Electronics, 5. 217-219, January (1973).

(6) Mohtadi, M.F. and Rowe, R.D., "A Rational Strategy for Control of
     SO_2 Emission in Alberta", 4th Joint Chemical Engineering Conference,
     Vancouver, September (1973).

PLUME DISPERSION RESEARCH AT NATURAL GAS

SULPHUR EXTRACTION PLANTS[1]

by

G. K. Lee[2] , H. Whaley[2] and J. G. Gainer[3]

ABSTRACT

The rise and dispersion have been determined for four plumes
emitted by three natural-gas sulphur-extraction plants in Alberta. This
report describes the data acquisition techniques employed and gives a
preliminary evaluation of the results. At one plant, two plumes were
studied, one under inversion conditions and the other under limited mix-
ing conditions. One plume from each of the other two plants was studied
under neutral conditions. The results indicate that the standard devia-
tions of plume spread cannot be reliably estimated for limited mixing
conditions and that plume behaviour is strongly influenced by local topography.

---

[1] Prepared for presentation to the Canadian Natural Gas Producers Association,
Calgary, Alberta, 2 March 1973; published as Fuel Report R-265; Department
of Energy, Mines and Resources, Mines Branch, Ottawa.

[2] Research Scientists, Canadian Combustion Research Laboratory, Fuels Research
Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa,
Canada.

[3] Senior Engineer, Exploration and Production Department, Gulf Oil Canada Ltd.,
Calgary, Alberta.

Computer Simulation of Pollutant Dispersion:

Single Stack and Air Shed Models

By

K. Aziz, J.K. Donnelly, J.P.A. Wallis

Department of Chemical Engineering
The University of Calgary
Calgary, Alberta

ABSTRACT

This study compares analytical, Sutton and numerical models on a consistent basis for a single stack. Diffusion coefficients are shown to affect discretization error considerably, small coefficients giving large errors and large coefficients small errors. In both cases the error decreased with increased downwind distance. Turbulent transport models did not compare favorably with the Sutton equation or analytical solutions. It is proposed to extend this work to a simple air shed model for Alberta. Various aspects of an air shed model are discussed.

INTRODUCTION

The increasing demands of the populace for a cleaner environment, in particular air and water, have caused governments to enact anti-pollution legislation. Consequently there has been an increased need for pollution models, not only to predict the behaviour of present day facilities, but to determine the pollution effects of future constructions. In Alberta an example would be the proposed Athabasca Tar Sands projects. Another important aspect is that a comprehensive air pollution model could be incorporated into an overall pollution strategy. This is shown in Figure 1 and is a modification of the method proposed by Plotkin and Lewis (1972).

At present most pollution models are the classical Gaussian type. The well known Sutton, Pasquil and Brookhaven models (see Aziz et al. (1973)) are all Gaussian, but use different values for the standard deviations. Unfortunately these are only valid for a single pollutant source over flat terrain under steady-state conditions where reaction and decay effects are negligible. The more complicated models are really simplifications of the momentum, mass and energy equations, e.g. Hino (1968), Randerson (1970), Shir (1970). In general the complex models can include terrain, multiple source, reaction, decay and transient effects. The price paid is the loss of the simplicity of the Gaussian expressions, the replacement being a large numerical model. Despite the number of model studies none have assessed the accuracy of computer simulations.

The purpose of this paper is to show that computer models do compare well with Gaussian models. Consequently the more general and complicated air shed models are worthy of further study.

Statement of the Problem

In general the pollution dispersion process may be taken as a material balance equation which in words is:

$$
\begin{bmatrix} \text{Accumulation} \\ \text{of Pollutant} \\ \text{in a Given} \\ \text{Volume} \end{bmatrix} + \begin{bmatrix} \text{Pollutant} \\ \text{Transported} \\ \text{by Convection} \\ \text{(Wind)} \end{bmatrix} = \begin{bmatrix} \text{Pollutant} \\ \text{Transported} \\ \text{by Diffusion} \end{bmatrix} + \begin{bmatrix} \text{Pollutant} \\ \text{from} \\ \text{Sources} \end{bmatrix} - \begin{bmatrix} \text{Pollutant} \\ \text{used up by} \\ \text{Reaction} \\ \text{and Decay} \end{bmatrix}
$$

In mathematical terms, with simplifications and assumptions, the pollutant concentration is governed by (see Aziz and Wallis (1973)).

$$
\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} = \frac{\partial D_x \frac{\partial C}{\partial x}}{\partial x} + \frac{\partial D_y \frac{\partial C}{\partial y}}{\partial y} + \frac{\partial D_z \frac{\partial C}{\partial z}}{\partial z} - R + Q_v \quad (1)^*
$$

(accumulation) + (wind transport) = (Diffusion transport) -

(reaction) + (sources)

Single Stack Study

For very simple cases, Equation (1) can be solved directly for C. For example, the Sutton model (Monin and Yaglom (1965)) can be

---

* Symbols are defined in nomenclature.

shown to be a solution of Equation (1) when v, w, D_x, R and $\frac{\partial C}{\partial t}$ are zero; there is a single source, u is constant, the terrain is flat, and D_y and D_z are power functions of x. An analytical solution may also be obtained for Equation (1) for the same conditions as the Sutton equation and for constant D_y and D_z (Monin and Yaglom (1965)).

Sutton (neutral atmosphere), Analytical and Turbulent Transport Theory (u, D_y and D_z are functions of z) were compared on a consistent basis by having the same average values for u, D_y and D_z. The computational method and application to Turbulent Transport Theory is described in papers by Aziz et al. (1973) and Aziz and Wallis (1973). It can be shown that this method of comparison gives a conservative estimate for the analytical diffusion coefficients. A point source of 1000 g/s (95 ton/day) at an effective stack height of 100 m. (340 ft) in a velocity field of u = 4.35 and 8.7 m/s (10 and 20 mph respectively) were the numerical constants used. They correspond approximately to conditions for a large sulfur plant in Alberta.

Some transient results ($\frac{\partial C}{\partial t} \neq 0$) were also determined for constant D_y and D_z, all physical parameters having the same values as steady-state case. All computations were done on a CDC 6400. Discretization error refers to the difference between the analytical solution and the numerical estimate of the analytical solution. Grid spacing refers to the increments in the variables x, y, z and t in the solution of equation 1. Converged solution means the most accurate numerical estimate of the analytical solution that can be obtained at a particular grid spacing.

Results

Figure 2 compares analytical, Sutton and numerical results (modified Euler) for short downwind distances (D_y, D_z small). The discretization error is considerable initially, but decreases for increasing downwind distances. Ideally the analytical and modified Euler lines should be the same. Notice the discretization error is much smaller for concentrations at the stack height. The Sutton equation gives a sharper concentration gradient than the constant diffusion coefficient simulations (analytical and modified Euler). The numerical results can be considered as converged results for the grid size given. Similar results were obtained for a wind speed of 8.7 m/s.

Figure 3 compares Turbulent Transport, analytical and Sutton theories for short downwind distances. The discretization error is much larger for the Turbulent Transport simulations (converged solution lines and Euler simulation line) and the correspondence with Sutton or Analytical simulations is poor. This is caused by the relatively small diffusion coefficients at ground level; remember that diffusion coefficients are increasing functions of z (see Aziz et al. (1973)). Similar results were obtained for a wind speed of 8.7 m/s.

Figure 4 compares Turbulent Transport, analytical and Sutton theories for larger downwind distances. The discretization error has decreased considerably (D_y and D_z are much larger) even though the distance between grid points has been considerably increased. Turbulent Transport Theory still deviates considerably

from the other methods. Numerical convergence would require even a smaller grid size; notice the curves cross and then diverge for the two different grid spacings. This was not experienced in the numerical simulation of the analytical solution. It should also be noted that the Sutton equation and the analytical solution correspond very well for distances greater than the point of maximum ground level concentration.

Figure 5 shows essentially the same things as Figure 4. However, the wind velocity is now 8.7 m/s compared with 4.35 m/s for Figure 4. Notice the increased wind causes a decrease in ground level concentrations. Converged numerical simulation results are the same for $\Delta x = 80$ in Figures 4 and 5.

Figure 6 shows the numerical transient solution for the constant diffusion coefficient case (transient solution of the results shown in Figure 4, compared with the converged numerical solution curve). Notice that steady-state values are achieved very quickly.

All figures show curves for the transverse distance $y = 0$. The source is located at $x = 0$, $y = 0$, $z = 100$ and the solution is symmetrical about $y = 0$. The results for Figures 2-5 are based on the results reported by Aziz et al. (1973) and Aziz and Wallis (1973). These references should be consulted for more detailed information. Euler and modified Euler are numerical methods for integrating Equation (1). Turbulent Transport Theory answers may only be obtained by numerical integration.

Conclusions for the Single Stack Study

1. The correspondence between the analytical model and Sutton's equation is good for distances greater than the point of maximum ground level concentration.

2. Numerical simulations are shown to have an acceptably low discretization error excepting those simulations where Turbulent Transport Theory was used.

3. Turbulent Transport Theory does not compare well with Sutton or Analytical models.

4. Grid size can have a significant effect on discretization error.

5. Simulations with large diffusion coefficients have small discretization errors.

6. Transient simulations are relatively uninteresting as steady-state is reached very quickly once the pollutant reaches a given position.

Air Shed Model

Since it has just been demonstrated that a single stack can be acceptably modelled numerically, there are firm grounds to extend the model to large areas with multiple sources. This is an

air shed model and means the integration of Equation (1) to find
ground level concentrations.

Limitations of the Proposed Air Shed Model

A map of Alberta is shown in Figure 7 and the model
would cover all of Alberta excepting the Rocky Mountains which are
to be treated as a barrier. Ideally topographical features should
be included in the model, but large grid sizes preclude accurate
topographical description; therefore for the first attempt Alberta
is to be assumed flat. Should contour description be needed, it
could be added at a later date. Because of the large area covered
by the model it should not be used to predict local concentrations.
Rather it should be used to determine pollution trends for the
province.

Accurate data are needed to make a model useful. Such
things as pollutant decay and ground level absorption rates must be
provided by the chemist and biologist. Diffusion coefficients can
be provided by the established literature, but even this gives
different values (e.g. Pasquill (1961), Sutton (1947) and Brookhaven
data (see Smith and Singer, 1966) do not agree). The meteorological
department will provide the wind conditions and other pertinent
atmospheric data. Source rates of pollutant will be estimated for
proposed plants and determined from operating data for existing
plants. This requires the cooperation of the industrial sector.

The actual computer model in block modules should be similar to the flow diagram in Figure 8.

General Conclusions

1. It has been demonstrated that numerical means can accurately determine ground level concentrations for single stacks.

2. Discretization error is small for large (meaningful) values of the diffusion coefficient.

3. An air shed model has been proposed for Alberta.

4. Extensive interdepartmental cooperation is required to make the air shed model a success.

ACKNOWLEDGEMENTS

NOMENCLATURE

C   concentration, g/m^3

D_x diffusion (turbulent transfer) coefficient in the downwind direction, m^2/s.

D_y transverse diffusion (turbulent transfer) coefficient, m^2/s.

D_z vertical diffusion (turbulent transfer) coefficient, m^2/s.

Q_v source rate per unit volume, g/m^3-s.

R   reaction rate term, g/s-m^3.

t   time, s.

u   velocity in the downwind direction, m/s.

v   velocity in the transverse direction, m/s.

w   velocity in the vertical direction, m/s.

x   downwind distance, m.

y   transverse distance, m.

z   vertical distance, m.

REFERENCES

Aziz, K., Carr, L.A., Rowe, R.D., Wallis, J.P.A., Computer Modelling of Pollution From Atmospheric Sources, The 4th Joint Chemical Engineering Conference, Vancouver, British Columbia, September 9 - 12, 1973.

Aziz, K., Wallis, J.P.A., Some Aspects of the Computer Modelling of Pollution From Atmospheric Sources, In Process of Publication, 1973.

Hino, M., Computer Experiment on Smoke Diffusion Over a Complicated Topography, Atmospheric Environment, $\underline{2}$, 541-558, 1968.

Monin, A.S., Yaglom, A.M., "Statistical Fluid Mechanics: Mechanics of Turbulence", 1965, vol. 1, The M.I.T. Press, Cambridge, Mass., 1971 (English Translation).

Pasquill, F., The Estimation of the Dispersion of Windborne Material, Meteor. Mag., $\underline{90}$, 33-49, 1961.

Plotkin, S.E., Lewis, D.H., Control Strategy Evaluation Using Models, A.I.Ch.E., 72nd National Meeting, St. Louis, Missouri, May 21-24, 1972.

Randerson, D., A Numerical Experiment in Simulating the Transport of Sulfur Dioxide Through the Atmosphere, Atmospheric Environment, $\underline{4}$, 615-632, 1970.

Shir, Ching-Cheung, A Pilot Study in Numerical Techniques for Predicting
Air Pollutant Distribution Downwind From a Line Stack, Atmospheric
Environment, 4, 387-407, 1970.

Smith, M.E., Singer, J.A., An Improved Method of Estimating Concentrations
and Related Phenomena from a Point Source Emission, J. Appl. Meteor.,
5, 631-639, 1966.

Sutton, O.G., The Problem of Diffusion in the Lower Atmosphere,
Quart. J. Roy. Soc., 73, 257, 1947.
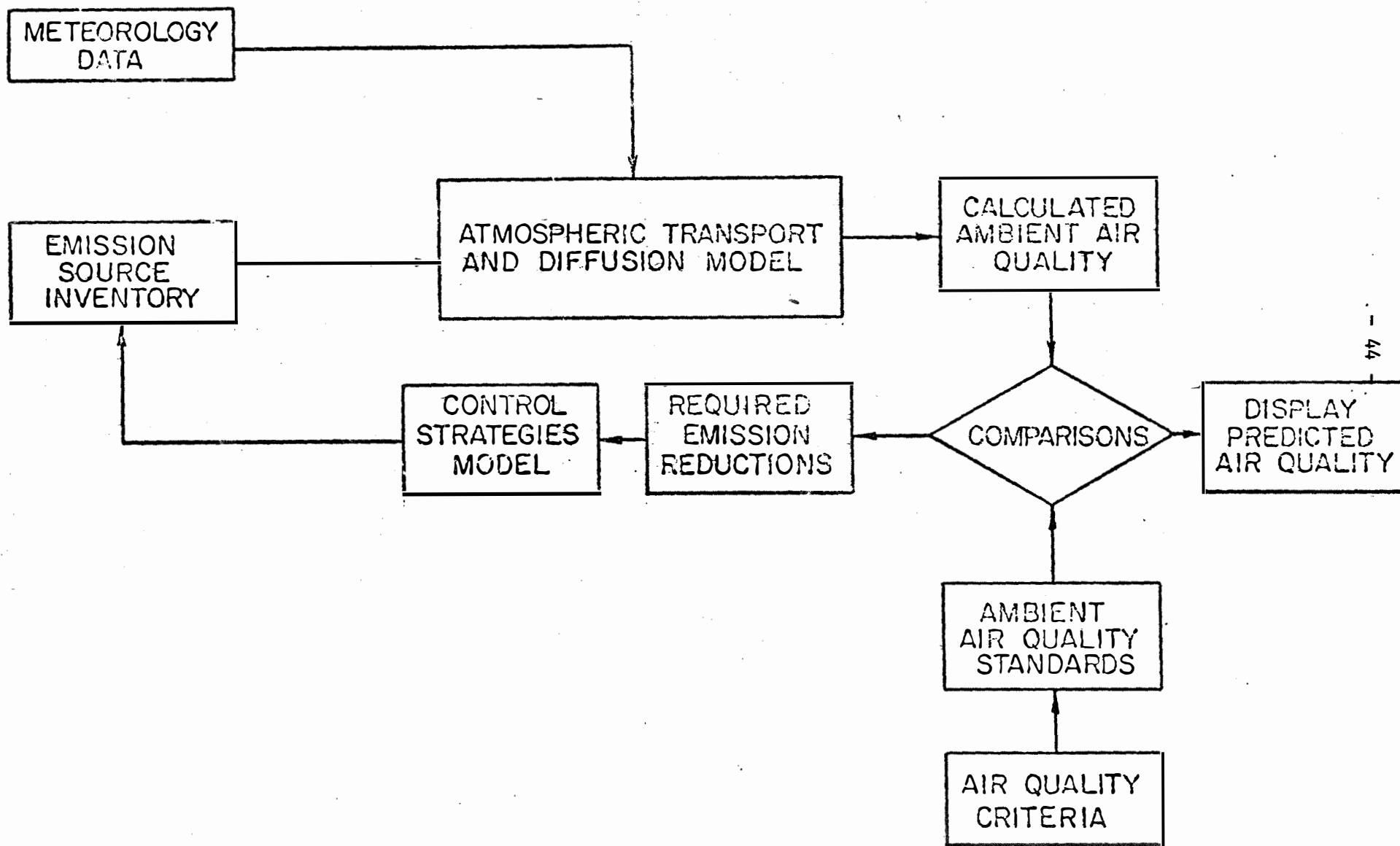
Figure 1 Air Quality Analysis Model
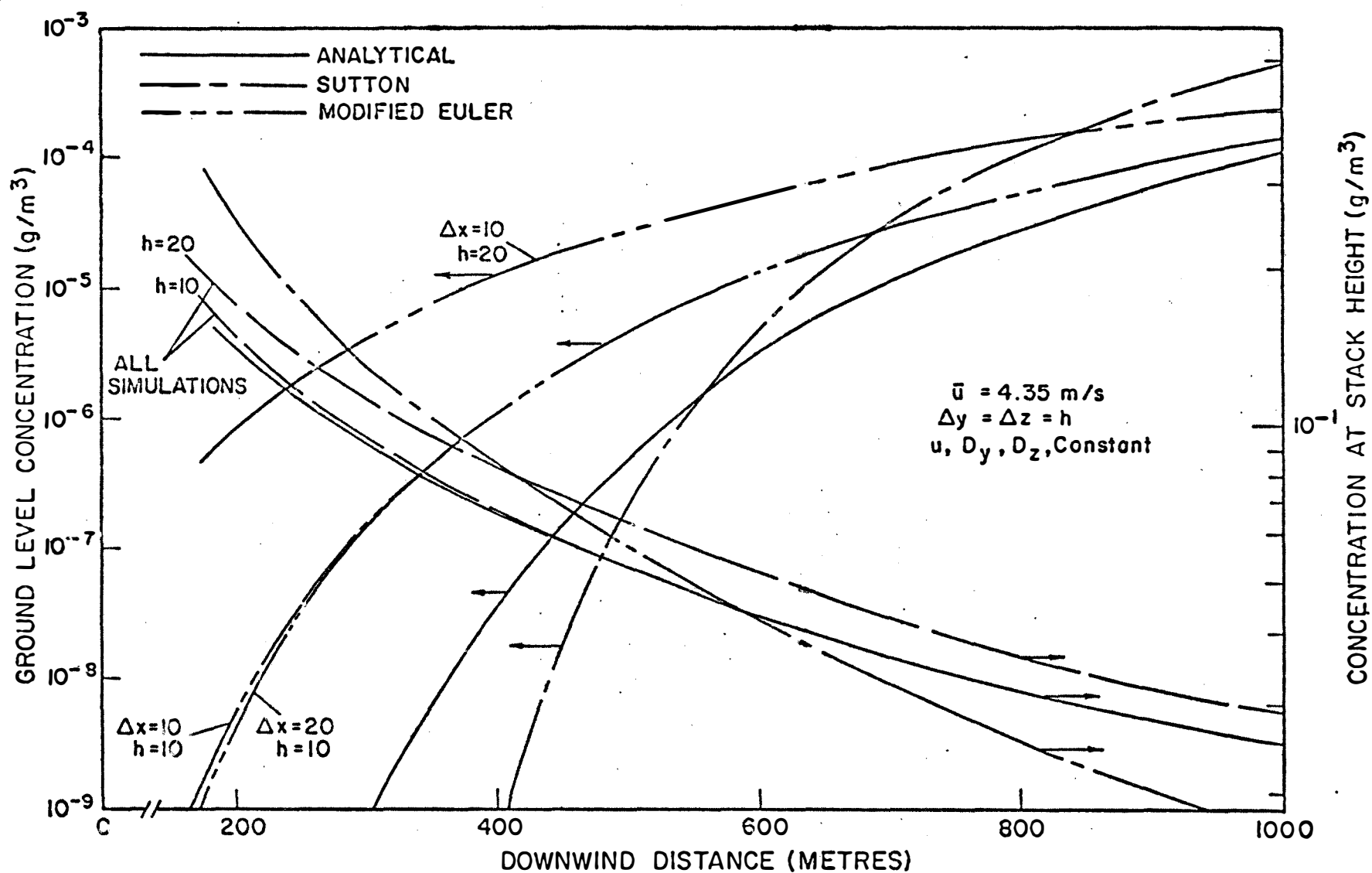
Figure 2 Effect of Grid Size on Concentration
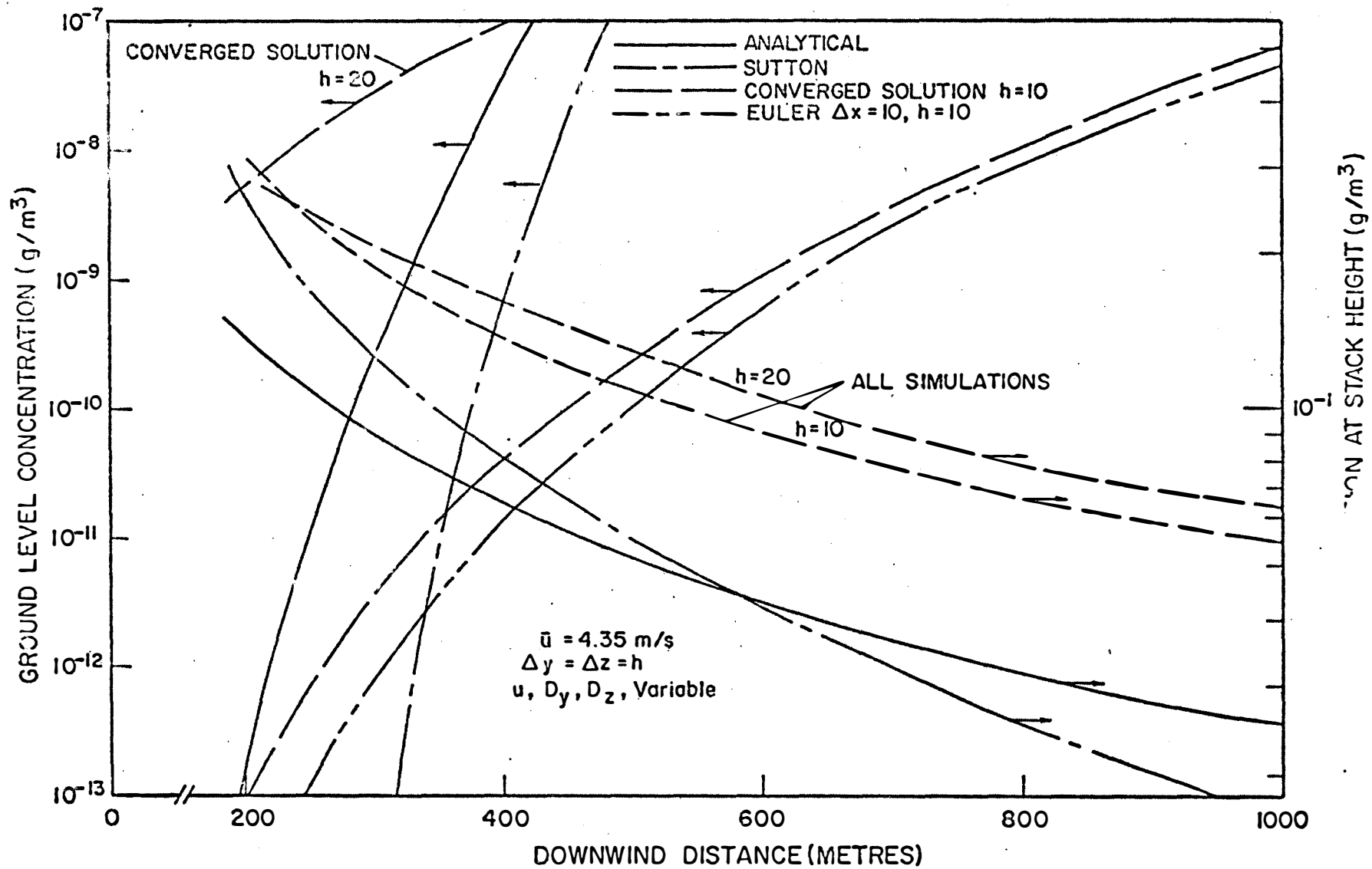
Figure 3 Effect of Variable u, D_y, D_z on Concentration
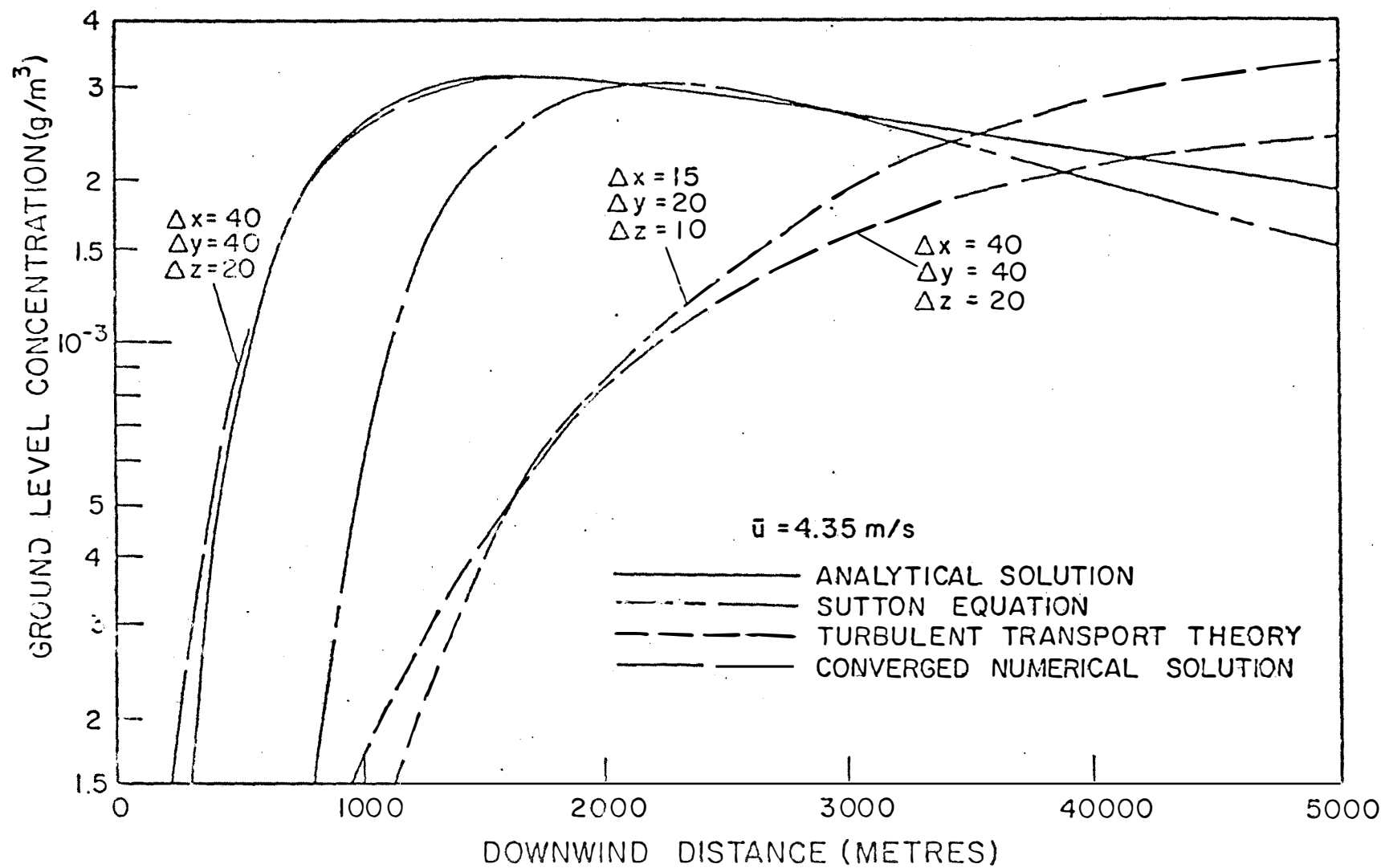
Figure 4   Ground Level Concentrations by Different Schemes
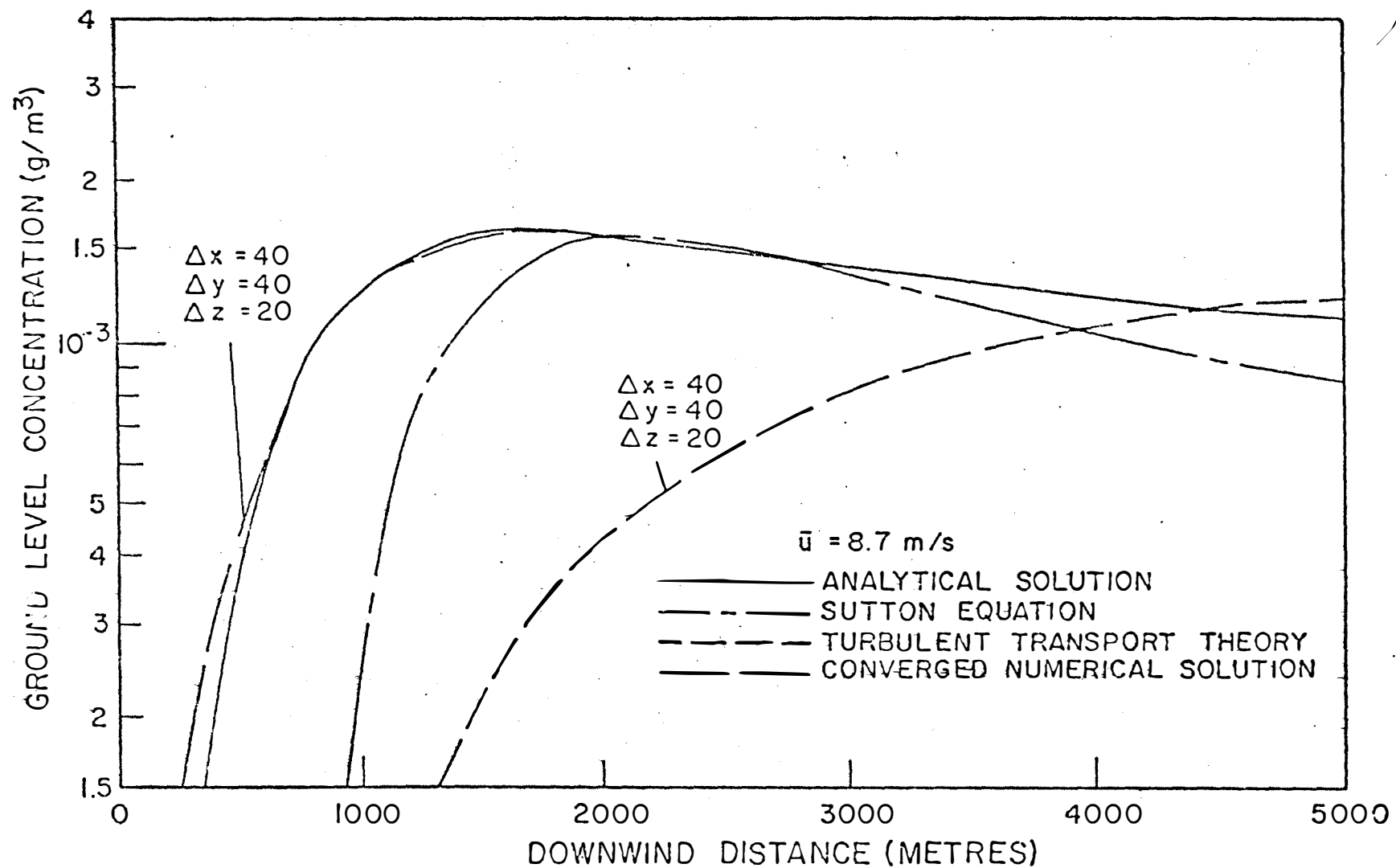
Figure 5   Ground Level Concentrations by Different Methods
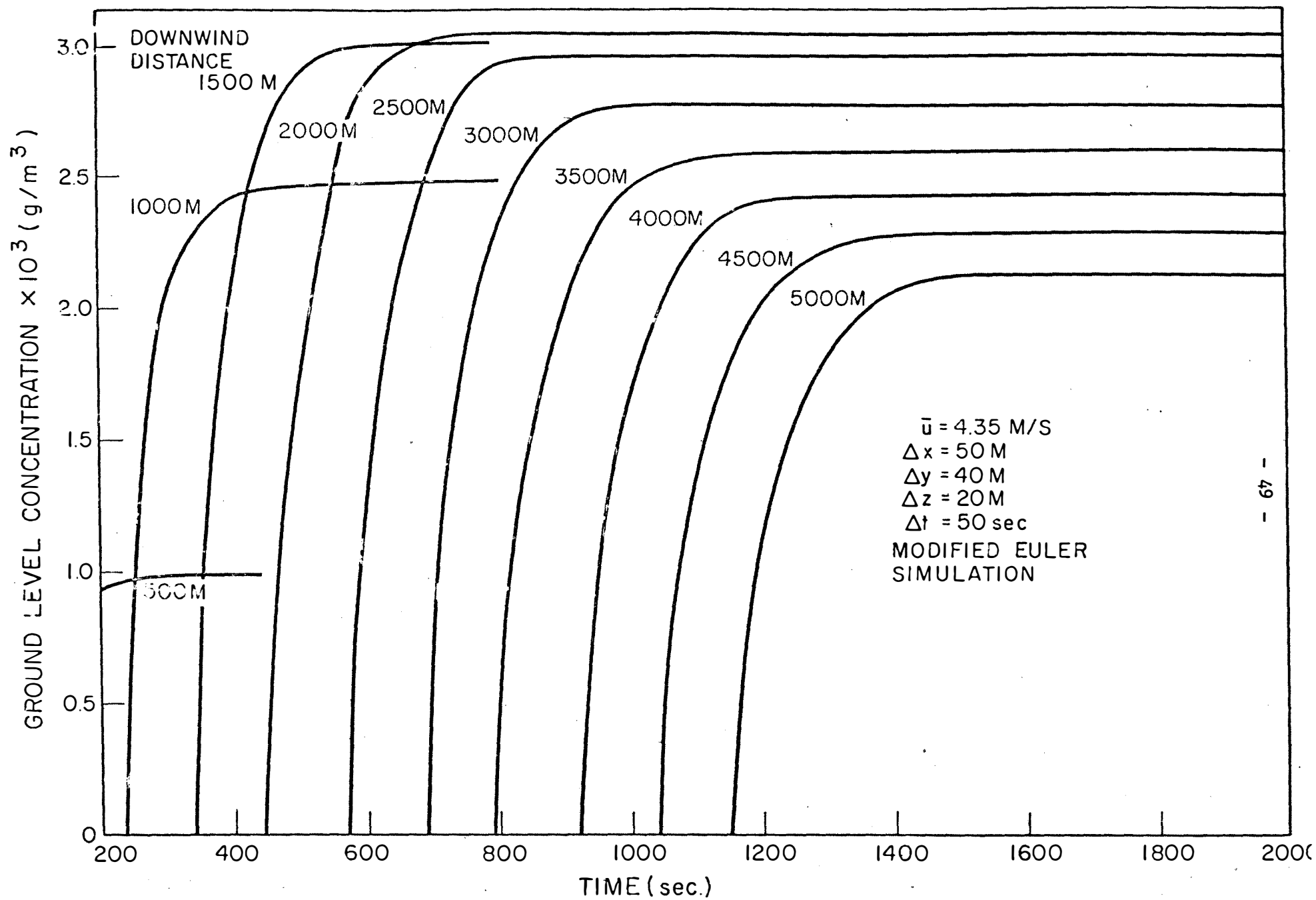
Figure 6 A Transient Simulation of Pollutant Dispersion
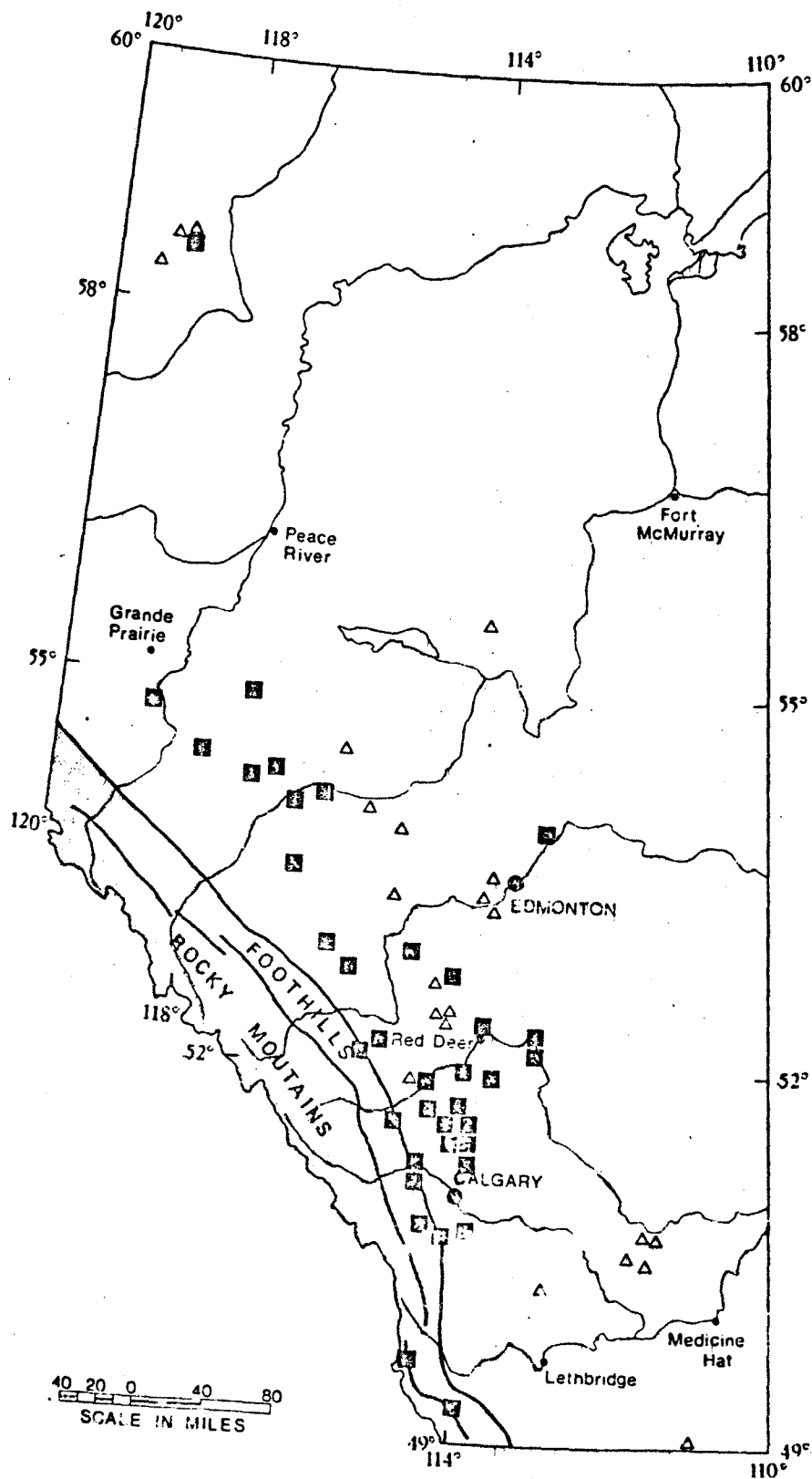
Figure 7 Map of Alberta

⬛ Sulfur producing plants

△ Sour gas plants that do not recover sulfur
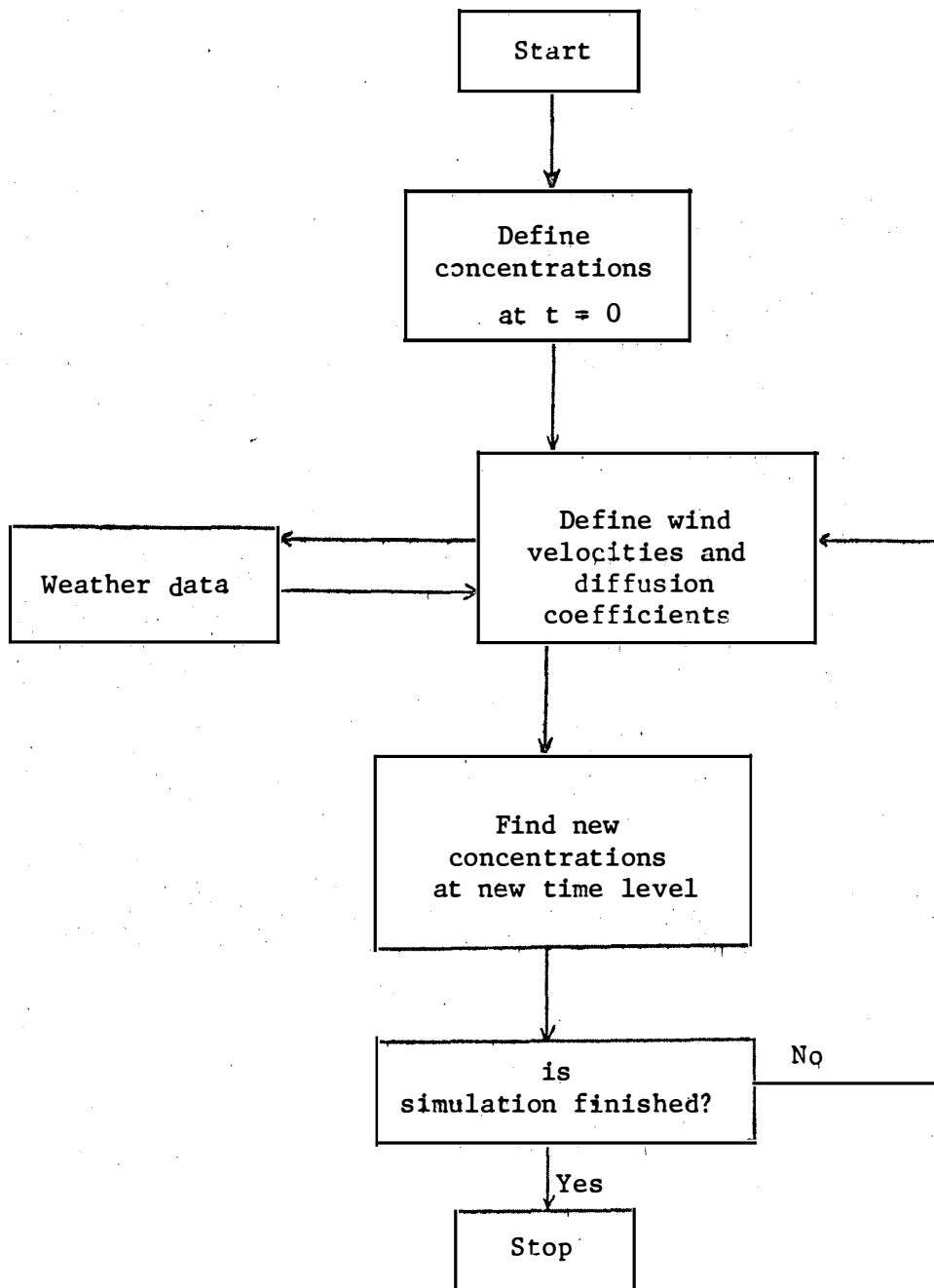
Figure 8 Air Shed Model Flow Diagram

Other Atmospheric Influences

THE FATE OF SULFUR DIOXIDE IN THE ATMOSPHERE

by

M. F. Mohtadi

Department of Chemical Engineering
The University of Calgary
Calgary, Alberta

ABSTRACT

Nearly 1,500 tons per day of sulfur dioxide is discharged into the atmosphere in Alberta, as a result of the operation of sour gas plants. This is equivalent to approximately 10 pounds sulfur per acre in the Province south of the 55th parallel. Only a few percent of the total SO_2 emitted falls directly to the ground in the 1,000 square miles surrounding the plants. The rest is either deposited on the ground by natural precipitation or dispersed in the atmosphere. Since SO_2 is a natural component of the atmosphere and its global recycling follows an intricate pattern through soil, water and vegetation, a careful study of its fate in the atmosphere is highly recommended.

THE ATMOSPHERIC PHOTOCHEMISTRY OF SO₂

by

H. S. Sandhu
Department of Chemistry
University of Alberta
Edmonton, Alberta

ABSTRACT

Recent ideas on the mechanisms of homogeneous oxidation of SO$_2$ are reviewed and methods are suggested for estimating the relevant rate data.

Introduction

Sulfur compounds are an important class of air pollutants. Much research has been published recently on how to minimize emissions and how to remove them from the atmosphere[1].

Sulfur dioxide is removed from the atmosphere by both physical and chemical processes, and the latter may occur heterogeneously or in the gas phase. The gas phase mechanisms are not well established and may be entirely thermal in origin or photochemically induced. A quantitative evaluation of the significance of these homogeneous processes has not been possible due to the lack of rate data particularly for the extremes of meteorological conditions prevalent in Alberta.

This report outlines recent ideas[2,3] on the photo-induced oxidation mechanisms of SO_2 and evaluates semi-empirical methods for calculating the necessary Arrhenius parameters where they are not available from experiment.

Excited States of SO_2 and its Quenching Mechanism

The absorption of solar radiation occurs either in the allowed band which extends from 3400-2900 A° or in the forbidden band from 4000-3400 A°. The former transition gives rise to a singlet molecule SO_2 ($^1B_1$) ($^1SO_2$) while the latter gives rise to a triplet species, SO_2 ($^3B_1$) ($^3SO_2$). Calvert and co-workers[3] have interpreted their results as a reaction scheme:

$$^1SO_2 + SO_2 \longrightarrow {}^2SO_2$$
$$\longrightarrow {}^3SO_2 + SO_2$$
$$+ M \longrightarrow SO_2 + M$$
$$\longrightarrow {}^3SO_2 + M$$

$$^1SO_2 \quad \text{------} \quad SO_2 + h\nu_f$$

$$\text{------} \quad SO_2$$

$$\text{------} \quad ^3SO_2$$

$$^3SO_2 \quad \text{------} \quad SO_2 + h\nu_p$$

$$\text{------} \quad SO_2$$

$$^3SO_2 + SO_2 \quad \text{------} \quad SO_3 + SO$$

$$\text{------} \quad ^2SO_2$$

$$^3SO_2 + M \quad \text{------} \quad Products$$
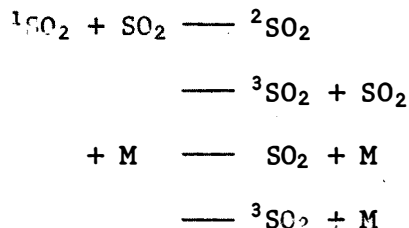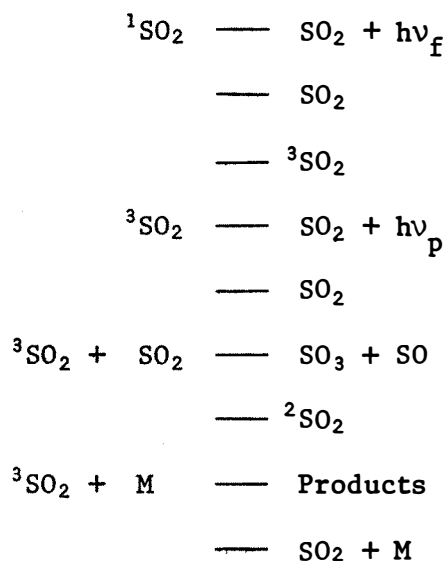
$$\text{------} \quad SO_2 + M$$

where M is a third body and ν_f and ν_p are the fluorescence and phosphorescence frequencies. The reported rate constants for the quenching of $^3SO_2$ molecules by NO and olefinic hydrocarbons, which are found in polluted atmospheres, are close to the collision number ($\sim 2 \times 10^{11}$ liters mole^{-1} sec^{-1}), whereas values for H_2O and O_3 are smaller by a factor of ~ 100.

Computation of Rate Constants

A reaction mechanism can be evaluated only if the concentration of the species involved and the values of the rate constants are known. In spite of the increased research activity in reaction kinetics over the past two decades, experimental kinetic data on certain reactions, relevant to air pollution, are inadequate or non-existent. One is forced to employ semi-empirical methods to estimate rate coefficients to make semi-quantitative predictions. The calculations of the preexponential factors of the rate constants for a variety of unimolecular and bimolecular reactions can be carried out successfully and the

computed values agree reasonably well with the available experimental results[4,5]. In addition, Bond-Energy-Bond-Order (BEBO) method has been widely used to calculate the potential energies of activation for atom transfer reactions[6,7,8] and is expected to yield reasonable estimates of activation energy in the sulfur systems.

Acknowledgement

I thank Dr. A. T. Blades and R. F. Klemm of the Research Council of Alberta for helpful discussions.

References

1. R. F. Klemm. Environmental Effects of the Operation of Sulfur Extraction Gas Plants, Consultant Report Submitted to Alberta Environment Conservation Authority, 1972.

2. M. Bufalini. Environ. Sci. Technol., 5, 685 (1971).

3. H. W. Sidebottom, C. C. Babcock, G. E. Jackson, J. G. Calvert, G. W. Reinhardt and E. K. Damon. Environ. Sci. Technol., 6, 72 (1972) and references therein.

4. S. W. Benson. Thermochemical Kinetics, Wiley, New York, N.Y., 1968, p. 97.

5. A. T. Blades and H. S. Sandhu. Int. J. Chem. Kin., 3, 187 (1971).

6. H. S. Johnston. Gas Phase Reaction Rate Theory, Ronald Press, New York, N.Y., 1966, p. 339.

7. S. W. Mayer. J. Phys. Chem., 74, 3941 (1969).

8. E. Jakubowski, M. G. Ahmed, E. M. Lown, H. S. Sandhu, R. K. Gosavi, and O. P. Strausz. J. Amer. Chem. Soc., 94, 4094 (1972).

SULPHUR ISOTOPE ABUNDANCES AND ENVIRONMENTAL ASSESSMENT —
Applications to Sulphur Gas Research in Alberta

by

H. Roy Krouse
Department of Physics
The University of Calgary
Calgary, Alberta T2N 1N4

ABSTRACT

Since S^{32} and S^{34} differ in their masses, their relative numbers are altered by mass-dependent processes. In Alberta, H_2S from different pools varies considerably in its S^{34}/S^{32} abundance ratios. This provides a means of monitoring gas industry emissions of sulphur compounds and their effects on the environment. Data from Alberta identify industrial contributions of SO_2 to the air and show that these are not readily mixed on a local meteorological scale. Isotopic studies also show that lichens derive sulphur from the atmosphere in a more direct manner than higher plants. Sources of sulphur compounds in streams can also be identified.

INTRODUCTION

Isotopes of an element differ in their masses. Since many physical, chemical, biological, and geological processes are mass dependent, the relative abundances of isotopes are altered in terrestrial processes. Thus, measurements of isotopic abundances provide information about the origin(s) of a given specimen and the conversions that it has undergone.

Isotopic compositions are usually measured with a mass spectrometer. Absolute abundances are difficult to determine to an accuracy of better than 0.1% whereas the relative isotopic abundances in two samples can be compared with precisions of better than ±.01%. For this reason, the isotopic composition of a sample is related to that of a reference using a δ-scale (del-scale). Of the four stable isotopes of sulphur, S^{32} and S^{34} are usually studied and the δ scale is defined as:

$$\delta S^{34} \text{ in } \%_o = \left[\frac{[S^{34}/S^{32}]_x}{[S^{34}/S^{32}]_{std}} -1 \right] \times 1000$$

The standard to which other samples are referred in laboratories the world over is troilite in meteorites, usually the Canyon Diablo meteorite. This choice will be discussed later.

SULPHUR ISOTOPE ABUNDANCES IN NATURE

Since sulphur exists naturally in many forms and valence states, there are numerous processes by which the S^{34}/S^{32} abundance ratio is altered. Since the initial report of THODE et al (1949),

Thode's group and many other researchers have utilized sulphur isotope data to elucidate problems in various research areas.

Figure 1 shows some of the terrestrial δS^{34} variations encountered. One sees the reason for selecting meteoritic troilite as a standard. Its isotopic composition varies little from meteorite to meteorite and falls near the terrestrial average. Deep seated primary sources such as basic sills tend to have narrow δS^{34} distributions near the meteoritic reference. In contrast, sulphur compounds in sedimentary rocks, coal, oil, etc. have large variations in isotope composition because of participation in the biological sulphur cycle. Generally, the more oxidized sulphur species tend to be more enriched in S^{34} compared to the reduced species. This is consistent with statistical thermodynamics (TUDGE and THODE, 1950). Exceptions are common because the world's sulphur isotope distribution is far from conditions of thermodynamic equilibrium.

Whereas present day ocean sulphate is remarkably uniform isotopically (except near freshwater contributaries), evaporite data attest to significant temporal isotopic variations in sulphate in the ancient oceans. Pb-Zn deposits of Western Canada (EVANS et al, 1968; SASAKI and KROUSE, 1969) and petroleum (THODE et al, 1958; THODE and MONSTER, 1965) as well as H_2S in sour gas wells are enriched in S^{34} to roughly the same extent as evaporites. THODE and MONSTER (1965) found petroleum and associated H_2S to be on the average some 15‰ depleted in S^{34} compared to related evaporites. However, more recent studies

(BROWN et al, 1973) on gas wells reservoired in the Devonian revealed many instances where the δS^{34} of the H_2S differed from $SO_4^=$ in the water by only 1 to 2‰.

Figure 1 contrasts with data compiled by previous authors which show narrower δS^{34} distributions particularly in air and water. This simply reflects the paucity of published data. For example, the full range of freshwater variation in Figure 1 is encountered in the Mackenzie River System (HITCHON and KROUSE, 1972). Similarly the range of δS^{34} values in the air of Alberta is considerably larger than that spanned by all previously reported data.

S^{34}/S^{32} ABUNDANCE VARIATIONS IN THE ATMOSPHERE OF ALBERTA

For some three years now, our laboratory has been measuring the sulphur isotope composition of sulphur oxides in the air of Alberta. Samples have been obtained from the Department of the Environment, Government of Alberta and more recently, samples from the Ram River area have been provided by Core Laboratories Ltd. under contract from Aquitaine Co. Ltd. In all cases, solutions from lead peroxide exposure cylinders were oxidized, and precipitated as $BaSO_4$. The $BaSO_4$ was converted to Ag_2S, which was then combusted to SO_2 for mass spectrometric analysis. Mass spectrometry involved simultaneous collection and digital recording of SO_2^+ ion currents at mass 64 and 66 (McCULLOUGH and KROUSE, 1965).

Figure 2 and Table 1 show data obtained in initial stages

of the study. The δS^{34} values ranged from +7‰ to +28‰. In Figure 2, the value at any location represents the average of several stations. These variations appeared as localized phenomena. This means that sulphur oxides near ground level in Alberta have not been mixed on a broad meteorological scale. Further, these isotopic compositions fall in the ranges associated with petroleum and sour gas. These findings are not surprising and can be concluded by conventional chemical analyses. Indeed, the data are biased since the Alberta Department of the Environment air monitoring sites are presumably chosen on the basis of known sources of atmospheric emissions.

Table 1 shows that in many cases, the isotopic composition did not change during consecutive samplings one month apart at the same station; e.g. Red Deer 4, Windfall 5, Okotoks 2, Coleman 8. On a given date, different stations in the same area sometimes gave consistent δS^{34} values, e.g. Red Deer 4,5 and Okotoks 2,4. On the other hand, there were cases where consecutive samples at the same station were noticeably different (e.g. Carstairs 4) and where a given station was not consistent with neighbouring stations, e.g. Red Deer 6.

Data obtained since these initial studies show that the δS^{34} value depends on the season at a given station. Further, this dependence is not uniform for stations throughout the province although adjacent stations tend to behave similarly.

We have plotted δS^{34} vs. sulphur oxide concentrations

to ascertain the isotopic composition of the "natural background" in Alberta. At higher concentrations, the isotopic variations should be greater because of varied industrial contributions whereas lower concentrations should be more indicative of the background. From these data, we conclude that the isotopic composition of the background in Alberta varies significangly from place to place and with season. If industrial contributions are not mixed on a broad meteorological scale, natural contributions should not behave otherwise.

For a given location, δS^{34} values usually converge with higher sulphur oxide concentrations. This is exemplified by data from Balzac (Figure 3).

To interpret Figure 3, consider a number of simplified situations illustrated in Figure 4. Sources A and B have different isotopic compositions which remain constant. In case 1, source A is constant in its emission rate and since it also has a fixed δS^{34} value, it plots as a point on a δS^{34} vs. sulphur oxide concentration graph. In case 2, source A varies in its emission rate and therefore plots as a horizontal line. In case 3, the emission rate for source A is constant while that of B varies. When the rate for B approaches zero, the isotopic composition of the emission approaches that of source A. As the emission rate increases, its isotopic composition approaches that of source B. In case 4, where both A and B can vary in their emission rates for a given concentration, the δS^{34} value can fall anywhere between that of A and B dependent upon the relative contributions

from each source. In case 5, A is a small source while the surroundings (natural background plus other man-made sources) are inhomogeneous isotopically and variable in emission rate. As the surroundings approach zero emission rate, the isotopic composition approaches that of source A. With increasing emission, the δS^{34} spread increases as the different surrounding sources contribute to the total emission. In case 6, source A generally dominates so the isotopic spread associated with the inhomogeneous surroundings appears at lower concentrations. At higher concentrations the δS^{34} values converge to that of source A. Other situations and combinations of these six cases can be envisaged. Further, the δS^{34} variations may be a function of location and/or time.

The data of Figure 3 can be identified with case 6 of Figure 4. We conclude that at Balzac, there is a dominant source which is uniform in its isotopic composition but varies in its emitted contributions to a given location. The surroundings consist of sources whose isotopic compositions and emissions vary considerably in time and space. The histogram of Figure 3 gives the frequency of encountering δS^{34} values. This distribution peaks while being independent of concentration. This provides further evidence for a dominant source of constant δS^{34} value which varies in its contributions to a given location.

The interpretation of sulphur isotopic abundance data and the identification of sources must be executed with care. Effluent sulphur gases from a stack may differ isotopically from the raw material being processed. If isotope exchange occurs, the order of S^{34} enrichment

would be $SO_4^= > SO_3 > SO_2 > H_2S$ (TUDGE and THODE, 1951).

Enrichments of S^{34} in SO_3 compared to SO_2 have been observed in flue gases and interpreted as exchange processes at elevated temperatures (BALDWIN et al, 1969). Generally, the process of adding oxygen atoms is not expected to alter the sulphur isotope composition significantly (LEWIS and KROUSE, 1969). In the atmosphere, sulphur isotope exchange among sulphur compounds should proceed rather slowly because of dilute concentrations and low temperatures. Therefore, if the isotopic composition of stack emissions are known, their fate should be traceable.

Temporal variations at a given sampling station can arise in many ways. We have already seen that a background which is isotopically inhomogeneous and varying in emission is one possibility. If an industrial operation is dominant, isotopic variations can result if it processes different raw materials. Isotopic analyses of stack gases for the individual raw materials combined with production log data would assist in interpreting the net effects. A given sampling station may experience contributions from more than one industrial operation. In that case, the isotopic composition in a given time interval is highly dependent upon the wind direction. In such a situation, a polar diagram with δS^{34} as the radial co-ordinate and wind direction as the angular co-ordinate might distinguish the sources.

Our studies to date have dealt with samples representing

one month exposure. In many cases, there was an insufficient sample
for a reliable sulphur isotope analysis. We have every hope of developing
an apparatus in the near future which can collect enough sample within a
time span of minutes. In this way, a given location could be effectively
monitored and the isotopic data correlated to other parameters such as
wind direction.

SULPHUR ISOTOPE ABUNDANCES IN VEGETATION

In our study in the Ram River area, we measured sulphur
isotope abundances in lichen and pine needles. These data are compared
to atmospheric data in Figure 5. The lichens have the same isotopic
range as the atmospheric samples. This suggests that lichens obtain
their sulphur directly from the atmosphere and/or as scavenged sulphate
in precipitation. The mean isotopic composition of the lichens is
higher than the associated atmospheric samples but we do not believe
that this negates the interpretation. Rather, there is the question
of how quickly lichens respond to an isotopic change in the atmosphere.
The atmospheric samples present a monthly mean isotopic composition
but the lichens may represent longer or shorter integration times.

In contrast, the definite shift to a lighter isotopic
composition for the pine needles must reflect the complex mechanisms
by which sulphur finds its way to the needles. Figure 6 illustrates
some of the possibilities. There is the question as to how the rate
of uptake from the air compares to transportation within the tree

system. In other words, is the net sulphur movement upwards or downwards? To what extent do all the needles of the tree isotopically equilibrate with each other? Is it a dynamic system or do older needles reflect the isotopic situation at some time in the past? In the soil, there are also a number of variables. Some of the sulphur is introduced to the soil from the atmosphere. There may also be other sources such as subsurface gypsum. Microbiological activity in the soil will redistribute sulphur isotopes. Experiments to eludidate some of these problems have been started.

Since the δS^{34} composition of the atmosphere of Alberta is quite positive as compared to the terrestrial average, we are also examining soil, lichens, and needles in the location where the atmospheric δS^{34} composition is nearer to zero (Wawa, Ontario). This study should test the validity of the interpretations made for the Ram River area.

SULPHUR ISOTOPES IN HYDROLOGY

Our studies of sulphur isotope abundances in streams have not been directly related to the sour gas processing industry. However, a brief summary of our findings illustrates the potential of this technique.

In studies of thermal springs of western Canada, the δS^{34} values for $SO_4^=$ fell in line with evaporite data. We were able to conclude that the sulphate did not arise by the chemical oxidation of sulphides at depth but rather ancient marine sulphate deposits were

dissolved by these waters. The H_2S in these springs was much lighter isotopically than the associated sulphates; this could be attributed to the preferential reduction of $S^{32}O_4^=$ by sulphate-reducing bacteria (KROUSE et al, 1970). In a study of the Mackenzie River System, HITCHON and KROUSE (1972) were able to relate the δS^{34} values encountered to different geological sources with the help of chemical data and factor analyses despite the fact that biological activity had undoubtedly altered the isotopic abundances. KROUSE and MACKAY (1971) used H_2O^{18}/H_2O^{16} abundances to verify that thorough lateral mixing of the Mackenzie and Liard rivers required a distance of the order of 200 miles.

More recently, HISLOP and KROUSE (1973) carried out a pilot study on the Calgary river system. Generally, we found that relatively smooth concentration profiles could be contrasted by large variations in the δS^{34} values. Figure 7 shows one interesting cross-section from our study. Note the δS^{34} fluctuations in the mainstream. Also note that the east branch (sample 7) has a much higher concentration and much lower δS^{34} value than samples in the main stream. These data point to a source on the east branch since contributions from Nose Creek or further upstream should have also affected sample 6. However, sample 6 is similar in concentration and δS^{34} value to other samples in the mainstream.

Contributions from the Sulphur Gas Industry and their fates in streams could be effectively monitored by S^{34}/S^{32} abundance measurements.

CONCLUDING REMARKS

Our studies of sulphur isotope variations have emphasized that identification of sources, dispersion, mixing phenomena and environmental impact are very complex problems. Our studies also give insight into the difficulties sometimes encountered with conventional techniques. The fact that we have measured different δS^{34} values for the same concentration at a given sampling site in both atmospheric and water studies means that concentration measurements alone are insufficient to provide unambiguous interpretations. The understanding of complex phenomena requires many measurements of a number of parameters. For example, close meteorological monitoring coupled with concentration measurements reduces the chances of misinterpretation (in comparison to using concentration data alone). Stable isotope abundances have the desirable property of providing a natural label. Like any other parameter it is most effective when other techniques are also done well.

ACKNOWLEDGMENTS

REFERENCES

Baldwin, Robert D. et al, "The Atmospheric Diagnostics Program at
    Brookhaven National Laboratory: Second Status Report."
    U.S. Department of Commerce, November 1969.

Brown, H.M., Hitchon, Brian and Krouse, H.R., Unpublished isotope data
    on Alberta gas wells (1973).

Evans, T.L., Campbell, F.A. and Krouse, H.R., "A reconnaissance study
    of some western Canadian Lead-Zinc deposits." Econ. Geol. 63,
    349-59 (1968).

Hislop, R. and Krouse, H.R., Unpublished Sulphur Isotope Data on the
    Calgary River System (1973).

Hitchon, B. and Krouse, H.R., "Hydrogeochemistry of the surface waters
    of the Mackenzie River drainage basin, Canada - III. Stable
    isotopes of oxygen, carbon and sulphur." Geochim. Cosmochim.
    Acta 36, 1337-57 (1972).

Krouse, H.R., Cook, F.D., Sasaki, A. and Smejkal, V., "Microbiological
    fractionation in springs of western Canada." Rec. Dev. Mass
    Spec., University Park Press, 629-39 (1970).

Krouse, H.R. and MacKay, J.R., "Application of H_2O^{18}/H_2O^{16} abundances
    to the problem of lateral mixing in the Liard-Mackenzie River
    system." Can. J. Earth Sci. 8, 1107-09 (1971).

Lewis, J.S. and Krouse, H.R., "Isotopic composition of sulfur and sulfate
    produced by oxidation of FeS." Earth and Plan. Sci. Lett.
    5, 425-428 (1969).

McCullough, H. and Krouse, H.R., "Application of digital recording to
    simultaneous collection in mass spectrometry." Rev. Sci. Instru.
    36, 1132-34 (1965).

Thode, H.G., MacNamara, J. and Collins, C.B., "Natural variations in the
    isotopic composition of sulphur and their significance." Can. J.
    Res. B27, 361-73 (1949).

Thode, H.G. and Monster, J., "Sulfur-isotope geochemistry of petroleum,
    evaporites and ancient seas." Amer. Assoc. Petrol. Geol. Mem.
    4, 367-377 (1965).

Tudge, A.P. and Thode, H.G., "Thermodynamic properties of isotopic
    compounds of sulfur." Can. J. Res. B28, 567-578 (1950).

Table 1

Isotopic composition of oxidizable sulfur
compounds in samples of air from Alberta

Location	Station	Date (1971)	δS^{34}
Red Deer	4	Aug. 13	+20.9
	4	Sept. 15	+20.3
	5	Sept. 15	+20.7
	6	Sept. 15	+14.0
Lone Pine Creek	2	Aug. 12	+27.1
	2	Sept. 16	+28.1
Windfall	5	Aug. 6	+15.6
	5	Sept. 9	+15.4
Okotoks	2	Aug. 4	+21.3
	2	Sept. 1	+21.5
	4	Sept. 1	+21.6
	3	Sept. 1	+18.2
Bigstone	1	July 8	+18.3
	2	July 8	+18.4
Coleman	8	July 27	+12.7
	8	Sept. 2	+12.8
Carstairs	4	Aug. 11	+16.7
	4	Sept. 16	+19.0

Figure 1:   Terrestrial δS^{34} Variations.

Figure 2: δS^{34} Variations in Oxidizable Sulphur Compounds in Alberta Air: July-August, 1971.

Figure 3: δS^{34} vs Sulphur Oxide Concentration for Stations near Balzac, 1972.

Figure 4: δS^{34} vs Sulphur Oxide Concentration for a number of hypothetical situations.

Figure 5:   Comparison of δS^{34} Values for Atmosphere, Lichen and Pine Needles: Ram River Area, 1972-73.

Figure 6:   Unknowns in Sulphur Transport in a Pine Tree.

Figure 7: δS^{34} and $SO_4^{=}$ Concentrations in a Cross-Section of the Calgary River System, April 1973.

Figure 1: Terrestrial δS^{34} Variations.

Figure 2: δS^{34} Variations in Oxidizable Sulphur Compounds in Alberta Air: July-August, 1971.

Figure 3: δS^{34} vs Sulphur Oxide Concentration for Stations near Balzac, 1972.

Figure 4: δS^{34} vs Sulphur Oxide Concentration for a number of hypothetical situations.

Figure 5: Comparison of δS^{34} Values for Atmosphere, Lichen and Pine Needles: Ram River Area, 1972-73.

SULPHUR OXIDES ?

BACTERIAL CONVERSIONS

? NUTRIENTS

? DEEP SOURCES

Figure 6: Unknowns in Sulphur Transport in a Pine Tree.

Figure 7: δS^{34} and $SO_4^=$ Concentrations in a Cross-Section of the Calgary River System, April 1973.

ATMOSHPERIC SULPHUR DIOXIDE: EFFECTS ON THE pH AND SULPHUR CONTENT OF
RAIN AND SNOW;   ADDITION OF SULPHUR TO SURFACE WATERS, SOIL, AND CROPS;
AND ACIDIFICATION OF SOILS

by

M. Nyborg
Soil Science Department
University of Alberta, Edmonton

and

McKinnon, Allen & Associates Ltd.

INTRODUCTION

Direct toxicity of SO_2 to humans, livestock, and vegetation has received much attention. Quite apart from direct toxicity, SO_2 may have important indirect effects on the environment. The sulphur content and acidity of rain, snow, soils and waters may be increased by SO_2 emissions with consequent effects on vegetation and aquatic life.

Sulphur gases that do not settle out are slowly oxidized to sulphate in the atmosphere. Neutral sulphate salts form to the extent that cations are available in the atmosphere (e.g. NH_4^+, Ca^{++}, Mg^{++}, K^+, Na^+) but any excess sulphate forms sulphuric acid. Rain and snow in New England and northwestern Europe frequently contain small amounts of sulphuric acid (Johnson *et al.* 1972, *Anon* 1971). Average pH of precipitation was found to vary from 3.9 to 4.3 at several stations in New York State, New Hampshire, Massachusetts and Connecticut (Likens 1972). By comparison, rains in areas distant from industry usually have pH values in the range of 5.5 to 7.0. In Sweden forest growth has been slightly reduced and some bodies of water have become too acid for certain types of fish (*Anon* 1971); and the cause is apparently the deposition of sulphuric acid in rain and snow (*Anon* 1971). Deposition in rain and snow is generally considered the main way that SO_2 emissions are brought to earth (Alway 1937, Hoeft 1972).

However, SO_2 can be adsorbed directly from the air by both plants (Coleman 1966) and soils (Johansson 1959).

In Alberta the processing of sour natural gas and the extraction of oil from the tar sands together result in emission of about 550,000 long tons of SO_2 annually (Tollefsen 1972). The long-term effects of those emissions on soils and waters depends entirely on the concentration and form in which the S comes to earth. Evenly distributed over the province annual emissions would result in a deposition rate of about 3 lbs. per acre. But emission sources are *not* evenly distributed and deposition is probably concentrated around the sources. If depositions were concentrated on only 5% of the province (about 10 million acres) the rate of deposition would then be about 60 lbs. per acre per year. Assuming the S were deposited mostly as sulphuric acid, the pH of most soils would drop by 0.5 to 1.5 units after 10 years. In many farm soils such a decrease would mean that soil-acidity sensitive crops (e.g. alfalfa and barley) would no longer grow well. Acidity in farm soils could be corrected by liming, but this would be difficult if not impractical in forests.

Sulphur depositions may be a benefit in some areas, especially if they are not acid-forming. Many soils in Alberta are deficient in S for farm and forest crops, and on those soils use of S fertilizers increases yield of cereal grains, rapeseed, and legumes (Nyborg 1968). Consistent deposition of about 10 lb. S per acre annually would eliminate much of the need for S fertilizers.

Relatively small amounts of S are brought down by precipitation in Alberta. Walker (1969) estimated that 2 to 4 lb. S per acre come down annually in rain and snow in Central Alberta. Summers and Hitchon (1973) estimated

that an average of 2.3 lb. S per acre was deposited by rain in 3 months within a 25 miles radius of a gas plant emitting 30 long tons of S daily. There is no information on the amounts of S being deposited by other means in the province.

Our objectives were to find how and where SO_2 comes to earth and in what concentrations. Specific objectives were to find if SO_2 emissions acidify precipitation, soils and waters under Alberta conditions; and to determine the amounts of SO_2 adsorbed directly by vegetation, soils, and waters at different distances from gas plants.

This paper brings together results to date from two separate projects. One project, supported by Shell Canada Limited, was begun in 1972 with work concentrated in the Pincher Creek-Waterton area. The other, sponsored by the Alberta Environmental Research Trust, was started in 1973 at various locations.

METHODS AND MATERIALS

In 1972, 12 stations were established near the Shell Waterton gas plant, which has a maximum emission of 124 long tons of sulphur per day. Eleven of the stations were located close to the plant (1.5 to 10 miles) while 1 control station was 25 miles away. In 1973, the number of stations was increased from 12 to 19. In 1973, 59 additional stations were established in other areas of Alberta and 4 control stations were placed in Saskatchewan. Thirteen were located near the Aquitaine Ram River gas processing plant, which has a maximum emission of 84 long tons of S per day.

Rainfall samples were obtained at each station, using plastic funnels mounted on plastic receiving bottles. Funnels were fitted with fine screens to exclude insects and debris. In 1972 samples were taken from each rainfall, but

in 1973 samples were taken of accumulated rainfall during each week.

New and old snow were sampled during January-March, 1973 near the
Waterton plant, near the Ram River plant, throughout north-central and north-
ern Alberta, and in northern Saskatchewan.

Rain and snow water were analyzed for pH, and for SO_4 by a modifi-
cation of Dean's method (1966). Some samples were also analyzed for content
of Ca, Mg, Na, K (by atomic absorption), and NH_4 and NO_3 (by steam distil-
lation).

Experiments to determine the amount of S added to soils by emissions,
and the effect of emissions on soil pH, were conducted at all stations in 1972
and 1973. However, only three experiments set out in 1972 near the Waterton
plant have been completely analyzed.

The amount of S added to soils was estimated by exposing a Gray Wooded
topsoil of loam texture (Breton series) in 1-gallon plastic pots at 6 stations
near the Waterton plant. The pots were kept free of plant growth and period-
ically brought to field capacity water content by adding distilled water. The
pots were exposed during June, July and August of 1972. The soil was then
analyzed for soluble SO_4-S.

The effect on soil pH was estimated in two experiments. In one
experiment, the Gray Wooded soil was placed in 2-gallon plastic pots, sown to
creeping red fescue and exposed at 10 stations without watering from late June,
1972, to early May, 1973. Soil pH was determined on samples from the 1- to 3-cm.
depth. (The top 1 cm. was discarded because of wind-blown soil and debris at
some stations.) In the other experiment, barley was grown on a slightly cal-
careous Dark Brown soil of loam texture in four 5-gallon plastic pots at each
of 12 stations. The pots were exposed from June 1 to September 1, 1972
and were periodically brought to field capacity with distilled water. Soil

pH was determined on the top 5 cm. and on the top 15 cm. of all pots. Barley grown in similar pots in 1973 was sampled at weekly intervals for determination of water-soluble SO_4-S.

Absorption of sulphur emissions by water was estimated in experiments near the Waterton and Ram River plants in 1973. Distilled water was exposed in plastic beakers (connected to a reservoir which maintained the water level), protected by a fine screen to exclude insects and debris and a roof to exclude rainfall. Exposure was during August near the Ram River plant, and from mid-August to late September near the Waterton plant. The water samples were then analyzed for SO_4-S content and pH.

The pH of soils was determined in a mixture of 1 part soil and 2.5 parts water. The soluble SO_4-S in soils was extracted with 0.1M $CaCl_2$ solution, and soluble SO_4-S in plant samples was extracted with water. The SO_4-S content of water, and soil and plant extracts was determined by a modification of Dean's (1966) method.

RESULTS

The pH and sulphur content of rain

From June 22 to August 1, 1972, the average pH of rain from four stations 1.5 to 10 miles downwind from the Waterton plant was 1.3 to 0.6 units lower than at the control station 25 miles away, or at two stations not downwind (Table 1). The SO_4-S content of rain downwind was moderate (1.5 to 2.8 ppm) and higher than at the control station (0.9 ppm).

Results were quite different in 1973. The SO_4-S content at the control station was similar to that in 1972. But downwind from the gas plant SO_4-S content was consistently higher than in 1972; while pH was *not* depressed signif-icantly (Table 1). Analyses of selected rains for Ca, Mg, K, Na, and NH_4 in-

dicated that SO_4-S in rains during 1973 occurred as $CaSO_4$ (and sometimes as

Na_2SO_4 or K_2SO_4), while acid rains in 1972 did not contain enough cations to

neutralize all the H_2SO_4 in the rain. We do not know which year was typical.

Table 1. The pH and sulphur content of rain at several stations in 1972 & 1973 as influenced by direction and distance from a gas plant.

Location of station		Average composition of summer rains			
	Distance from	pH		SO_4-S (ppm)	
Direction	gas plant (miles)	1972	1973	1972	1973
Directly downwind	1.5	4.8	6.4	2.8	2.6
	4	4.6	6.2	1.5	2.4
	6	4.9	6.2	1.5	2.1
	10	5.3	6.3	2.5	3.6
Not downwind	8	5.9	6.6	1.3	1.6
	9	5.9	6.8	1.5	1.9
Control site	25	5.9	6.5	0.9	0.8

The SO_4-S content of rains at 19 stations operated from June 14 to

August 10, 1973 in the vicinity of the Waterton plant (Fig. 1) demonstrated

that a large plant increased the S content of rain for a considerable distance.

The average at the control site was 0.6 ppm, and at two stations located 16 and

18 miles downwind from the plant 2.5 and 2.1 ppm, respectively (Fig. 1).

Elevated S content and slightly decreased pH of rain were found near

the Ram River plant in 1973 (Fig. 2). Rain at sites remote from SO_2 emissions

had substantially lower SO_4-S content and slightly higher pH than rain at sites

near the two plants (Table 2). Despite increased concentration of S in rain

● 2.5

2.0 TO 2.9 PPM

● 2.1

0.6 ppm at
control site
25 miles from
gas plant

● 1.3

MORE THAN 3.0 PPM

● 3.2

● 5.2

● 1.6   ● 2.5

●
1.7

● 3.0

● 2.5

● 1.8

● 2.2

GAS PLANT

● 2.1

●
1.5

● 1.8   ● 1.2

LESS THAN 2.0 PPM

N

Scale: 1 inch = 5 miles

● 1.1
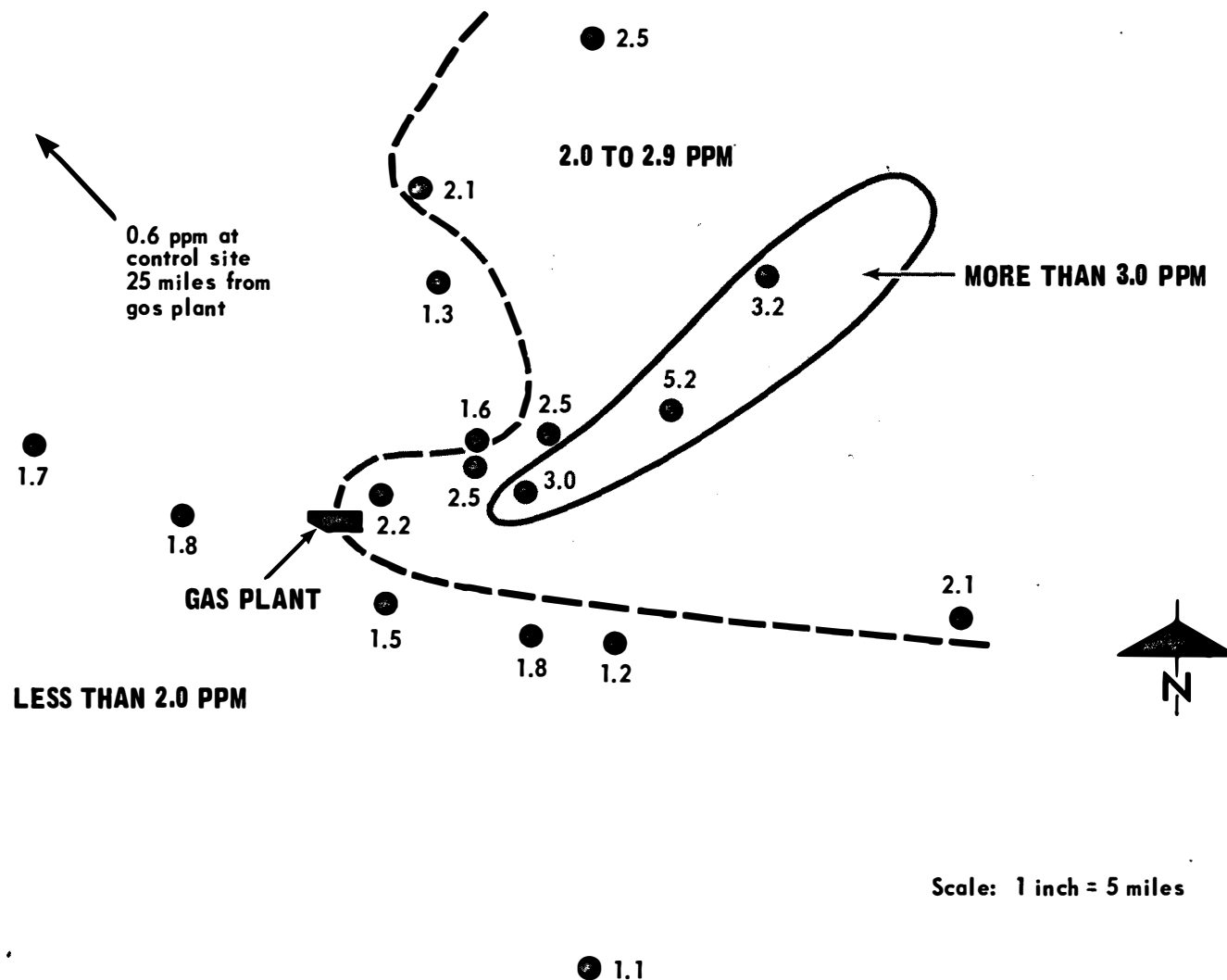
Figure 1   Average content of SO$_4$ – S (ppm) in rainfall from June 14 to August 10, 1973, at 18
stations in the vicinity of a gas processing plant. (Location stations shown by dark circles)

pH 5.7
0.8 ppm S

pH 6.1
1.3 ppm S

pH 5.8
0.9 ppm S

N

pH 5.9
0.8 ppm S

pH 5.7
0.9 ppm S

— GAS PLANT

pH 5.6
1.6 ppm S

Scale: 1 inch = 2 miles

pH 5.2
2.2 ppm S

pH 5.5
1.9 ppm S

pH 5.6
1.7 ppm S

pH 5.5
1.5 ppm S
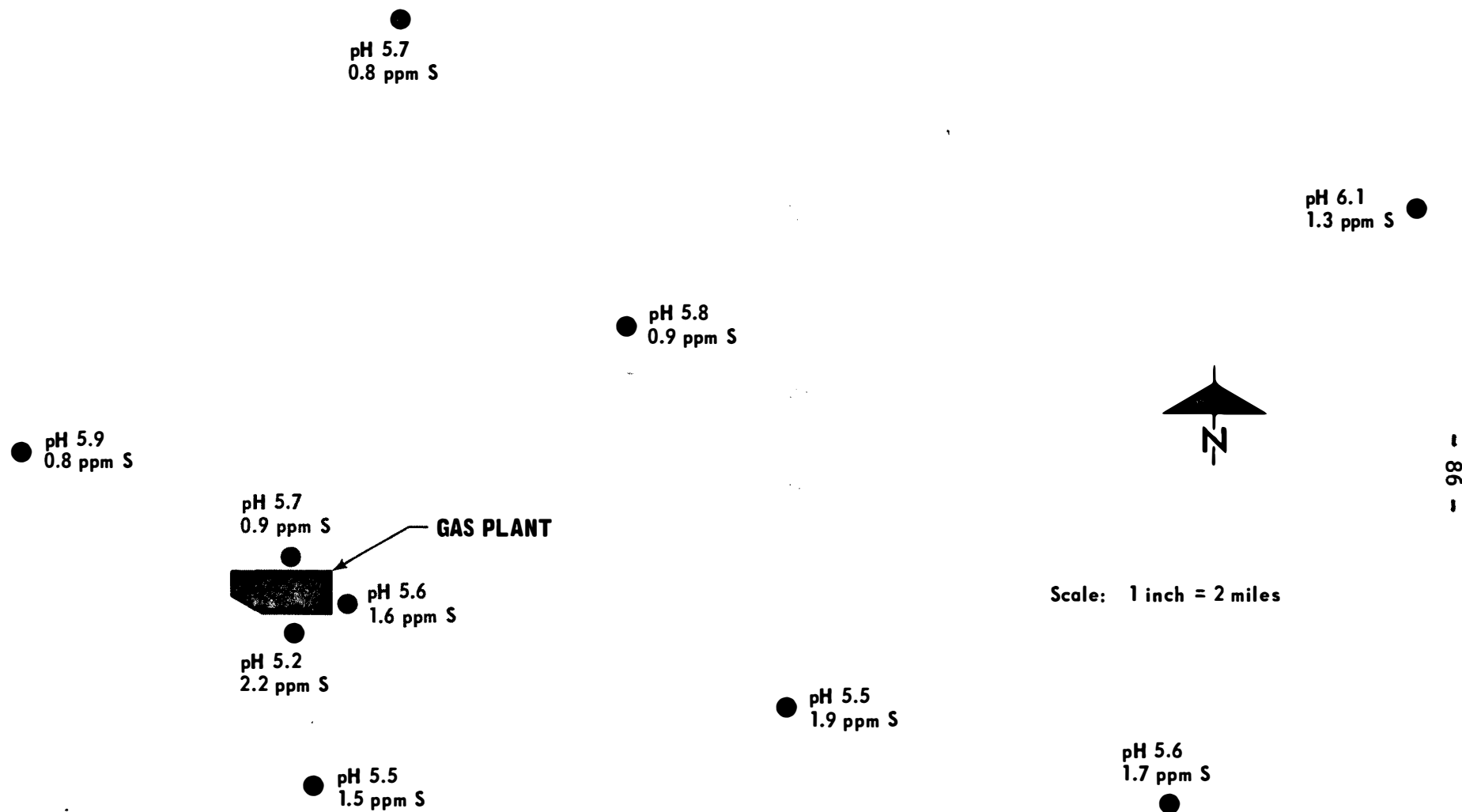
Figure 2:   Average pH and SO$_4$ – S content of rainfall from July 5 to August 30, 1973, at 10 stations in the vicinity of a gas processing plant.

near the two plants, the amounts brought down were quite small: less than 2

lb. S per acre (Table 2).

Table 2. Characteristics of rain during 1973[1] at stations remote from and
near to sources of SO_2 emissions.

Location	Average pH	Average SO_2-S content (ppm)	Amount of sulphur brought down by rain (lb. S/acre)
Lundbreck, Alta.	6.5	0.8	0.6
Thickwood Hills, Alta.	6.0	0.7	0.5
Canwood, Sask.	6.3	0.6	0.7
Fiske, Sask.	6.4	0.7	0.3
Waterton plant[2]	5.6	2.4	1.3
Ram River plant[3]	5.5	5.5	1.6

[1] For the periods May 1 to September 7 at Lundbreck, July 10 to September 13 at

Thickwood Hills, June 27 to September 5 at Canwood, and June 28 to September 5

at Fiske.

[2] Average for 4 downwind stations, June 1 to August 30, 1972 and May 1 to

September 7, 1973.

[3] Average for 6 downwind stations, July 5 to August 30, 1973.

The pH and sulphur content of snow

Samples of newly-fallen and old snow were taken at some 100 sites

in Alberta and Saskatchewan. Typical results showing pH and S content of

the winter's accumulated snow are given in Table 3. At two sites remote

from SO_2 sources (Beaverlodge, Alta.; and Canwood, Sask.) the winter's snow

(as sampled in March, 1973) contained less than 0.2 lb. S per acre, and pH of

the snow water averaged 5.5. At sites in central Alberta, which are close to

several plants, S content increased to only 0.6 lb. S per acre and pH was approximately 6.0. Likewise, in the vicinity of the Ram River plant the winter's snow had only about 0.6 lb. S per acre, and pH was about 6.0. The results in Table 3 show that gas plants added less than 1 lb. S per acre to snow, and did not make the snow acid (instead there was a tendency for the pH of snow to *increase* with increasing S content).

Newly-fallen snow typically had S contents of 0.1 to 0.4 ppm whether taken near plants or in remote areas. Older snow had slightly higher contents, especially near plants, indicating that atmospheric S was either absorbed by the snow or deposited on it. Experiments near one gas plant demonstrated snow surfaces absorbed small amounts of S directly from the air over a period of several weeks.

Table 3. The pH and sulphur content of the winter's accumulated snow, at various locations sampled in March, 1973.

Location	pH of snow	Sulphur in the winter's snow (lb. S/acre)
Distant Sites		
Beaverlodge, Alberta	5.4	0.14
Canwood, Saskatchewan	5.6	0.16
Sites in the Region of Gas Plants		
Lacombe, Alberta	6.2	0.42
Stettler, Alberta	5.9	0.40
Ram River Plant		
control*	5.6	0.22
downwind**	5.8	0.63

*Average of 2 remote sites.
**Average of 6 sites at 1 to 12 miles from the gas plant.

Amounts of sulphur gained by soils

Sulphur gained by bare soil, and deposited by rain during 3 months, is given in Table 4. Total S gained by the soil was 8 to 10 times greater than the amount in rain at 3 stations directly downwind from the Waterton gas plant, and it was 3 to 5 times greater at 3 other stations not directly downwind. The amounts of sulphur gained by the soil were substantial, varying from 9 to 18 lb. S per acre at three stations located from 6 to 1.5 miles downwind from the plant.

Table 4. Sulphur brought down in rain and gained by soil from June 1 to August 30, 1972, at stations near the Waterton plant.

Location of station		Sulphur (lb. S/acre)	
Direction	Distance from gas plant (miles)	Brought down in rain	Gained by soil
Directly downwind	1.5	1.8	18.3
	4	1.4	11.0
	6	1.2	9.4
Not directly downwind	3	1.6	7.3
	7	0.9	4.9
	7	1.3	3.5

Depression in soil pH

After exposure of the Gray Wooded soil for 10 months, pH of the 1- to 3-cm. depth was an average of 0.10 units lower at 5 stations directly downwind from a plant than at 5 stations not directly downwind (Table 5). Likewise, after exposure of the Dark Brown for 3 months near the plant, pH of the top 5 cm. of soil was an average of 0.06 units lower at 6 sites with high

sulphation cylinder readings, than at 6 sites with lower readings (Table 6).
A difference of 0.08 units was found for the top 15 cm. of the Dark Brown soil.
While differences were very small for the Dark Brown soil, they were statis-
tically significant.

Two exploratory experiments, one with a poorly-buffered subsoil
and another with a Black topsoil, also showed slight but consistent lowering
of soil pH on exposure for 6 weeks directly downwind from the plant.

Table 5. The pH of the 1- to 3-cm. depth of a Gray Wooded soil exposed for
10 months at stations near a gas processing plant.

Location of station

Direction	Distance from gas plant (miles)	pH of the 1- to 3-cm. depth of soil
Directly downwind	1.5	6.05
	4	6.12
	6	6.16
	7	6.05
	10	6.10
	Average	6.10
Not directly downwind	3	6.22
	7	6.12
	7	6.27
	9	6.16
	9	6.23
	Average	6.20

Table 6.   The pH of the top 5 cm. of a slightly calcareous Dark Brown soil
           after exposure for 3 months at stations near a gas processing plant.[1]

Pair No.	pH at sites with high sulphation readings	pH at sites with lower sulphation readings
1	8.02	8.10
2	7.91	7.97
3	7.75	7.89
4	7.80	7.92
5	8.00	7.92
6	7.82	7.97
Average	7.88	7.94

[1]Stations were located in pairs, with the stations of each pair at sites of
similar land elevation but different sulphation cylinder readings.

Absorption of sulphur gas emissions by crops

The SO_4-S content of barley samples fluctuated markedly with time and
sampling station (Table 7). Mapping of values showed that areas of concentration
shifted from one week to the next, suggesting shifts in the emission pattern.
The rapid fluctuations of SO_4-S in barley indicated substantial absorption of
SO_2 by plants.

Absorption of atmospheric sulphur gases by surface water

Distilled water protected from rain, but exposed to the air, absorbed
substantial amounts of S near the Waterton plant (Figure 3). Directly downwind
(northeast), water gained 10 to 16 lb. S per acre expressed on a basis of 6
months' exposure. The gain was 6 to 9 lb. at the sites not downwind. Near the
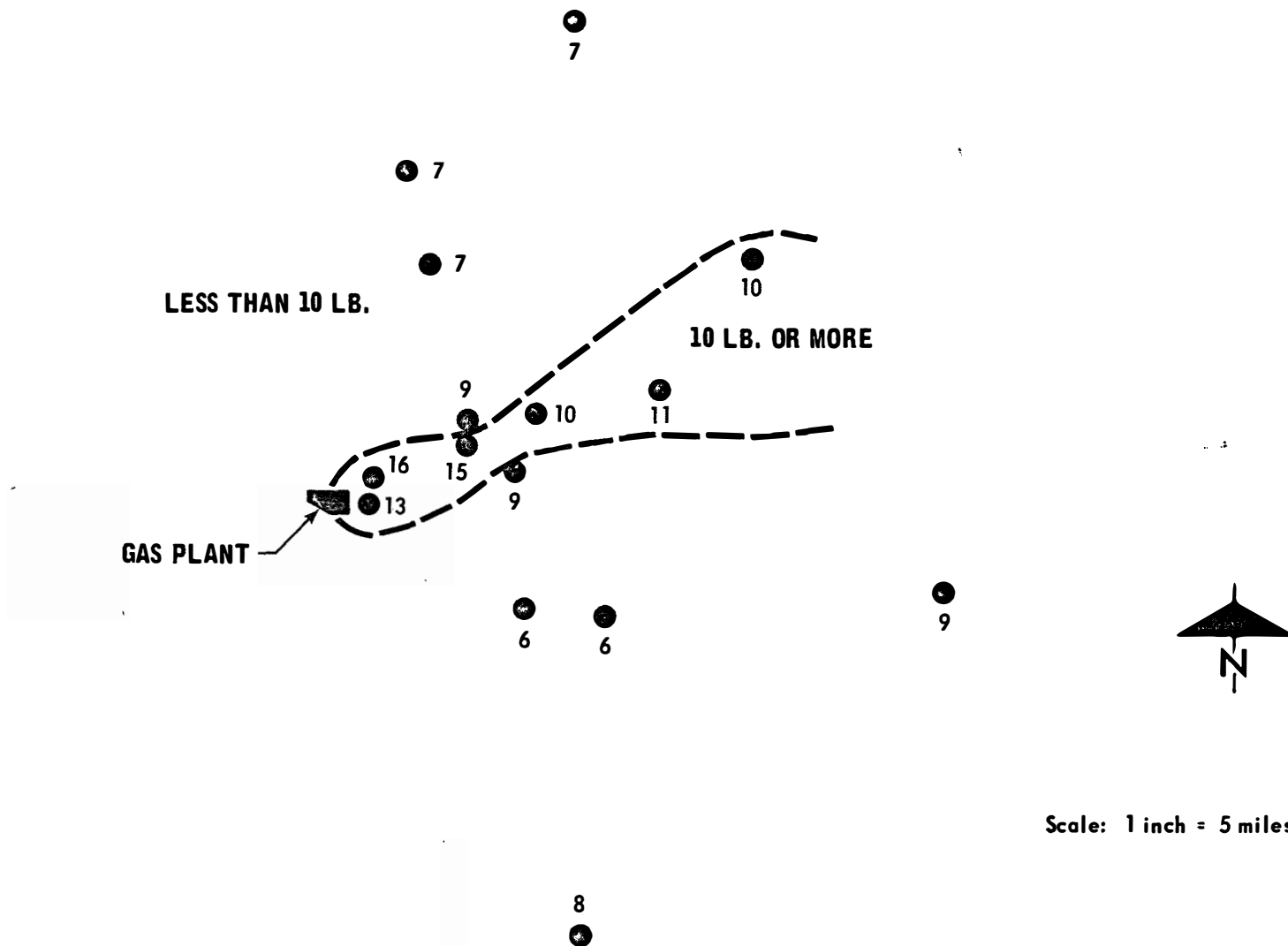
Figure 3 Amounts of sulphur gained by water exposed to the air but protected from rain. Results are expressed as lb. S per acre for a 6-month period.

Ram River plant 1 to 6 lb. S per acre was absorbed, expressed on a basis of 6 months. The highest values were obtained at stations in open areas, suggesting that forest cover reduced absorption by water. The pH of water after exposure showed no consistent pattern, apparently because other substances were absorbed besides S.

Table 7. Water soluble SO_4-S in barley near a gas processing plant at four sampling dates.

Location of station		Water soluble SO_4-S (ppm)			
Direction	Distance	May 31	June 19	June 28	July 18
North	9	1,540	970	600	1,210
Northeast	1.5	1,050	1,210	1,100	1,200
Northeast	4	1,240	620	710	880
Northeast	5	1,320	950	440	1,020
East	6	1,680	1,140	580	740
Southeast	7	900	650	620	650
South	3	650	1,150	680	590

DISCUSSION

Some rainfalls near gas processing plants were as acid as pH 4.0, but acid rain here is much less frequent and severe than in parts of the world which are heavily industrialized. For example, Johnson, *et al.* (1972) report *average* pH values of 4.0 and some rainfalls of pH 3.0. Rainfall near plants often contained as much as 2 to 5 ppm SO_4-S, which produces very acid rain if S occurs as H_2SO_4 rather than sulphate salts. Analysis of rain samples for Ca, Mg, K, and Na showed that most rains had a high enough cation content to prevent

extreme acidity.

Snow acquired very small but significant amounts of S from gas plant emissions. However, we did not encounter snow that had been acid.

Rain and snow in areas of Alberta and Saskatchewan distant from SO_2 sources had very low S contents, close to the world-wide background of 0.5 ppm (Junge 1963). Consequently, those remote sites received little or no S in precipitation from gas plants or other industries.

The amounts of S deposited by rain and snow immediately downwind from two plants with heavy SO_2 emissions were surprisingly small -- only 2 to 4 lb. S per acre annually. Walker (1969) found annual S deposition of 2 to 4 lb. per acre in rain and snow throughout a large area in Central Alberta, but his sampling sites, unlike ours, were not concentrated near gas plants. Summers and Hitchon (1973) estimated deposition of 2.3 lb. S per acre in rain during 3 months near a plant with annual S emissions of about 30 long tons. Our measurements indicated slightly lower amounts near two plants with much heavier SO_2 emissions.

In some parts of the world S is brought to earth mostly by snow and rain (Alway 1937, Hoeft 1972). Amounts can be large, and Hoeft (1972) found annual depositions by rain and snow in Wisconsin were 16, 42, and 168 kg S per ha for rural, urban and industrial locations, respectively. Obviously, the situation is quite different in Alberta.

In Alberta most S reaches the soil by means other than deposition in rain and snow. *At three stations located from 1.5 to 6 miles directly downwind from a plant, bare soil gained from 9.4 to 18.3 lb. S per acre in 3 months, of which only 1.3 to 1.8 lb. S per acre were deposited by rain.* Thus S content of rain is a very poor indicator of the amount of S coming to earth in Alberta. Our results are similar to those of Johansson (1959) who found that in Sweden, at distances of 1 to 8 km from an oil-burning power plant, much more S was

absorbed directly from the air by soils than was brought down in precipitation.
Several experiments indicated a slight but consistent lowering of soil pH
downwind from S gas emissions. Our results are preliminary, but by extrapola-
tion, the pH of the plowlayer of farm soils could be lowered by about one pH
unit after a period of 15 to 30 years. This would not be especially serious
for farm land because applying lime at about 1 ton per acre would correct the
acid condition which had developed. Soil acidity in farm land is not unusual.
Approximately 20 per cent of the farm land in Alberta is naturally too acid
for the best growth of alfalfa (Nyborg 1972), and liming is becoming an
agricultural practice. The consequences of soil acidification by S emissions
would be more serious in forests, because soils are poorly-buffered and difficult
to treat with lime.

Plants can absorb SO_2 directly from the air through their leaves, but
not usually enough for their total S requirements (Coleman 1966). Our preliminary
results indicate significant absorption of S gas emissions by barley at distances
of up to 10 miles or more from a gas plant with heavy SO_2 emissions.

Sulphur gases may be directly absorbed by water. Our results gave
absorption rates of 1 to 16 lb. S per acre of water surface in 6 months at
distances of up to 15 miles downwind of two gas plants.

There is still another mechanism by which S gases may come to earth.
Baker *et al.* (1973) suggest that SO_2 is adsorbed on vegetation and then washed
off by rain.

In summary, we have found that in Alberta S gas emissions are brought
to earth through direct absorption by soils, vegetation and water, as well as
by deposition in rain and snow. The amounts of S deposited in rain are very
small, and the problem of acid rain is much less severe than in heavily indust-
rialized parts of the world. Our preliminary results indicate that soils down-

wind from emission sources receive enough S (primarily through absorption) to cause gradual lowering of soil pH.

ACKNOWLEDGEMENTS

REFERENCES

Alway, F.J. *et al*. 1937. Sufficiency of atmospheric sulphur for maximum crop yields. Soil Sci. Soc. Amer. Proc. 2:229-238.

Anon 1971. Royal Ministry of Foreign Affairs (Sweden). 1971. Air pollution across national boundaries. Kungl. Boktrycheriet, P.A. Norstedt och Soner, Stockholm.

Baker, J. *et al*. 1973. Effect of atmospheric sulfur dioxide on the pH of rain intercepted by forest trees. Proceedings of the Workshop on Sulphur Gas Research in Alberta, Nov., 1973.

Coleman, R. 1966. The importance of sulphur as a plant nutrient in world crop production. Soil Sci. 101:230-239.

Dean, G.A. 1966. A simple colorimetric finish for the Johnson-Nishita microdistillation of sulphur. Analyst. 91:530-532.

Hoeft, R.G. *et al.* 1972. Nitrogen and sulphur in precipitation and sulphur dioxide in the atmosphere in Wisconsin. J. Environ. Quality. 1:203-208.

Johansson, O. 1959. On sulphur problems in Swedish agriculture. Ann. Agr. Coll., Sweden. Vol. 25:57-169.

Johnson, N.W. *et al.* 1972. Atmoshperic Sulphur: Its effect on the chemical weathering of New England. Science. 177:514-516.

Junge, C.E. 1963. Air chemistry and radioactivity. Academic Press, New York.

Likens, G.E. 1972. Acid rain. Environment. 14:33-40.

Nyborg, M. 1972. Soil acidity and liming in Alberta. Agriculture Bulletin, University of Alberta. Number 17, page 8-11.

Summers, P.W., and Hitchon, B. 1973. Source and budget of sulphate in precipitation from Central Alberta. Can. Journal of the Air Pollution Control Association. 23:194-199.

Tollefsen, E.L. 1972. Sources of air pollutants and future trends in air quality standards. Second Annual Quarterly meeting, Canadian Natural Gas Processors Association, Edmonton, June 9, 1972.

Walker, D.G. 1969. Sulphur in precipitation in Central Alberta. Can. J. Soil Sci. 49:409-410.

EFFECT OF ATMOSPHERIC SULFUR DIOXIDE
ON THE pH OF RAIN INTERCEPTED
BY FOREST TREES

by

J. Baker and D. Hocking
Canadian Forestry Service
Northern Forest Research Centre, Edmonton

and

M. Nyborg
Soil Science Department
University of Alberta, Edmonton

INTRODUCTION

Sulphur gas emissions may depress the pH of rain (Likens 1972) but little is known of their effects on intercepted rain (throughfall and stemflow) in forests. The Aquitaine Ram River gas processing plant, located in a lodgepole pine-dominated forest, emits up to 84 long tons of SO_2 per day. The plant and surrounding environment provide a satisfactory location for investigating the influence of the forest on acidification of rain by SO_2.

METHODS

Eight collection sites were established up to 8 miles from the gas plant. Three control sites were later established 10 to 12 miles upwind from the plant and separated from it by a long, high ridge of land. Rainfall was collected in clearings and intercepted rain in immediately adjacent stands of lodgepole pine. Samples of open rain and intercepted rain were collected in plastic bottles fitted with funnels having screens to exclude insects and debris. At each site, stemflow was gathered from

one tree with a trunk diameter of approximately 18 inches. Collection devices were left in place and the entire sample was removed at weekly intervals. Analyses performed on samples included pH and sulfate, the latter by a modification of Dean's method (Dean 1966).

RESULTS

During the period July 5 to August 16, the average pH value of rain at the eight test sites was 5.6. The average pH values of throughfall and stemflow were 5.0 and 4.1 respectively (Table 1). Samples of rain and intercepted rain were obtained at all sites on August 23 and August 30. The average pH value of rain over the sampling period (August 17-30) at or near the gas plant was 0.6 pH units lower than that of the control sites. However, pH values of both throughfall and stemflow were an average of 1.8 units lower at the sites near the plant than those at the control sites (Table 1).

Table 1. Average pH values of rain and intercepted rain.

Location	Period of time	Rain	Intercepted Rain	
			Throughfall	Stemflow
8 sites near the gas plant	July 5 to Aug. 16	5.6	5.0	4.1
	Aug. 17 to Aug. 30	5.7	4.6	4.0
	Aug. 31 to Oct. 15	5.9	5.7	3.9
3 control sites	Aug. 17 to Aug. 30	6.3	6.4	5.8
	Aug. 31 to Oct. 15	6.6	6.7	5.4

Results for the samples collected on August 30 are shown in Figure 1. The pH values of throughfall from control sites ranged from 7.1 to 6.6, while those from exposed sites ranged from 5.2 to 4.4. At the control sites pH of stemflow varied from 5.0 to 7.0; at test sites, from 4.6 to 3.4.

During the period August 31 to October 15, rains were lighter and less frequent than earlier in the season. Rain and intercepted rain could not be sampled consistently at all sites, so detailed comparisons between control and test sites were impossible. However, pH was still depressed at test sites (Table 1).

Intercepted rain was consistently higher than open rain in total sulphate-S content. Actual data are not given here because our method did not distinguish between inorganic and labile organic sulphate and figures may be misleading.

DISCUSSION

The increased acidity of intercepted rain could possibly be due to the adsorption of emitted SO_2 on the surface of needles and/or bark of trees, which subsequently dissolves in water forming sulfurous acid (H_2SO_3). Data on sulphate content are consistent with this hypothesis, but not yet supportive of it owing to the deficiency in analytical method. Other analytical methods will have to be used to determine the precise source of increased acidity of intercepted rain.

Although results are preliminary, they suggest two important possibilities: (1) Sulphur dioxide emissions did acidify intercepted rain more than open rainfall. Stemflow was the most acid. The impact of the very acid stemflow on soil acidity, however, would likely be limited to an extremely small area at the base of the tree (Bollen et al. 1968). (2) This increased acidity of intercepted rain may help to explain the fate of some of the sulphur dioxide. Emissions in forests may be adsorbed and later washed off in intercepted rain.

REFERENCES

Bollen, W.B., C.S. Chen, K.C. Lu, and R.F. Tarrant. 1968. Effect of stemflow precipitation on chemical and microbiological soil properties beneath a single alder tree. *In*: Biology of Alder. Proceedings of Northwest Scientific Association Annual Meeting, April 14-15, 1967. Pp. 149-156.

Dean, G.A. 1966. A simple colorimetric finish for the Johnson-Nishita microdistillation of sulphur. Analyst. 91:530-532.

Likens, G.E. 1972. Acid rain. Environment 14:33-40.

6.0 (5.2) [4.6]

6.4

● 6.0 (4.3)

6.1 (5.2) [3.6]

5.9 (4.4) [4.1]

N

GAS PLANT ──→ ● **5.7 (5.0) [3.4]**

5.5 (4.8) [3.8]

5.9 (4.4) [3.6]

5.4 (4.7) [3.6]

5.8

● 6.6 (7.1) [5.3]

● 6.5 (7.2) [7.0] } **CONTROL SITES**

● 6.1 (6.6) [5.0]

Scale: 1 inch = 3 miles
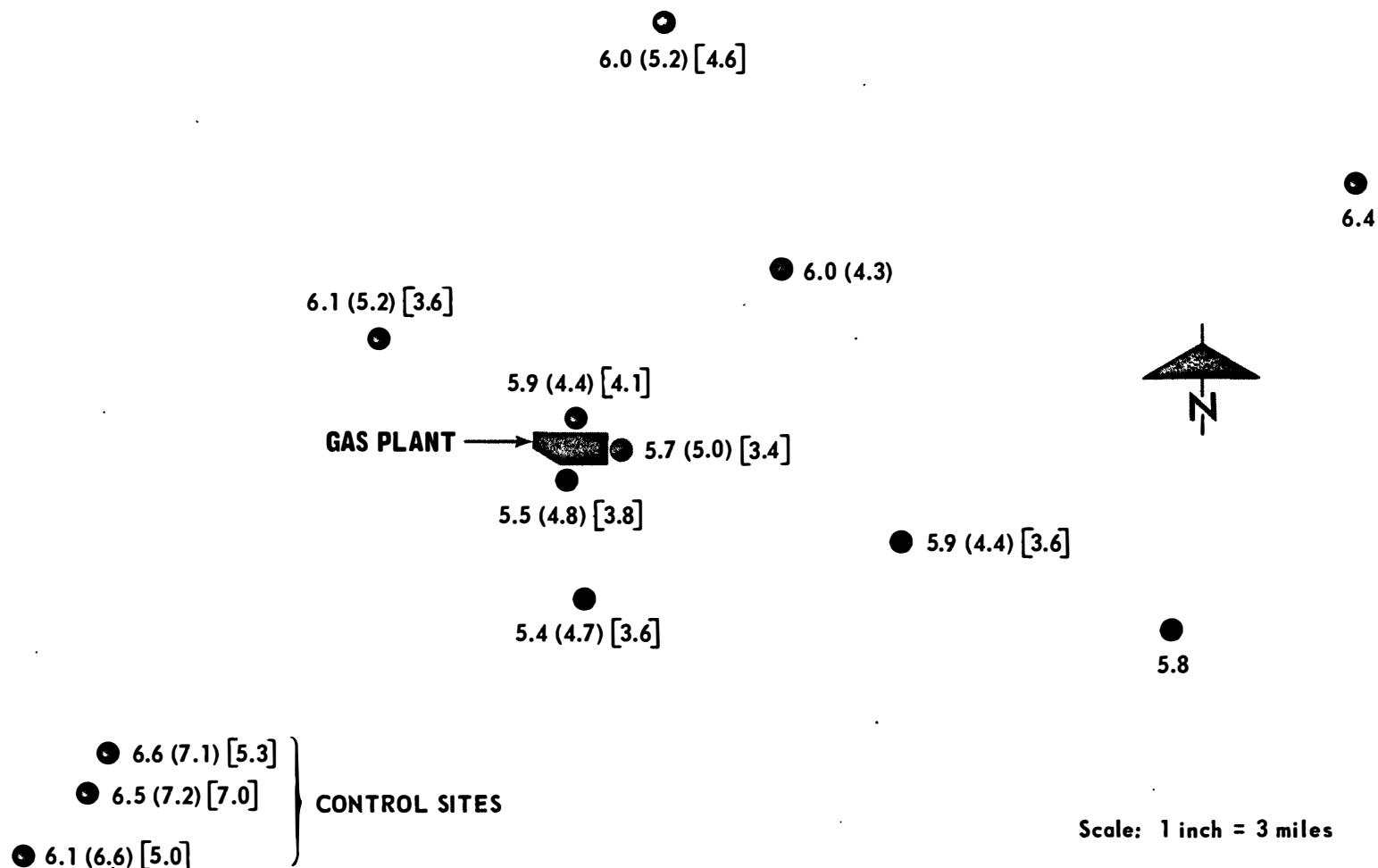
Figure 1:   The pH of rain, through-fall ( ), and stem-flow [ ] from one rainfall collected August 30, 1973, in the vicinity of
a sour natural gas processing plant.   (Collection sites are shown by dark circles)

Biological Impacts of

Sulphur Gases

Introductory Editorial:

SOME TERMS FOR SYMPTOMS ON PLANTS EXPOSED TO SULPHUR GASES

D. Hocking

The biological impacts of sulfur gases are very diverse. This workshop deals only with impacts on vegetation.

In the biological literature, exposure to an air pollutant is universally referred to as a *fumigation*. This is often qualified by a descriptive adjective: *experimental, acute, injurious, intermittent, chronic, mild*. *Fumigation* is also sometimes used as an adjective with *episode, incident or accident*.

The Glossary of Meteorology (Huschke 1959) does not define the term fumigation. In 1968, however, a specialized listing of terms used in air pollution meteorology (Schafer et al. 1968) defined *fumigation* as an inversion breakup that returns trapped pollutants to ground level. But the same listing also recognized a general meaning as any experimental exposure to an air pollutant, so the meteorological sense is not exclusive. Therefore, based on thirty years prior use in the biological literature, *fumigation* can continue as the generic term for any exposure to an air pollutant, recognizing that in certain contexts it defines a particular type of exposure.

Impacts of air pollution on vegetation cover a wide range for which the terminology is much less clear.

Symptoms on foliage might be described in qualitative (e.g. colour, shape) and quantitative (e.g. duration, severity) terms. Adequate description depends on both but it is hard to generalize about the qualitative aspects, which depend so much upon species. The two key quantitative dimensions are duration and severity.

Almost all authors use *chronic* and *acute* to describe *markings,*
injuries, damage, or *symptoms.* Both terms connote rate of onset, dura-
tion and severity in their standard definitions and in the implied mean-
ings of most authors (for a sampling, see Katz 1949, Brandt & Heck 1968,
Barrett & Benedict 1970, Tamm & Aronsson 1972).

Because of the many connotations of the terms, authors seldom
define them adequately and never without some ambiguity, overlap or con-
flict. A compilation of the uses will illustrate this.

acute symptoms: necrosis; leaf cells are *killed,* generally in
distinctive patterns with sharp edges. Usually characteristic of a sudden
exposure to a high concentration for a short period: an *acute* fumigation.
Standard dictionaries define *acute:* coming sharply to a climax, serious,
urgent, characterized by sharpness or severity.

chronic symptoms: chlorosis, sometimes called chlorotic symp-
toms; leaf cells are not killed, only the chlorophyll is affected--a
gradual bleaching of the leaves, often resembling normal aging. Usually
characteristic of prolonged or intermittent exposure to low concentrations:
chronic fumigation. Standard dictionaries define *chronic:* marked by
frequent recurrence and/or long duration and often by slowly progressing
seriousness.

So the difficulty with these terms is that they overlap and
conflict. Acute symptoms are also chronic: they persist unless enough
of the leaf is killed to cause it to fall off. And chronic symptoms may
be transient: chlorophyll *can* be regenerated. Furthermore chronic and
acute symptoms may be found on the same plant, even on the same leaf;
leaves of different ages respond differently to the same fumigation condi-
tions.

Although the *general sense* of acute and chronic, is reasonably
common, objective use of them must include rigorous qualification.

In summary, foliage responses to sulfur gas fumigations are
much too complex to be adequately described with two rather vague and
general terms. Use of specific terms with well-defined meanings such as

necrosis and chlorosis, with suitable modifiers such as *mild, severe, transient* and *permanent,* is much to be preferred.

References

Barrett, T.W. and H.M. Benedict. 1970. Sulfur dioxide. *In:* Jacobson and Hill (Eds.). Recognition of air pollution injury to vegetation: A pictorial atlas. Air Pollution Control Assoc., Pittsburgh. pp. C1-17.

Brandt, C.S. and W.W. Heck. 1968. Effects of air pollution on vegetation. *In:* Stern (Ed.). Air Pollution Vol. I:401-443. Academic, N.Y. & London.

Huschke, R.E. (Ed.) 1959. Glossary of Meteorology. Amer. Met. Soc., Boston.

Katz, M. 1949. Sulfur dioxide in the atmosphere and its relation to plants and soils. Ind. Eng. Chem. 41:2450-2465.

Schafer, V. et al. 1968. Glossary of frequently used terms in air pollution. Amer. Met. Soc., Boston.

Tamm, C.O. and A. Aronsson. 1972. Plant growth as affected by sulphur compounds in polluted atmosphere. A literature survey. Res. Note No. 12; Royal College of Forestry, Stockholm.

SULPHUR DIOXIDE AND FOREST VEGETATION[*]

by

A. A. Loman

ERA Sciences Limited, Calgary

In Alberta, sulphur dioxide symptoms have been observed to appear and disappear on forest vegetation in the vicinity of sour gas plants. The range of symptoms observed on coniferous and deciduous foliage cannot be adequately described in terms of the two existing categories, "chronic" and "acute" symptoms, which are presented in the editorial of these Proceedings. A third category of symptoms, which is most frequently observed in Alberta, is therefore used by scientists of ERA Sciences Ltd.

Foliar sulphur dioxide symptoms are temporary symptoms on the green plant: the foliage itself abscisses at the end of the growing season in deciduous species, and at the end of three to seven years in coniferous species. However, one frequently observed group of symptoms in Alberta is transient on the foliage itself. Foliar symptoms of this category will appear and disappear within weeks following sulphur dioxide episodes during the growing season. These symptoms may be defined as follows:

1. Transient symptoms are transitory on the foliage during the growing season. On deciduous species transient symptoms are characterized by a light intercostal chlorosis of the leaves. On conifers, transient symptoms are characterized by a light chlorosis on the distal portions of one-year-old and older needles. No leaf cells are permanently destroyed in this category. Current year's needles are healthy.

*Submitted to ALBERTA SULPHUR GAS RESEARCH WORKSHOP, Edmonton, Nov. 2, 1973.   Not to be quoted without written permission of the author.

Transient sulphur dioxide symptoms are common in Alberta, They cannot be found from one observation period to the next on the same trees. No reductions in growth rate have been detected in trees with transient symptoms.

In contrast to transient foliar symptoms which disappear within weeks during the growing season, chronic symptoms are slightly more severe, and persist until the foliage abscisses. Chronic symptoms may be defined as follows:

2. <u>Chronic symptoms</u> remain on the foliage for the duration of its functional life. On deciduous species, chronic symptoms are characterized by severe intercostal chlorosis, and frequently by necrotic leaf margins. On conifers, chronic symptoms are characterized by severe chlorosis on the distal portions of one-year-old and older needles, frequently with necrotic tissues at the tips. Current year's needles are healthy in this category.

The most severe category of symptoms found in Alberta is exclusively associated with industrial accidents, and is therefore found in the immediate vicinity of a sulphur dioxide source. The foliar symptoms in this category are called "acute" symptoms.

3. <u>Acute symptoms</u> are characterized by severe necrosis or killing of foliar tissues of conifers and deciduous trees. Little or no chlorotic symptoms develop. On most deciduous species encountered in Alberta, acute symptoms are quickly followed by abscission of the killed leaves, and by flushing of a second crop of foliage. On conifers, acute symptoms are found on all needles, including current year's needles. This is important, as it distinguishes the acute category from the two lighter categories of symptoms, in which current year's needles remain healthy.

To date, no sulphur dioxide episodes have been severe enough to kill the buds of forest trees in Alberta.

Continuous monitoring of ambient air in the vicinity of gas plants has shown that sulphur dioxide "episodes" frequently consist of "pulses" of high sulphur dioxide concentrations lasting a few seconds, inter-spersed with short sulphur dioxide free periods. Periods of steady levels of elevated concentrations of this gas in the atmosphere appear to be less common than previously believed. Greenhouse and growth chamber studies, however, employ steady levels of fumigation only. It is not known how soon symptoms appear on forest vegetation after a sulphur dioxide episode. It has therefore not been possible to relate sulphur dioxide concentrations and duration of episode to the three observed categories of symptoms.

Merchantable forest species in Alberta may be ranked in order of decreasing susceptibility to sulphur dioxide (Table 1). Since tolerance levels of vegetation to sulphur dioxide are known to fluctuate with differing environmental conditions, exceptions to this ranking will occur.

The development of visible symptoms on the foliage of forest species is a short term effect of sulphur dioxide episodes, at concentrations in excess of the capacity of the green plant to assimilate this gas. The impact of short term effects on forest associations is a function of the frequency of occurrence of sulphur dioxide episodes on the same plants during one growing season.

Long term, cumulative effects of sulphur dust fall or sulphur dioxide washout on vegetation must be assessed by regularly monitoring the buffering capacity of forest soils. Forest soils have considerable ability to absorb and transform industrial effluents into harmless

compounds providing they are not overtaxed. A regular soil monitoring system which incorporates measurements of pH, conductivity and total sulphur content is required in conjunction with growth rate analyses, assessments of vigor of individual species, and changes in forest associations, in order to assess long term sulphur and sulphur dioxide effects on the forests of Alberta.

TABLE I		
FOREST VEGETATION IN ALBERTA IN ORDER OF DECREASING SUSCEPTIBILITY TO SULPHUR DIOXIDE EPISODES		
MERCHANTABLE SPECIES		DECIDUOUS
CONIFERS	DECIDUOUS	
1. Abies lasiocarpa 2. Abies balsamea 3. Pinus banksiana 4. Pinus contorta 5. Picea mariana 6. Picea glauca 7. Larix laricina	1. Betula papyrifera 2. Populus balsamifera 3. Populus tremuloides	1. Alnus spp. 2. Salix spp.

SULFUR GAS IMPACT SURVEYS AND RESEARCH AT THE
NORTHERN FOREST RESEARCH CENTRE

R. A. Blauel and D. Hocking

The Canadian Forestry Service has an active program of surveys
and research on the effects of sulfur gases (and other pollutants) on
the forest. The objectives are to gather basic and applied data on
forest responses to pollutants, to evaluate these responses in terms of
environmental quality, and to provide consulting and other services to
resource management agencies.

These objectives are pursued by several means. Discussions
and meetings such as this workshop stimulate general interest. In
response to specific requests from various agencies, the impact of
pollution incidents can be assessed through preliminary surveys and
field examination.

Governmental management agencies and industry contribute
technical and logistical support to surveys.

Field examinations may follow surveys that are interesting
or that reveal problems of diagnosis or impact assessment. These are
usually cooperative and sometimes involve universities and consulting
firms as well as the agencies initially concerned.

General examples of pollution incidents involving sulfur
gases which require surveys are: sulfur fires, oil and gas well blowouts,
battery site releases, valve and line leaks, servicing releases and
sulfur stockpiling incidents. Data collected include site details,

meteorology, photographic documentation, and vegetative and soil samples. Analysis involves describing symptoms, rating species sensitivity, evaluating injury and damage, and estimating predispositions, morbidity and mortality.

Also, the Canadian Forestry Service awards Research and Development Contracts to further the program objectives. These may specify problems in applied knowledge or may require the generation of new knowledge.

The impact of sour gas emissions on forest vegetation is studied in an area S.W. of Rocky Mountain House around the Gulf Strachan and Aquitaine Ram River gas processing plants. Cooperators include:

1. Federal government agencies:

   Canadian Forestry Service
   Atmospheric Environment Service
   Environment Protection Service

2. Provincial government agencies:

   Department of the Environment
   Department of Lands and Forests

3. Industrial consulting firms:

   Gulf
   Aquitaine
   Core Laboratories

4. Universities (also contractors):

   Calgary (departments of chemical engineering, physics, and
       environmental sciences).
   Alberta (departments of botany and soil science).

Elements of the study include:

1. studying plume delineation and dispersal;

2. location of impingement areas;

3. observation of visual symptoms on trees, shrubs and lower vegetation;

4. measurements of chemical changes in precipitation, throughfall and stemflow;

5. studying alterations to soil chemistry;

6. conducting a preliminary sulfur budget study;

7. development and testing of a bio-monitoring system using lichens and bryophytes.

Vegetative response is also being studied in the Athabasca Tar Sands, at the request of the Alberta Department of Environment, the Alberta Forest Service and Great Canadian Oil Sands. This study includes aerial surveys with ground truthing, and permanent observation plots near continuous SO_2 monitors.

Remote sensing techniques have been used more extensively in surveys of impacts on forests by emissions from the smelters at Thompson and Flin Flon in Manitoba. Missions were flown by the Canadian Centre for Remote Sensing, using high and low level, multi-spectral imagery. Ground truthing was conducted in smoke impingement areas. Particularly useful for delineating severe damage was false color infra-red film with the Wratten 12 filter package. Oblique angle photography was important in detection of partial defoliation since tree top foliage tends to remain longest, concealing bare branches below.

The situation around the smelters is complicated owing to the mixture of toxic agents in emissions. As well as SO_2, several heavy metals (especially nickel) also affect vegetation.

Our program of research includes controlled experimentation in the laboratory and greenhouse. Symptoms are to be diagnosed under a variety of environmental and pollutant exposure conditions. Threshold injury levels (under different conditions and for different receptors) and the mechanisms of injury will be examined. Cooperative work will continue to play an important part.

DESIGN OF A GAS-EXCHANGE SYSTEM
FOR THE STUDY OF THE EFFECTS
OF SULPHUR DIOXIDE ON VEGETATION.

by

Allan H. Legge

Environmental Sciences Centre, The University of Calgary

A gas-exchange system has been developed for the intimate analysis of the effects of sulphur dioxide on vegetation in the Whitecourt area of the sour-gas corridor in the province of Alberta. This work is sponsored by the Whitecourt Environmental Study Group, the Provincial Department of the Environment and ERA Sciences Ltd. of Calgary. Research is underway on one-year-old seedlings of white spruce, *Picea glauca* (Moench), Voss, and lodgepole pine, *Pinus contorta* Louden. The main objective is to determine quantitatively the effects of varying concentrations of SO_2 under differing environmental conditions. We are attempting to correlate basic plant physiology and the onset of visible plant symptom development with air quality.

Primary production in green plants is determined by the photosynthetic assimilation of CO_2. The rate at which CO_2 is taken up by the plant is determined by physiological factors which are closely bound to environmental conditions. The gas-exchange system was designed to continuously record processes of photosynthesis, respiration and

transpiration of intact plants within a wide range of controlled

environmental conditions. The purpose was to provide experimental

conditions similar to those found in the field. A Beckman IR315A

non-dispersive infrared gas analyzer is utilized for the measurement

of CO_2. Lithium chloride hygrometers are used to measure water vapor

concentration.

The heart of the system is double-linked growth chambers

(Fig. 1). Environment 1 is the Sirigor Gas-Exchange Chamber developed

as the result of collaboration between the Botanical Institute of the

Forestry Research Institute, Munich, and the Siemens Research Center

in Erlangen, West Germany. This internal chamber controls such factors

in the above-found or "stem environment" as air temperature, relative

humidity (dewpoint) and wind velocity. The plant root environment is

controlled in the outer chamber. Controlling root temperature avoids

the production of isothermal conditions common to most growth chamber

experiments and introduces a thermal gradient between the root system

and shoot apex similar to that in the field. This growth chamber is a

modified M-13 manufactured by Environmental Growth Chambers, Chagrin

Falls, Ohio. Its high intensity light package produces near daylight

conditions of 1250 microeinsteins/m^2/sec. for the internal Sirigor

chamber (10,000 ft. candles).

External air is drawn in through a series of mixing vessels

to dampen out local ambient fluctuations of CO_2 concentrations which

may vary from 315-340 vpm (volume per million). An electromagnetic pump

(P_1) (Reciprotor, Edward, Copenhagen) is used to maintain a constant

flow rate of air entering the system. Continuous air flow adjustment is

possible by changing the voltage with a rheostat. Fine adjustment in the flow rate is made with a precision needle valve. After P_1 the air stream is split with part of the stream passing through a two-stage humidifier with the flow rate adjustable by a needle valve. The by-passed air recombines with the humidified air in a mixing vessel (MV_2) at which point the relative humidity is determined (HS_1). By carefully adjusting flow rates at this initial split in the air stream, relative humidities between 10% and 100% are readily obtainable. Since the air source is external, the humidification loop is primarily used under winter conditions of very low outside relative humidity. Just after MV_2 the input air stream is split again to allow for the introduction of specific concentrations of SO_2 into the system. SO_2 is generated by means of a Dynacal gas permeation tube (Metronics Associates Inc., Palo Alto, California). The permeation characteristics are such that by varying the temperature of the permeation tube and the flow rate of air past it, SO_2 concentrations may be varied and accurately controlled. By adjusting the input valve in front of the flow meter (FM_2) and the temperature of the water bath surrounding the permeation tube the desired concentration of SO_2 is achieved when the non-SO_2 stream recombines in mixing vessel 3 in a predetermined dilution ratio. At this point the air stream is equally split into a sample stream (solid line) and a reference stream (dotted line). The sample stream, after passing through the input humidity sensor (HS_2), goes directly into the Sirigor Gas-Exchange Chamber.

The air temperature inside the measuring chamber can be adjusted by means of a temperature controller in three different ways:

1. Set-valve control. The temperature is kept constant

irrespective of the external chamber temperature.

2. Follow up control. The internal chamber is kept the
   same as external temperature.

3. Program control. Chamber temperature varies according
   to a preset program.

In the double chamber configuration, set-valve control of
temperature is utilized. The other methods are noted only to illus-
trate the flexibility of the system.

Since a plant gives off water-vapor via the process of trans-
piration, the by-pass loop through the water vapor trap is utilized to
prevent condensation in the chamber. (Condensation is a sink for both
CO_2 and SO_2 and must be avoided.) The internal chamber humidity is deter-
mined by the output humidity sensor (HS_4). Humidity control is achieved
by the adjustment of the dew point of the water vapor trap via a differen-
tial electrical signal from the output humidity sensor as it is increased
by transpiration relative to the input humidity sensor. The transpired
water in the circulating by-pass is condensed out, thus equalizing the
humidity difference.

A quantum sensor (Lambda Instruments Co. Inc., Lincoln, Nebraska)
is utilized to measure the photosynthetically active radiation (PAR)
incident upon the plant in the gas-exchange chamber. This sensor measures
the light spectrum for photosynthesis in the 400-700 nm waveband.

Air is pulled from the gas-exchange chamber at a constant flow
rate by a rheostat controlled pump (P_3). The mass flow of gas from the
chamber to the infrared gas analyzer (IRGA) is measured by a Matheson
Linear Mass Flowmeter Model 8116-0214 (Matheson Gas Products, East

Rutherford, New Jersey). This measures the true mass flow without necessity of corrections or compensations for the temperature and pressure of the gas. After both the reference and sample streams are dried by passing through $CaSO_4$ (anhydrous) to prevent the interference of water vapor, they pass through the IRGA. This differential measurement between the CO_2 content of the two streams is referred to as open-system analysis. Net-photosynthetic CO_2 assimilation can now be directly calcualted from the mass flow record.

The SO_2 sampling points are indicated as S_1 through S_6.

S_1 - background ambient air

S_2 - mixed input before entry into gas-exchange chamber

S_3 - concentration in gas-exchange chamber

S_4 - loss in water vapor trap

S_5 - output from gas-exchange chamber

S_6 - loss to $CaSO_4$ (anhydrous) after air is dried and
input to IRGA

All these points are utilized to determine the fate of and concentration of SO_2 in the overall gas-exchange system.

NOTE: Teflon*, rather Tygon, tubing must be used to prevent loss of
SO_2 by diffusion and absorption.

Continued testing with this gas-exchange system will help provide the data needed by the Government of Alberta in the establishment of more meaningful ambient air quality standards.

*Trade marks reg.

THE USE OF LICHENS AS BIO-INDICATORS OF SULPHUR DIOXIDE

by James W. Case
Department of Biology
University of Calgary
Calgary, Alberta
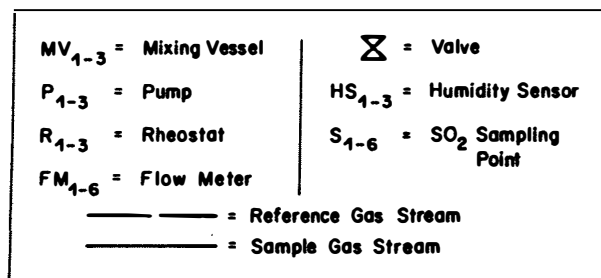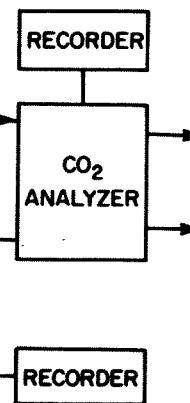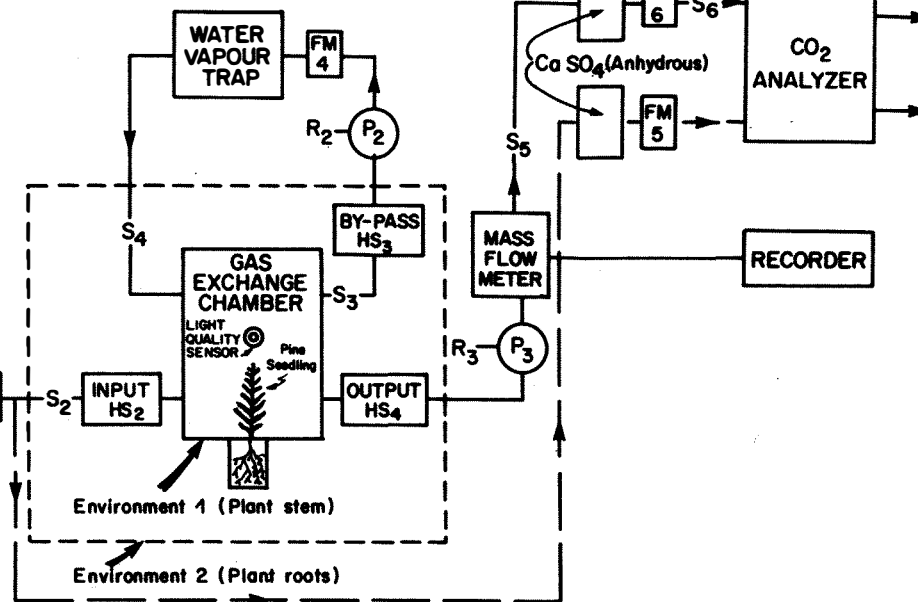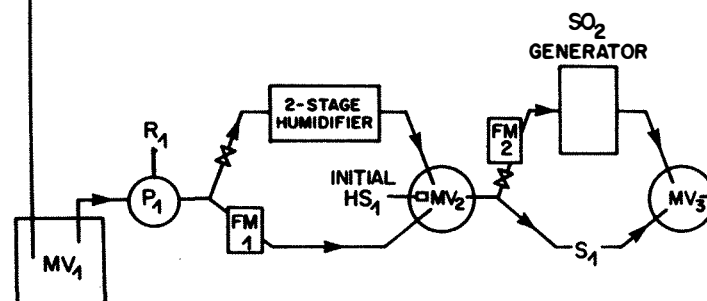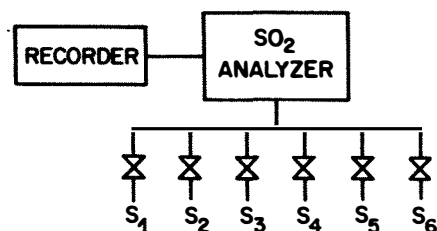
Figure 1: Block diagram of gas-exchange system for monitoring and/or controlling the following parameters: sulfur dioxide and carbon dioxide concentrations, leaf temperature, air and soil temperature, light quality, relative humidity, wind velocity and plant transpiration. All parameters are recorded, but for the sake of clarity only three are indicated: carbon dioxide and sulfur dioxide concentration and mass flow of air through the sample gas stream.

Lichens are unique in being composed of an algae and a fungus living in a symbiotic relationship. They are very slow-growing, primitive plants but despite this are found in all countries and habitats of the world. Alberta alone has over 500 species occurring in habitats ranging from badlands and short grass prairie to the boreal forest and the bare rock of the Canadian Shield. They are found on a variety of substrates including trees, rotting wood, soil, and rock. Many organisms depend on lichens for food and protective micro-habitats. Recent work reveals the importance of some lichens as nitrogen fixers in forest communities (Denison, 1973).

It was early recognized that lichens were damaged or destroyed by air pollution and could be used as a reliable indicator of the degree of air pollution (Grindon, 1859; Nylander, 1866). At that time, smoke and particulate matter were considered to be the damaging agents of air pollution, but that has not been confirmed. Temperature and humidity changes have been considered important in cities but cannot be used to explain field observations where no such discrepancies exist (LeBlanc and Rao, 1973). Now, all available evidence from laboratory and field studies demonstrates that sulphur dioxide is the principal factor affecting lichens over large areas.

Lichens are, in general, more sensitive to sulphur dioxide than are higher plants (Hawksworth, 1971). They absorb air very efficiently over their entire surface (Gilbert, 1969; Smith, 1962). Also, since lichens are perennial and evergreen plants they continue to absorb sulphur dioxide whenever they are metabolically active, even in the winter.

Vascular plants, on the other hand, have protective cuticles and closable stomatal pores which restrict absorption of sulphur dioxide from the air, especially during the night. Further, the higher plants obtain their water mostly from the soil, whereas bark-dwelling lichens absorb water from the surface of the substrate before the pollutant can be removed. If a vascular plant is fumigated with a high level of sulphur dioxide, it suffers acute damage, but can replace the damaged leaves as early as the next spring. Because of the lichen's slow rate of growth, damage to the photosynthetic apparatus is chronic and may take up to two years to repair, and then only if no further fumigations occur.

Sulphur dioxide present on a long term basis gradually reduces the pH of soils and other substrata on which lichens grow. Reduced pH and high concentration of sulphur dioxide, built up by the lichen, will lead to the oxidation of the chlorophyll of the algal component, especially chlorophyll 'a' (Puckett, et al., 1973).

Depending on humidity and temperature, lichens generally suffer more damage as the long term average sulphur dioxide concentration increases above 0.01 ppm, and they almost never grow in an area where average concentration is greater than 0.21 ppm.

In recent years, the correlation between air pollution and lichen distribution has been substantiated. Over two hundred and twenty-five papers dealing with lichen vegetation of areas affected by air pollution have been published. Some of the better known studies have been produced in continental Europe by Skye (1965, 1968), De Sloover (1969), De Sloover and LeBlanc (1968, 1970); in Britain by Coker (1967), Gilbert

(1969, 1970), Hawksworth and Rose (1970); and in North America by Brodo (1961. 1966), Dreisinger and McGovern (1970), LeBlanc (1971), LeBlanc and De Sloover (1970), LeBlanc, Rao and Comeau (1972) and Rao and LeBlanc (1967, 1973). Many techniques have been employed to correlate the distribution of lichens around air pollution sources with mean levels of air pollutants and, in some cases, to utilize their behaviour as a means of monitoring the distribution and severity of the pollutant emissions (James, 1973). Three of the most popular techniques used in mapping are Zone mapping, IAP (Index of Atmospheric Purity) mapping and Transplants.

Zone maps are constructed on the basis of the distribution and frequency of individual indicator species. The four zones most frequently distinguished are: (1) an inner 'lichen desert' with few or no lichens present; (2) an 'inner struggle zone'; (3) an 'outer struggle zone' that is approaching normality; and (4) a 'normal unaffected zone'. Satisfactory Zone maps depend on the presence of recognized species which are sensitive to different levels of air pollution, and require a good knowledge of their ecology.

The IAP Mapping techniques (De Sloover, 1964) lead to numerical assessments of the degree of air pollution at sample sites and can provide a quick, efficient, and economical method for preparing a pollution map of the area. This map, with some consideration of meteorology and topography, would present a relative picture of the pollution concentration, of the intensity of damage caused, and of the total area affected by the pollutant (LeBlanc, Rao and Comeau, 1972).

The IAP is defined by the recently modified formula (LeBlanc and De Sloover, 1970):

$$IAP = \sum_{i}^{n} (Qxf)/10 \quad \text{where}$$

n is the number of species at each site

f is the frequency-coverage index of each species at each site

Q is the average number of epiphytic lichens concurrently present with that species at all sites.

The numerical IAP values produced for each site are plotted on a base map, and zones based on ranges of IAP values are constructed. The IAP method is as, or in some case more, reliable than other methods.

Transplant studies are a recent development. Generally, lichen-bearing discs of bark are cut from one tree or a group of trees and are then secured in holes of the same diameter cut in the bark of similar trees in an affected area and of control trees in an unaffected site. If there are no trees, the lichen-bearing discs can be attached to posts instead (Schoenbeck, 1969). This technique has clearly demonstrated that individual species differ in their tolerance to sulphur dioxide (LeBlanc and Rao, 1966) as predicted by Q factors of the IAP technique.

Although transplant experiments can be used in making practical assessments of air pollution levels over large areas, they are usually too time-consuming since visible damage or death of the lichen in less polluted areas may take one to two years (Brodo, 1966; LeBlanc and Rao, 1966; Hawksworth, 1969).

During the public hearings on the environmental impact of sulphur extraction gas plants in Alberta, representatives of industry pointed out that ground monitoring is sometimes unsatisfactory because of factors such as unusual meteorological conditions. An IAP map would show the total area

affected, would present a relative picture of the pollution concentrations, and would show the long term effect of the sulphur dioxide emissions on the epiphytic lichens. This map could then be used in settling disputes as to the effects that sulphur dioxide from the sulphur extraction gas plant has on various components of the surrounding countryside. Zone mapping, however, has limited application in Alberta because the ecology of most lichen communities has not been adequately studied. Transplant studies are more time-consuming than the IAP mapping method, although they are useful as a back-up to IAP mapping.

BIBLIOGRAPHY

Air pollution. 1961. World Health Organization, Monograph series no. 46.

Brandt, C.S. and W.W. Heck. 1968. Effect of air pollutants on vegetation. IN. Air Pollution. 2d ed. Edited by A.C. Stern. Acad. Press, New York.

Brodo, Irwin Murray. 1961. A study of lichen ecology in Central Long Island, New York. American Midland Naturalist 65 (2): 290-310.

Brodo, Irwin M. 1966. Lichen growth and cities: a study on Long Island, New York. Bryologist 49: 427-449.

Coker, P.D. 1967. The effects of sulphur dioxide pollution on bark epiphytes. Trans. Brit. Bryol. Soc. 5: 341-347.

Denison, W.C. 1973. Life in tall trees. Sci. Amer. 228 (6): 74-80.

De Sloover, J. 1969. Pollutions atmosphériques et tolérance spécifique chez les lichens. Bull. Soc. Bot. Fr. Mém. 1968: 205-217.

De Sloover, J. and LeBlanc, F. 1968. Mapping of atmospheric pollution on the basis of lichen sensitivity, IN, Misra, R. and Gopal, B. (eds.) Proc. Symp. Recent Adv. Trop. Ecology, 42-56. Varanasi: The International Society for Tropical Ecology.

De Sloover, J. and LeBlanc, F. 1970. Pollutions atmosphériques et fertilité chez les mausses et chez les lichens épiphytiques. Bull. Acad. Soc. lorr. Sci. 9: 82-90.

European Congress on the Influence of Air Pollution on Plants and Animals, 1st, Wageningen, 1968. Air pollution, proceedings.

Gilbert, O.L. 1969. The effect of SO_2 on lichens and bryophytes around Newcastle upon Tyne. IN, Air Pollution, Proceedings of the First

European Congress on the influence of air pollution on plants

and animals, Wageningen 1968: 223-35. Wageningen: Centre for

Agricultural Publishing and Documentation.

Gilbert, O.L. 1970. Further studies on the effect of sulphur dioxide on

lichens and bryophytes. New Phytol. 69: 605-27.

Grindon, L.H. 1859. The Manchester Flora. London: White.

Hawksworth, D.L. B.W. Ferry, and M.S. Baddeley. 1973. Air Pollution and

Lichens. University of Toronto Press.

Hawksworth, D.L. 1969. The lichen flora of Derbyshire. Lichenologist 4:

105-93.

Hawksworth, D.L. 1971. Lichens as litmus for air pollution: A historical

review. Int. J. Environ. Studies 1: 281-96.

Hawksworth, D.L. and Rose, F. 1970. Qualitative scale for estimating

sulphur dioxide air pollution in England and Wales using epi-

phytic lichens. Nature, Lond. 227: 145-8.

James, P.W. 1973. Introduction. IN, Air Pollution and Lichens. Edited

by B.W. Ferry, M.S. Baddeley, and D.L. Hawksworth. University

of Toronto Press.

LeBlanc, Fabius. 1971. Possibilities and methods for mapping air pollution

on the basis of lichen sensitivity. Mitteilungen der Forstlichen

Bundesversuchsanstalt Wien 92: 103-126.

LeBlanc, Fabius and Jacques De Sloover. 1970. Relation between industrial-

ization and the distribution and growth of epiphytic lichens and

mosses in Montreal. Can. J. Bot. 48: 1485-1496.

LeBlanc, Fabius and D.N. Rao. 1966. Réaction de quelques lichens et mousses

épiphytiques à l'Anhydride sulfureux dans la région de Sudbury, Ontario. <u>Bryologist</u> 69: 338-347.

LeBlanc, F. & D.N. Rao. 1973. Evaluation of the pollution and drought hypotheses in relation to lichens and bryophytes in urban environments. <u>Bryologist</u> 76: 1-19.

LeBlanc, Fabius, D.N. Rao, & Gilberte Comeau. 1972. The epiphytic vegetation of <u>Populus balsamifera</u> and its significance as an air pollution indicator in Sudbury, Ontario. <u>Can. J. Bot.</u> 50: 519-528.

Linzon, S.N. 1971. Economic effects of sulphur dioxide on forest growth. <u>J. Air. Poll. Cont. Assoc.</u> 21 (2): 81-86.

Nylander, W. 1866. Les lichens du Jardin du Luxembourg. <u>Bull. Soc. bot. Fr.</u> 13: 364-72.

Puckett, K.J., E. Nieboer, W.P. Flora, & D.H.S. Richardson. 1973. Sulphur dioxide: its effect on photosynthetic fixation in lichens & suggested mechanisms of phototoxicity. <u>New Phytol.</u> 72, no. 1, 141-154.

Rao, D.N., & Fabius LeBlanc. 1967. Influence of an iron-sintering plant on corticolous epiphytes in Wawa, Ontario. Bryologist 70 (2), Summer.

Schönbeck, H. 1969. Eine methode zur Erfassung der biologischen Wirkung von Luftverunreinigungen durch transplantierte Flechten. <u>Staub</u> 29: 14-18.

Skye, E. 1965. Botanical indicators of air pollution. <u>Acta phytogeogr. suec.</u> 50: 285-7.

Skye, E. 1968. Lichens and air pollution. <u>Acta phytogeogr. suec.</u> 52: 1-123.

Smith, D.C. 1962. The biology of lichen thalli. <u>Biol. Rev.</u> 37: 537.

Thomas, M.D. 1961. Effect of air pollution on plants. <u>IN</u>, Air Pollution. World Health Organization, Geneva.

A PRELIMINARY STUDY OF THE EFFECTS OF AIR POLLUTION ON LICHEN AND BRYOPHYTE VEGETATION NEAR EDMONTON, ALBERTA

Thomas Lee and Dale H. Vitt

Department of Botany, The University of Alberta, Edmonton, Alberta.

INTRODUCTION

Epiphytes are self-sufficient plants that live on the bark of trees, manufacturing their own food through photosynthesis. In temperate regions, lichens and bryophytes (particularly mosses) are the dominant epiphytes.

In 1866, the Finnish botanist Nylander noted that lichens were responsive to air quality. Since then, the abundance and distribution of epiphytic mosses and lichens has been studied in 96 cities around the world. Only six such studies have been completed in North America, five of these in Canada. In each case the center of the urban area lacks epiphytic lichens and bryophytes; it is a "lichen desert". From this zone outwards, epiphytes tend to increase until the normal distribution of the region is reached.

Rydzak and Stasiak, (1971) suggest that such paucity of epiphytic lichens and mosses is due to city-induced microclimatic drought. Microclimate does have some effect on epiphytes (Brodo, 1966). But air quality is a limiting factor as well. Studies of an iron-sintering plant at Wawa, Ontario (Rao and LeBlanc, 1967), a steel producing plant in South

Wales (Pyatt, 1970), and a shale-oil works in Sweden (Skye, 1958) have
all demonstrated a correlation between the frequency of epiphytes and
air pollution levels.

Though many pollutants affect lichen and moss plants, sulfur
dioxide (SO_2) is the most ubiquitous and abundant. It bleaches chloro-
phyll, causes permanent plasmolysis and sporadic brown spots on the
chloroplasts of the algal cells, with chlorophylls degraded to phaeo-
phytins (Rao and LeBlanc, 1966). Hill (1971) observed that sulfur
dioxide may act on chlorophyll indirectly through the formation of sul-
fite.

Lichens are also sensitive to hydrogen flouride (Nash, 1971,
LeBlanc et. al. 1971). Whenever flouride concentrations exceed 80 ppm,
chlorosis of the lichen thallus occurs (Nash, 1971). Subsequently,
all the pigments are degraded and the thallus disintegrates.

Lichens have been fumigated with 5 ppm (Rao and LeBlanc, 1966)
and with 100-10,000 ppm SO_2 (Pearson and Skye, 1965) each for 24 hrs.
Lichen response was evident in both treatments, but the concentrations
were higher than are found in nature. The highest 24 hour concentrations
observed in cities are in the order of 1 ppm, (Blade and Ferrand, 1969;
Wilkins, 1954).

Nash (1973) fumigated a variety of lichens at 0, 0.5, 1.0, 2.0
and 4.0 ppm SO_2 for 24 hours. Responses ranged from significant chloro-
phyll reduction at 0.5 ppm in Parmelia caperata, to no significant re-
duction of chlorophyll until 2.0 ppm or higher in Physcia millegrana and
Cladonia furcata. Such different responses of lichens permits individual
species to be used as indicators of pollution intensity.

Field studies indicate that lichens are more sensitive to SO_2 than laboratory studies have shown. In the Tyne Valley (Gilbert, 1965) lichens were absent from areas where mean SO_2 concentration exceeded 0.10-0.15 ppm.

Several approaches have been employed in analyzing epiphyte distribution around cities and pollution centers. Maps have been produced by LeBlanc (1961) for Montreal and Rao and LeBlanc (1967) for Wawa, Ontario. Distribution maps reveal the response of individual species to air quality (LeBlanc and De Sloover, 1970) and provide indicator species. As another approach, The Index of Atmospheric Purity (I.A.P.) is a mathematical representation of the relationship between epiphytes and pollution (LeBlanc and De Sloover, 1970). Transplanting lichens from unpolluted areas to contaminated zones has also been a successful approach. Brodo (1966) found that _Parmelia caperata_ could not be transplanted to within 20 miles of New York City without damage to the thallus.

POLLUTION IN EDMONTON

Edmonton is the capital and largest city of Alberta, having a population of about 500,000. There are gas and oil refineries and chemical plants, as well as a pipeline terminal, east of the city in an area known as Refinery Row. Fort Saskatchewan, 13 miles to the northeast, also has several chemical plants.

Alberta Environment (1973) Air Pollution Control maintains a continuous monitoring system in the central city and at Refinery Row Data are reported as hourly peak and as monthly means which integrate the continuous data to 2 decimal places for SO_2 and 3 places for H_2S. Sulfur dioxide levels

in both areas have monthly means of 0.00 ppm, although in the Refinery
Row area hourly peaks of 0.04 ppm for July and 0.03 ppm for August are
reported. Hourly peaks within the city were 0.00 ppm for July and 0.02
for August. Hydrogen sulfide levels at Refinery Row have monthly means
of 0.003 ppm and 0.004 ppm for July and August 1973, and hourly peaks of
0.23 ppm for both months.

Sulfur dioxide is not continuously monitored at Fort Saskatchewan.
Exposure cylinders indicate that total sulfation there (0.0489 mg/day/100
cm^2) is one quarter of that at Refinery Row (0.1633 mg/day/100 cm^2). But
the Fort Saskatchewan area has higher concentrations of flourides and am-
monia than either central Edmonton or Refinery Row (Alberta Environment,
Air Pollution Control).

METHODS

Sampling was confined to aspen and balsam poplars. In the
Edmonton area, (Populus tremuloides Michx. and Populus balsamifers L.) are
the most common trees in the area. They develop a furrowed bark at matur-
ity which is suited to colonization by epiphytic lichens and mosses. Sam-
ple sites consisted of species undisturbed, mature groves containing less
than 5% coniferous trees and unshaded by buildings or other structures.
Thirteen sites were selected. Within each grove, ten trees were sampled,
selected by the following criteria: diameter at breast height of at least
15 cm, furrowing of the bark to a height of two meters from ground level
and at least two meters from the edge of the grove (to minimize edge ef-
fects). Each tree was examined from its base to a height of two meters
from ground level with a 10 X hand lens to determine the abundance of

epiphytes. Species growing on humus or soil over roots were not
included. Species were counted and assigned an estimated coverage
value (F) from 1 to 5 depending on the amount of bark surface
covered: 1) present at one location, 2) present at two or three
locations with little area covered, 3) found in one or two large
patches or at more than three locations about the trunk, 4)
abundant, but scattered about the bark surface and in no one
place being continuous, and 5) abundant, covering large continuous
sections of bark. Frequency of occurrence (F) was determined for
each species in each stand by the following:

$$F_{(Absolute)} = \frac{\text{No. of trees on which each species of epiphyte occurred}}{\text{Total No. of trees sampled}}$$

Stands were grouped according to their locations (see figure 1):
1, 4 as Refinery Row sites; 5, 6 as Near Refinery Row sites (these
are then considered together as Total Refinery Row sites); 2, 3,
7, 8, 9, 13 as Rural sites; and 10, 11, 12 as Fort Saskatchewan
sites.

For each stand, an Index of Atmospheric Purity (I.A.P.)
was computed: I.A.P. = Σ_n (Q x f)/10 (LeBlanc and De Sloover,
1970) where n is the number of species, Q is the Ecological Index
of each species and f is the coverage value assigned to it by the
5 point scale described above. The Ecological Index, Q, for each
species is the average of the total numbers of epiphyte species
occurring at the sites in which the species is present. The mean
I.A.P. values for each locality was calculated. Specimens of
each taxon are deposited in the University of Alberta herbarium.
(ALTA).

RESULTS

In the Fort Saskatchewan area, there were eight species of epiphytes while near Refinery Row, there were 17 species. In rural areas there were 24 species (Table 1).

Most lichens had low mean frequencies in the Fort Saskatchewan area that increased in the Refinery Row area and were highest in rural sites (Table 1). For example, Parmelia sulcata had a mean frequency of 0.0 in the Fort Saskatchewan area, 2.0 around Chemical Row and 3.8 in the rural area. Only 1 species, Pyrenula leucoplaca, tended to decrease in frequency outside of the Fort Saskatchewan area.

Mosses, while almost absent from the Fort Saskatchewan area, did not increase significantly on rural sites over their frequencies near Refinery Row.

The Index of Atmospheric Purity (Table 2) is lowest for the Fort Saskatchewan area (11.0), highest for the rural areas (38.6) and close to the rural area values in the vicinity of Refinery Row (35.7). The two sites at Refinery Row are 12% lower than the rural area (a difference of 4.8 IAP points), while the two sites *near* Refinery Row are 3% lower (1.1 points).

Mean total cover values (Table 2) closely parallel the IAP values: lowest for Fort Saskatchewan (8.9) and highest for rural areas (29.1), although Refinery Row values are close (28.7, 25.9).

DISCUSSION AND CONCLUSIONS

LeBlanc and Rao (1973) summarized the research of the last 100 years on responses of lichens and mosses to pollution. They

concluded that "the distribution pattern of lichens and bryophytes in a city can be related to the degree and extent of pollution." In the Edmonton area, lichens and mosses are distributed rather evenly except in Fort Saskatchewan. Our measures also indicate a low degree of air contamination around Refinery Row.

The epiphytic flora of Fort Saskatchewan is under severe stress. Only eight species are found there, as compared with 18 in Refinery Row and 24 in rural sites. Cover is about 33% of that in Refinery Row and rural localities, while I.A.P. values are also only about 1/3 of those computed for the other two areas.

LeBlanc and Rao (op. cit.) also concluded that "in cities and industrial areas, the absence or decline of epiphytic flora, especially of lichens, appears to be due to the pollution of air by SO_2, HF or another pollutant produced during fuel combustion or industrial operations." In any survey of epiphytes and pollution an immediate inclination might be to correlate levels of SO_2 with epiphyte abundance. However, in Edmonton, total sulfation as determined by exposure cylinders are *higher* in the Refinery Row area than at Fort Saskatchewan. In fact, in August, 1973, Fort Saskatchewan had a total sulfation 1/4 that of the Refinery Row. Since continuous monthly monitoring of SO_2 in the Refinery Row area indicates mean SO_2 levels to be below that required to affect lichens (see Gilbert, 1965), it would not be unreasonable to assume that SO_2 values at Fort Saskatchewan are also below that needed to have an adverse effect on epiphytes. Fluorides and ammonia have been reported in higher concentrations at Fort

Saskatchewan than at Refinery Row and the absence of epiphytes at
Fort Saskatchewan may be due to these compounds (Nash 1971).

One species, _Pyrenula leucoplaca_, is unusual in that it
shows higher frequency in the Fort Saskatchewan area. This peculiar
crustose lichen is usually found on the smooth bark of young poplar
trees. Thus, its presence is probably influenced more by the amount
of smooth bark available.

That "the absence of certain common, but sensitive, lichen
species in an area can serve as in indicator of the pollution of it's
air," was a third conclusion of LeBlanc and Rao. Three species show
fairly high frequencies in the Fort Saskatchewan vicinity, although
each of them has higher frequencies in all other areas. These three
species, _Physcia orbicularis_, _Xanthoria fallax_ and _Lecanora_ sp. might
be regarded as 'tolerants', since many species common to Refinery Row
or rural areas are not present in Fort Saskatchewan. This correlates
with the data of LeBlanc and De Sloover (1970), who reported _Xanthoria_
fallax, _Physcia orbicularis_ and several species of _Lecanora_ as being
present in the most polluted zone of Montreal. Species such as _Parmelia_
flaventior and _sulcata_ are not found in Fort Saskatchewan but are common
elsewhere and may be used as rough indicators of pollution.

LITERATURE CITED

Alberta Environment. 1973. Air monitoring report, Edmonton, July
and August, 1973. Air Pollution Control.

Blade, E. and E.F. Ferrand. 1969. Sulfur dioxide air pollution in
New York City: statistical analysis of twelve years. Jour.
Air Pollut. Control Assoc. 19: 873-878.

Brodo, J.M. 1966. Lichen growth and cities: A study on Long Island,
New York. The Bryologist 69: 427-449.

Gilbert, O.L. 1965. Lichens as indicators of air pollution in the
Tyne Valley. pp 35-47, In. Ecology and the Industrial
Society. Blackwell Sci. Publ., Oxford.

Hill, D.J. 1971. Experimental study of the effect of sulphite on
lichens with reference to atmospheric pollution. New
Phytol. 70: 831-836.

LeBlanc, F. 1961. Influence de l'atmosphère polluée des grandes
agglomérations urbaines sur les épiphytes corticoles.
Rev. Canad. Biol. 20: 823-827.

LeBlanc, F. and J. De Sloover. 1970. Relation between industrializa-
tion and the distribution and growth of epiphytic lichens
and mosses in Montreal. Canad. Jour. Bot. 48: 1485-1496.

LeBlanc, F., Gilbert Comeau, and D.N. Rao. 1971. Fluoride injury
symptoms in epiphytic lichens and mosses. Can. Jour. Bot.
49: 1691-1698.

LeBlanc, F. and D.N. Rao. 1973. Evaluation of pollution and drought hypotheses in relation to lichens and bryophytes in urban environments. The Bryologist 76: 1-19.

Nash, T.H. III. 1971. Lichen sensitivity to hydrogen fluoride. Bull Torrey Bot. Club 98: 103-106.

Nash, T.H. III. 1973. Sensitivity of lichens to SO_2. The Bryologist 76: 333-339.

Pearson, L. and E. Skye. 1965. Air pollution affects pattern of photosynthesis in _Parmelia_ _sulcata_, a corticolous lichen. Science 148: 1600-1602.

Pyatt, F.B. 1970. Lichens as indicators of air pollution in a steel producing town in South Wales. Environ. Pollut. 1: 45-56.

Rao, D.N. and F. LeBlanc. 1966. Effects of sulfur dioxide on the lichen algae, with special reference to chlorophyll. The Bryologist 69: 69-75.

Rao, D.N. and F. LeBlanc. 1967. Influence of an iron sintering plant on corticolous epiphytes in Wawa, Ontario. The Bryologist 70: 141-157.

Rydzak, T. and H. Stasiak. 1971. Badania nad stanem flory porostów w rejonie przemyslue azotewego w Pulawach. Ann. Univ. Mariae Curie-Sklodowska 26C: 329-342.

Skye, E. 1958. Luftföroreningars inverkan pa bush-och bladlavfloran kring skifferoljeverket i Närkes Kvarntorp. Svensk. Bot. Tidskr. 52: 133-190.

Wilkins, E.T. 1954. Air pollution in London smog. Mech. Eng. 76: 426-428.

Table 1. Mean Frequency of occurrence (F) for five localities
in the Edmonton Area. Number's in parentheses indicate
number of stands. Total Refinery Row category equals
sum of Refinery Row plus near Refinery Row group.

Species	Fort Sask. (3)	Refinery Row (2)	Near Ref. Row (2)	Total Ref. Row (4)	Rural (6)
Lichens					
Caloplaca cerina (Ehrh.) T. Fries	0	2.5	1.5	2.0	8.3
Caloplaca holocarpa (Hoffm.) Wade	0	0	0.5	0.2	0.8
Lecanora sp.	7.0	10.0	10.0	10.0	9.0
Parmelia albertana Ahti.	0	7.5	8.0	7.8	5.3
Parmelia flaventior Stirt.	0	0.8	1.0	0.9	2.8
Parmelia subrudecta Nyl.	0	0	0	0	0.7
Parmelia sulcata Tayl.	0	2.0	2.0	2.0	3.8
Physcognia grisca (Lam.) Poelt	0	1.5	0	0.8	0.7
Physcia adcendens Bitt.	3.0	8.5	9.0	8.8	9.8
Physcia aipolia (Ehrh.) Hampe	1.7	8.0	9.0	8.5	7.7
Physcia orbicularis (Neck.) Poetsch.	5.8	10.0	10.0	10.0	10.0
Pyrenula leucoplaca (Wallr.) Korb.	1.0	0	0	0	0.3
Ramalina crinalis (Ach.) Gyeln.	0	0	0	0	0.2
Ramalina fastigiata (Pers.) Ach.	0	0	0	0	0.3
Ramalina pollinaria (Westr.) Ach.	0	0	0	0	0.2
Usnea hirta (L.) Wigg.	0	0	0	0	0.2
Xanthoria fallax (Hepp.) Arn.	6.7	10.0	10.0	10.0	10.0
Xanthoria polycarpa (Ehrh.) Oliv.	0.3	2.5	3.0	2.8	4.7
Mosses					
Brachythecium salebrosum (Web. & Mohr) B.S.G.	0	4.0	6.7	5.2	4.2
Eurhynchium pulchellum (Hedw.) Jenn.	0	3.0	5.0	4.0	1.3
Orthotrichum obtusifolium Brid.	0	1.5	0	0.8	0.8
Orthotrichum speciosum var. elegans (Hook. & Grev.) Warnst.	0	3.5	7.0	5.2	3.2
Plagiomnium cuspidatum (Hedw.) Koponen	0	3.5	4.5	4.0	2.0
Pylaisiella polyantha (Hedw.) Grout	6.0	10.0	10.0	10.0	9.8
Total Number of Species	8	17	16	18	24

Table 2. Index of atmospheric purity of stands and localities in the Edmonton Area. Numbers in parentheses relate to stand numbers given in Figure 1.

	Fort Saskatchewan	Refinery Row	Near Refinery Row	Total Refinery Row	Rural
I.A.P.	2.2 (4)	34.8 (1)	37.2 (5)	34.8 (1)	25.6 (13)
For Individual Sites (stands)	10.6 (10)	32.8 (4)	38.1 (6)	32.8 (4)	29.3 (7)
	20.1 (12)			37.2 (5)	42.8 (2)
				38.1 (6)	46.7 (3)
					45.2 (8)
					42.2 (9)
Mean I.A.P. For Localities (± standard deviation)	11.0 (8.9)	33.8 (1.4)	37.6 (0.6)	35.7 (2.4)	38.6 (8.9)
Mean Total Cover (mean of Σr^i (1) for all sites)	8.9	25.9	28.7	27.3	29.1

Monitoring and Regulation
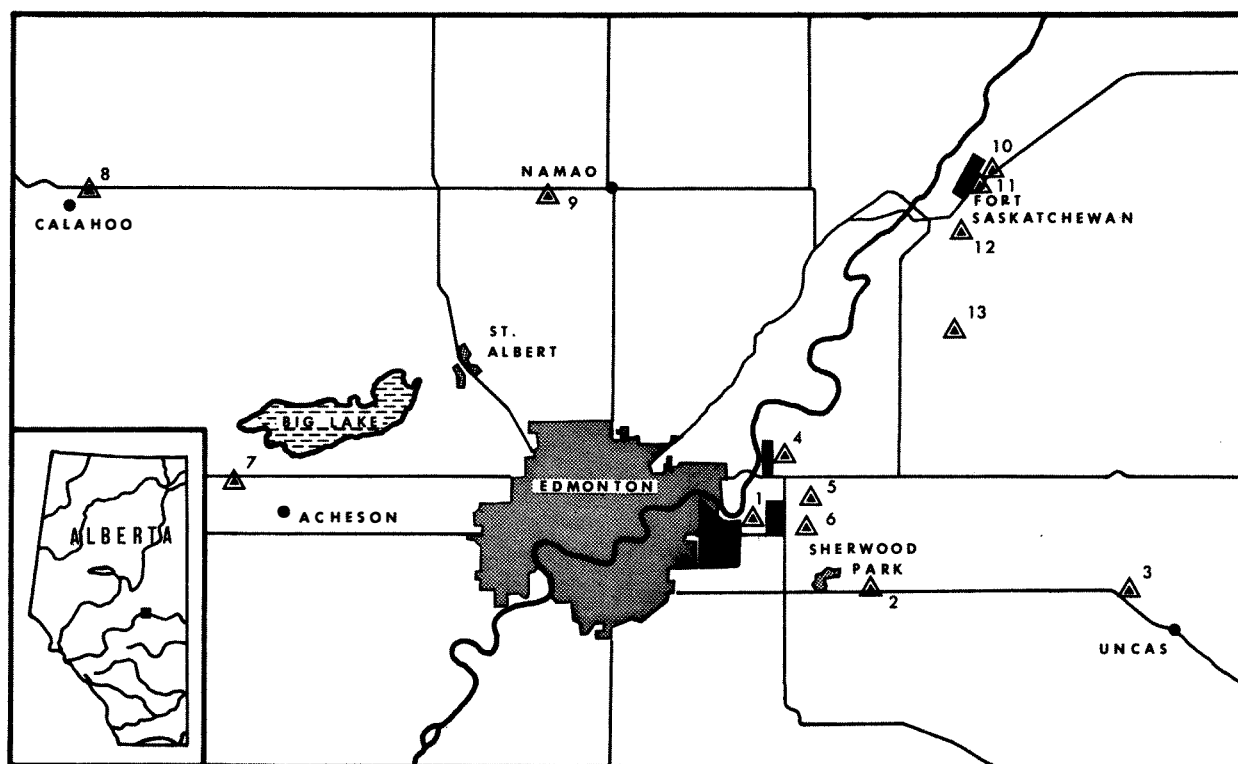
Figure 1: Map of the Edmonton Area showing the localities of the 13 study sites (triangles). Specific industrial areas noted in the text are shown as black areas.

ENVIRONMENTAL STUDIES

GULF OIL CANADA LIMITED

GULF OIL CANADA LIMITED

RESEARCH AND DEVELOPMENT DEPARTMENT

ENVIRONMENTAL STUDIES MOBILE LABORATORY

This versatile unit is capable of monitoring ambient air quality and source emissions for all of the major air pollutants.

The monitors are mounted in instrument racks and on benches in a specially designed 30' Bluebird bus powered by an 8 cylinder gasoline engine.

The Mobile Laboratory is completely self-contained and can operate either from shore-line power or from its own stabilised 22 kilowatt diesel powered generator. Air conditioning and heaters allow year round operation of the Laboratory. The bench mounted analyzers and instrument racks are shock-mounted to minimize the effect of road vibrations.

Instrument air is provided by an oil-free com-pressor mounted in the rear compartment. Most gas services are provided from cylinder storage contained in a sealed compartment while hydrogen is obtained from an electrolytic generator.

The Laboratory is equipped with an explosimeter which isolates the electrical power in the event that explosive vapor levels reach 60% of the lower explosive limit in critical areas of the Laboratory.

Samples of the outside ambient air are drawn
in through a sample port on a mast 25' above the
ground. The sample is pumped via a teflon sample
line to a manifold and flow panel where it is dis-
tributed to the various monitors.

Source samples are pulled from the sample point
through an electrically heated teflon sample line to
a sample conditioning box and then pumped to the
monitors.

Pollution levels will be correlated with weather
parameters. Wind speed and direction are measured by
a rotating cup anemometer and weather vane mounted on
top of the sample inlet mast. A centrally located
weather station will measure the parameters listed in
Table 1 below.

TABLE 1

Weather Station Parameters

Parameter	Principle of Measurement
Rainfall	Volumetric
Humidity/Temperature	Hygrothermograph
Solar radiation	Pyroheliometer
Barometric Pressure	Aneroid

The air quality monitors available in the
Laboratory are shown in Table 2.

TABLE 2

Ambient Monitors

	Pollutant	Range	Principle of Measurement
1.	Sulfur dioxide	.005-1.15 p.p.m.	Coulometry
2.	Sulfur cmpds.	>3 p.p.b.	G.C./F.P.D.
3.	Hydrogen sulfide	2-100 p.p.b.	Photometry
4.	Hydrogen sulfide	0.2-500 p.p.b.	Colorimetry
5.	Particulates	0-2,000 + mg/M^3	Gravimetry
6.	Particulates	>0.2 C.O.H. units	Photometry
7.	Oxides of nitrogen	.001-10 p.p.m	Chemiluminescence
8.	Ozone	0.2-200 p.p.b.	Chemiluminescence
9.	Total hydrocarbons	0.2 p.p.m.-2%	Flame Ionisation Det.
10.	Hydrocarbons	>0.5 p.p.m.	G.C./F.I.D.
11.	Carbon monoxide	0.5-50 p.p.m.	Non dispersive I.R.

Strip chart recorders and a data acquisition
system are used to record and process the signals
from these monitors.

The source monitoring facilities have been
integrated into the Laboratory by the use of dual
purpose analyzers. These instruments together with
the other monitors used in source measurement are
shown in Table 3.

TABLE 3

Source Monitors

Component	Principle of Measurement	
1. Sulfur dioxide	G.C./F.P.D.	*D*
Sulfur cmpds.	G.C./F.P.D.	
2. Hydrocarbons	G.C./F.I.D.	*D*
3. Oxides of nitrogen	Chemiluminescence	*D*
4. Flue gas	G.C./T.C.	
5. Flow	Pitot tube	
6. Differential Press	Variable inductance	
7. Temperature	Type K thermocouple	

NOTE: *D = Dual purpose*

Vehicle Specification

Bluebird bus	30' long by 8' wide
Height with mast down	11'6"
Air conditioning	20,000 B.T.U.
Heating	20,000 B.T.U.
Power generator	22 kilowatts
Gross vehicle weight	24,000 lbs.

--o0o--

REVIEW OF MONITORING DATA AVAILABLE FROM THE

ALBERTA DEPARTMENT OF THE ENVIRONMENT: WITH

SPECIFIC TABULATIONS FOR SOUR GAS PROCESSING

PLANTS.

by

J. C. Lack and W. J. Schnitzler

Air Quality Control Branch, Alberta Environment, Edmonton.

ABSTRACT

This paper summarizes the current air quality monitoring being conducted by the Department of the Environment and by the Sour Gas Industry.

Included is a summary of the minimum requirement guidelines which have been established for all Air Licences issued to sour gas plants. These requirements apply to all new plants and also existing plants when the existing approval is ammended.

Also included is a consolidation of the Air Monitoring Directives (AMD) which have been issued during 1972 and 1973. This AMD summarizes the reporting requirements for sour gas plants.

All data are public information and can be viewed or copied upon reasonable written request.

I. CURRENT AIR QUALITY MONITORING

Responsibility for monitoring of air quality has been placed jointly onto government and industry. The paragraphs below describe government operations and industry requirements. The Directive in part II, with attachments, details the methods used.

(a) Government of Alberta.

(i) Continuous Ambient Monitoring:

The Alberta Department of the Environment is responsible for conducting continuous monitoring surveys for sulphur dioxide and hydrogen sulphide near sour gas plants. There are four mobile laboratories, one each in the regions of Whitecourt, Edmonton, Red Deer and Calgary. The four laboratories are able to cover all the major four gas plants once each year and the small plants on a less frequent basis. The surveys which the Department conducts usually last 3 - 4 weeks.

Each mobile laboratory is equipped to monitor continuously, the SO_2 and H_2S concentrations in the ambient air, wind velocity and direction, ambient temperature, pressure and humidity. The mobile laboratory is maintained by the Department technologists from the appropriate regional office.

(ii) Static Ambient Monitoring:

The Department of the Environment has established a network of 180 exposure cylinders for measurement of total sulphation and hydrogen sulphide near most of the sour gas plants in Alberta.

(b)   Minimum Industry Requirements

Specific requirements for individual gas plants are detailed in Table 2, determined according to the principles below.

(i)   Continuous Ambient Monitoring:

The Department of the Environment has established a set of guidelines, dependent on the maximum allowable sulphur emission rate, for continuous monitoring of the ambient air for SO_2 and H_2S (Table 1). The locations of the continuous monitors are chosen by the plant. However, the Department may specify in the Air License a particular location or locations at which continuous monitoring must be conducted.

(ii)   Static Ambient Monitoring:

The industry is also responsible for conducting exposure cylinder monitoring for total sulphation, hydrogen sulphide and sulphur dustfall (Table 1). Those plants shipping their total sulphur producation in liquid form are exempted from sulphur dustfall monitoring. Those plants stockpiling but not shipping solid sulphur are permitted to reduce the number of sulphur dustfall stations to one half of that shown in the schedule provided that the minimum is not less than four. Those plants exempted in part 2 above must expand their network to the full compliment at least three months prior to break up of the sulphur stockpile.

(iii) Stack Emission Monitoring:

The incinerator stack(s) at each sulphur plant must also be surveyed each year according to the schedule established by the Standards and Approvals Division (Table 1).

TABLE 1   MINIMUM GUIDELINES

                                                          for

                                          MONITORING REQUIRED OF INDUSTRY

Maximum Allowable Sulphur Emission Rate LTS/D	Continuous Monitoring No. of Stations	Mo./yr.	No. of Total Sulphation and H_2S Exposure Cylinders	No. of Stack Surveys Per Year
120-149	5	12	40	8
90-119	4	12	35	7
60-89	3	12	30	6
30-59	2	12	25	5
15-29	1	12	20	4
10-14.9	1	9	16	3
5-9.9	1	6	12	2
3-4.9	1	3	8	1
1-2.9	1	2	4	As required
Less than 1	As required	As required	2	As required

Sulphur Production LTS/D	No. of Sulphur Distfall Exposure Cylinders
Greater than 1000	12
100 - 1000	8
Less than 100	4

TABLE 2   <u>CURRENT AMBIENT AIR MONITORING IN VICINITY OF SOUR GAS PLANTS</u>

PLANT (Operator)	LOCATION	SO_2 EMISSION LIMIT (LT/D)	AMBIENT MONITORING NETWORK *			
			Exposure T.S.&H_2S	Cylinders Sulphur	Continuous Monitoring No.	No./Yr.
Acheson (Cdn. Nat. Gas Liquids)	2-53-26W4	.79	1	0	0	
Balzac (Petrogas)	1&2-26-29W4	136 (1973) 102 (1974)	40	12	7	12
Bigoray (Amoco)	22-51-8W4	5.82	4	0	1	2
Bigstone (Amoco)	10-61-22W5	31.6 at 1000°F 38.2 at 1200°F	25	8	2	12
Bonnie Glen (Texaco Exp.)	17-47-27W4	2.58	4	4	1	2
Brazeau River (H.B.O.G.)	12-46-14W5	18.12	12	4	1	6
Burnt Timber (Shell)	13-30-7W5	41.6	20	8	1	12
Caroline (Aitana)	36-34-6W5	1.6	4	0	0	
Caroline (H.B.O.G.)	20-34-4W5	7.12	10	4	0	
Carstairs (Home)	3-30-2W5	5.52	5	4	0	
Crossfield (Amoco)	14-28-1W5	151.5 at 1000°F 196.9 at 1200°F	30	12	3	12
Daysland (Francana)	14-44-17W4	1.70	8	0	1	1 (1974-75)
Edson (H.B.O.G.)	11-53-18W5	39.0	10	8	1	2

* Refers to the current network except for a few plants which have new approvals in the past two months and may not have yet instituted the new network.

- 150 -

TABLE 2 (cont.)   CURRENT AMBIENT AIR MONITORING IN VICINITY OF SOUR GAS PLANTS

PLANT (Operator)	LOCATION	SO₂ EMISSION LIMIT (LT/D)	AMBIENT MONITORING NETWORK			
			Exposure Cylinders T.S.&H₂S	Sulphur	Continuous No.	Monitoring No./Yr.
Elkton (Home)	3-31-4W5	0.96	1	0	0	
Fort McMurray (G.C.O.S.)	17-92-10W4	44.(Sulphur plant) 350.(Power plant)	19	12	2	12
Gilby (Atlantic)	5-40-3W5	0.42	5	0	0	
Gilby (Pacific)	27-40-3W5	0.56	2	0	0	
Gilby (Texaco)	22-40-3W5	1.28	2	0	0	
Gold Creek (Atlantic)	26-67-5W6	4.36	7	4	1	2
Golden Spike (Imperial)	22-51=27W4	.21	9	0	1	1
Greencourt (Petrofina)	26-59-9W5	10.0	6	0	0	
Harmatten (Canadian Superior)	27-31-4W5	50.6	20	10	2	12
Hartell (Sun)	12-19-2W5	1.91	6	2	1	2
Hope Creek (Shell)	17-64-13W5	14.7	5	0	0	0
Innisfail (Shell)	3-35-1W5	18.4	13	8	1 1	12 6
Joffre (Imperial)	17-39-26W4	6.06	8	4	1	12

TABLE 2 (cont.)   CURRENT AMBIENT AIR MONITORING IN VICINITY OF SOUR GAS PLANTS

PLANT (Operator)	LOCATION	SO$_2$ EMISSION LIMIT (LT/D)	AMBIENT MONITORING NETWORK			
			Exposure T.S.&H$_2$S	Cylinders Sulphur	Continuous No.	Monitoring Mo./Yr.
Judy Creek (Imperial)	25-64-11W5	.36	1	0	0	
Jumping Pound (Shell)	13-25-5W5	53.7	9	10	3	12
Kaybob South #1&2 (H.B.O.G.)	12-62-20W5	172	30	12	3	12
Kaybob South #3 (Chevron)	15-59-18W5	215	35	12	4	12
Leduc (Imperial)	20-49-25W4	4.0	11	4	0	
Lone Pine Creek (Canadian Superior)	27-29-28W4	15.92	12	8	1	6
Lone Pine Creek (H.B.O.G.)	23-30-28W4	23.2	16	4	1	2
Minnehik - Buck Lake (CanDel)	5-46-6W5	5.64	4	4	1	2
Nevis (Chevron)	22-39-22W4	12.5	21	8	1	6
Nevis (Gulf)	33-38-22W4	27.4	25	8	1	12
Newell (Loydean)	15-18-14W4	.18	4	0	0	
Nordegg (Tenneco)	10-44-12W5	8.96	4	4	0	
Okotoks (Texasgulf)	27-20-29W4	52.4	8	10	1	2

TABLE 2 (cont.) <u>CURRENT AMBIENT AIR MONITORING IN VICINITY OF SOUR GAS PLANTS</u>

PLANT (Operator)	LOCATION	SO2 EMISSION LIMIT (LT/D)	AMBIENT MONITORING NETWORK			
			Exposure T.S.&H_2S	Cylinders Sulphur	Continuous No.	Monitoring No./Yr.
Olds (Amerada)	18-32-1W5	40.6	20	8	1	12
Paddle River (Canada Cities)	6-57-8W5	2.84	7	4	1	2
Pincher Creek (Gulf)	23-4-29W4	23.6	34	8	1	12
Quirk Creek (Imperial)	4-21-4W5	30.2	10	5	1	2
Rainbow (Aquitaine)	10-109-8W6	20.0	3	4	1	2
Rainbow (Mobil)	10-110-6W6	.50	3	0	0	
Rainbow (Imperial)	23-110-7W6	0	2	0	0	
Ram River (Aquitaine)	2-37-10W5	336	40	12	4	12
Redwater (Imperial)	29-57-21W4	4.46	10	0	1	2
Rimbey (Gulf)	5-44-1W5	54.4	30	5	1	2
Saratoga (Saratoga)	11-8-5W5	60	10	4	1	1
Simonette (Shell)	6-63-25W5	26.7	16	4	1	9
Strachan (Gulf)	35-37-9W5	76.4	38	12	2	12

TABLE 2 (cont.)   <u>CURRENT AMBIENT AIR MONITORING IN VICINITY OF SOUR GAS PLANTS</u>

PLANT (Operator)	LOCATION	SO2 EMISSION LIMIT (LT/D)	AMBIENT MONITORING NETWORK			
			Exposure T.S.&H2S	Cylinders Sulphur	Continuous No.	Monitoring Mo./Yr.
Sturgeon Lake (H.B.O.G.)	2-69-22W5	12.28	12	4	1	6
Sylvan Lake (H.B.O.G.)	32-37-3W5	5.10	10	4	0	
Turner Valley (Western Decalta)	6-20-2W5	6.3	13	4	1	3
Vulcan (Dome)	24-15-22W4	3.0	6	0	0	
Waterton (Shell)	20-4-30W4	248	42	12	5	12
West Whitecourt (Amoco)	17-60-15W5	210	20	6	1	12
Whitecourt (Pacific)	26-59-11W5	14.7	12	0	1	6
Wildcat Hills (Petrofina)	16-26-5W5	30.2	24	8	1	12
Wilson Creek (Amerada)	29-43-4W5	3.4	4	0	1	2
Wimborne (Mobil)	12-34-26W4	43.3	20	4	1	12
Zama (H.B.O.G.)	12-116-6W6	9.5	8	4	1	3

II. AIR QUALITY REPORTING REQUIREMENTS

   Consolidated Air Monitoring Directive:

      The items contained in the following directive constitute
a consolidation of all previous air monitoring directives issued in
1972 and 1973. This directive applies specifically to air monitoring
requirements in the vicinity of sour gas processing and sulphur recovery
plants throughout Alberta.

I. GENERAL

1.   All air monitoring reports are to be addressed as follows:

                  Mr. R. N. Briggs, M.Sc., P.Eng.
                  Director, Division of Pollution Control
                  Department of the Environment
                  6th Floor, Milner Building
                  10040 - 104 Street
                  Edmonton, Alberta
                   T5J 0Z6

On receipt, the reports are forwarded to the Head of the Air Quality
Control Branch for inspection and approval.

2.   To facilitate review, the heading of the covering letter of each
monthly submission should make reference to the plant name, applicable month
and year, as well as plant Air Approval and License number.

3.   All air pollution monitoring data must be compiled and forwarded
to this office before the end of the month following that for which the
observations were made. If a delay is necessary, a letter outlining the
reason must be received in this office before the data reporting deadline.
Continued negligence in this regard may necessitate prosecution.

4.   One single report should be forwarded each month, rather than
several partial reports. The single report should contain the following.

a. Exposure cylinder data.

b. Sulphur dustfall cylinder data (where applicable).

c. Continuous H_2S, SO_2 and wind monitoring date (where applicable).

d. Map of the plant area. Attachment A lists the detail to be included on the map.

e. Plant operating data. (Energy Resources Conservation Board forms S-30 and S-30A plus any additional information required by Air Licence.)

f. An explanation for all monitoring results in excess of the Clean Air (Maximum Levels) Regulations and the Department guidelines for total sulphation and hydrogen sulphide.

5.   The air monitoring data received must be clearly legible and contain the necessary detail as outlined in these directives. Where the data is the result of irresponsible monitoring methods or inadequate monitoring equipment, the data received will not be accepted as fulfilling the monitoring requirements specified in the Energy Resources Conservation Board Approval and the Department of the Environment Air Licence.

II TOTAL SULPHATION AND HYDROGEN SULPHIDE EXPOSURE STATIONS

1.   The function of H_2S and total sulphation and hydrogen sulphide exposure cylinders is to provide qualitative and relative data rather than quantitative pollutant measurements. The importance of careful handling, preparation and analysis and the continuous operation of the exposure cylinder stations is apparent in that only exposure cylinder data that is valid can be effectively compared to previous data. Attachment B contains additional detail in this regard.

2.   A suggested layout for reporting the exposure cylinder results is included. (Attachment C)

3.   The monthly submission of exposure cylinder data shall not be considered complete and acceptable unless it includes an explanation for possible sources of high exposure cylinder levels. The guidelines to be utilized are included in Attachment A. An explanation should also be included for possible sources where any one exposure cylinder records a substantial increase over the usual level, even though the reading is below the guideline specified.

4.   We wish to emphasize that exposure cylinders should be exposed as close as possible to the calendar month period. The individual exposures shall not extend for more than one month.

5.   To assure uniform laboratory procedures and comparable results a common reference station has been set up in Edmonton. Each laboratory which prepares and analyzes total sulphation or hydrogen sulphide exposure cylinders must send one exposure cylinder of each kind to our Edmonton office each month. Our staff then changes the individual stations and returns the exposed cylinders to your laboratory for analysis. In the case where on laboratory prepares and analyses the exposure cylinders for a number of plants, only one set of exposure cylinders is required. Data from laboratories analyzing total sulphation and H_2S exposure cylinders or total sulphation plates will not be accepted unless the laboratory is submitting one set of exposure cylinders to this office on a monthly basis for exposure at the Edmonton reference station.

6.   Change over to total sulphation plates from the glass jar cylinders is acceptable provided that both systems are maintained for a minimum of three months at each station, and the results are comparable.

7.   The use of tiles or any method other than the glass jar exposure cylinder for the detection of H_2S is unacceptable at this time.

8.   All exposure cylinder data sheets shall include a reference to the laboratory responsible for the specific analyses, as well as the signature of the laboratory personnel certifying the results.

III.   SULPHUR DUSTFALL MONITORING

1.   All plants producing elemental sulphur are required to conduct sulphur dustfall monitoring (with the exception mentioned below). A suggested layout for reporting the results is included (Attachment D).

2.   Exposure cylinders for sulphur dustfall are to be established at a distance of 1/8 to 1 mile (or starting at the property line) from the sulphur stock pile in locations approved by this office according to the following schedule:

Maximum SO_2 Emission*	No. of Sulphur Dustfall Cylinders Required
> 100 LT/D SO_2	12
100 " "	10
50 " "	8
20 " "	6
10 " "	4

* Plant maximum as per Energy Resources Conservation Board approval.

The sulphur dustfall analysis procedure which is to be followed is included. (Attachment E). The exposure period is 30 days and should be concurrent with the total sulphation and H_2S exposure

cylinders. The format for the reporting of sulphur dustfall levels is attached. Where a company is reporting relatively few total sulphation and H_2S exposure cylinders, one page can be utilized to report all of the exposure cylinders (total sulphation, H_2S, sulphur distfall).

3.   Those plants flaring rather than recovering the acid gas and producing no elemental sulphur and those plants shipping their total sulphur production in liquid form and having no solid sulphur storage facilities are exempted from the sulphur dustfall monitoring requirement.

4.   Those plants stockpiling solid sulphur but not shipping elemental solid sulphur are permitted to reduce the number of sulphur dustfall exposure cylinders to be implemented to one-half of the schedule set out in paragraph 1., above, provided the minimum number of exposure cylinders set out under this condition is not less than four.

5.   Those plants which have been utilizing the reduction in paragraph 3., above, must expand the sulphur dustfall monitoring net work to the full schedule three months prior to break up of the sulphur stockpile.

6.   Those plants shipping and stockpiling solid elemental sul- phur must implement the full schedule of sulphur dustfall exposure cylinder requirements outlined in paragraph 1 above.

7.   The sulphur dustfall levels throughout the Province of Alberta will be summarized by this office and mailed out to all plant operators on an annual basis.

8.   A description is included of the dustfall cylinders that are utilized for the monitoring of sulphur dustfall. (Attachment F).

9.   Locations of the sulphur dustfall stations shall be pro-
posed and forwarded to this office for approval prior to installation.
The locations should be representative, mainly in the primary downwind
direction and within a reasonable distance of the sulphur stockpile or
shipping area (within approximately one mile).

10.   The plastic polyethylene juice containers utilized by this
Department are available from:

> Western Varieties and Dry Goods Ltd.,
> 10187 - 103 Street,
> Edmonton, Alberta

The containers are listed as No. 88LT Plastic Juice Containers. Similar
containers may be available from other sources, however, this has been
our most dependable source.

11.   The location of all sulphur dustfall exposure cylinders
should be clearly indicated either on a separate map or on the general
plant area map, showing the H_2S and total sulphation exposure cylinder
locations. The format of this map should be restricted to 8 1/2 x 11".

12.   In expressing the concentration of sulphur dustfall, the
units of short tons sulphur per square mile per 30 days, (tons S/sq.mi./
30 days) should be utilized in order to provide a uniform basis for
comparison. (One short ton being 2,000 lbs.).

IV. CONTINUOUS AMBIENT MONITORING

1.   To constitute valid and representative data, each SO_2 and
H_2S instrument must be operational a minimum of 90% of the total com-
mitment. The percentage of time that each instrument was operating
each month must be stated in the instrumentation data form. Note that
the time periods utilized for calibration are not considered downtime.

A. Monitoring 12 months/year

    If the above criterion is not met, back up equipment may be required.

B. Monitoring less than 12 months/year

    If the above criterion is not met, the survey shall be extended until the number of days in excess of the 10% downtime have been made up; e.g., if a monitor is inoperable for 5 days during a 30 day survey, the survey shall be extended by 2 days.

2.   The SO_2 instruments must be calibrated at three or more concentrations and a legible photocopy of the recorder chart during calibration shall be submitted as part of the monthly report. So that the equipment sensitivity deviations may be analyzed, the photocopy of the recorder charts should include the initial calibration check, the final calibration verification when adjustments are necessary, and the baselines before and after calibration. Notes to assist in interpretation should be included.

3.   As an H_2S Regulation has been established for 1/2 hour periods, the spot tape type monitoring instrumentation must be adjusted accordingly. Arrangements therefore must be made to change the spot cycle on the conventional H_2S tape samplers to 30 minutes from 1 hour. This new requirement will be given a trial period of one year following which the results will be reviewed by the joint industry - government committee.

4.   Where the regulations are exceeded, the following proce-
dure shall be followed:

(i)   Immediate Notification

During office hours, immediately upon detection and confirmation

of excessive readings, this office shall be notified by T.W.X. or

telephone. This notification is to include the following infor-

mation:

(a) identification of plant and monitor site and date of excessive

     level monitored.

(b) indication of the specific regulation exceeded, as well as

     frequency of same, e.g.: 3 hours exceeded the SO_2 hourly

     regulation of 0.17 ppm, indication of the actual readings

     observed, wind speed and direction, and general atmospheric

     conditions.

(c) source of high readings and remedial action taken. During

     non-office hours, the procedure to be followed is outlined

     in section V of this directive.

(ii) Confirmation Letter

The information required in item (i) must be confirmed in writing

and forwarded to this office within 72 hours of the occurrence.

A detailed analysis of the violation (as per item (i) above, as

well as a description of the effectiveness of the remedial action

taken, the preventative measures taken to prevent recurrences,

and the readings two hours before and two hours after the ex-

cessive levels) is to be included and a carbon copy forwarded
to the Assistant Manager, Environment Protection, Energy Resources
Conservation Board, Calgary.

5. The reporting format for continuous monitoring is :

(i) All SO_2 average concentrations of 0.05 ppm or greater for 15
minutes shall be listed in addition to the peak value of 0.10
ppm previously utilized by some companies. All H_2S average
concentrations of 0.003 ppm or greater for 30 minutes shall
be listed.

(ii) The average SO_2 concentration during each period shall be
listed on the same page as the peaks; however, in no case
shall the averaging period exceed 30 minutes. In the case
where the observed peak exceeds 0.5 ppm, the averaging period
must not exceed 15 minutes.

(iii) In view of the new Regulations, the hourly average H_2S and
SO_2 tables must be replaced by half-hourly average tables.

(iv) A separate page should be utilized to list any occurrences
of H_2S or SO_2 concentrations which exceeded any of the Clean
Air (Maximum Levels) Regulations. These tables are to present
any running average concentration which exceeded the Regulations.

(v) A 24 hour running average tabulation must be included for SO_2
on every occasion of the hourly average exceeding 0.10 ppm.
i.e.: The running 24 hour average is to be calculated such
that in the first calculation the hourly average exceeding
0.10 ppm is the 24th hour, and in the final calculation the
hourly average exceeding 0.10 ppm is the initial hour.

6.   Where plants are conducting air monitoring surveys for less than 12 months per year, this office should be notified by mail of the intent to set up the monitoring trailer, before the survey commences. If the survey report period differs substantially from the proposed monitoring period, an explanation should be forwarded with the survey report.

7.   Telemetry of the continuous SO_2 and H_2S monitor levels to the plant control room allows a continuous check of the atmospheric pollution levels in the specific area of the monitor location. In this manner the necessary remedial action can be implemented immediately when high atmospheric SO_2 and H_2S levels are detected.

8.   One continuous monitoring survey is to be conducted during each annual plant turnaround. The survey shall cover the turnaround period and one week prior to one week after turnaround. For plants operating a continuous monitoring system for 12 months per year this item does not apply. Those plants required to operate a continuous monitoring system for less than 12 months per year may apply this item requirement as one month of the annual continuous monitoring requirement (as per Energy Resources Conservation Board approval).

9.   Attachment G illustrates the format of part of the Department of the Environment air monitoring surveys. We recommend that a similar format be established for the Industry submissions in order to facilitate rapid review.

V   STACK EMISSION MONITORING

(a)   Stack Surveys

The Air Approvals and Licences to Operate, which have been issued since 1972, require that a copy of each stack survey report be forwarded to the Director of the Pollution Control Division.

VI   ANNUAL REPORT

Following is an outline of minimum information requested in the Annual Reports, as required by Air Approvals and Licences.

1. General commentary as to the operation of the plant as it pertains to atmospheric emissions and general environmental considerations. A tabulation of significant studies conducted by industry may be included at their option.

2. A statistical summary of SO_2 and H_2S monitored readings in excess of the Clean Air Maximum Levels Regulations. Information should be in Table Form.

TABLE I

NUMBER OF OCCURRENCES

	1st Quarter	2nd Quarter	3rd Quarter	4th Quarter	Total
1/2 hr. SO_2	1	1	7		9
1 hr. SO_2		1	3		4
24 hr. SO_2					
1/2 hr. H_2S					
1 hr. H_2S					
24 hr. H_2S					

TABLE II

CAUSE OF OCCURRENCES

SOURCE	CAUSE	1st Quarter	2nd Quarter	3rd Quarter	4th Quarter	Comments
STACK	Low Top Stack Temperature		2 SO_2			
FLARE	Power Failure	1 SO_2		10 SO_2		Installed New Stand-by Generator
ETC.						
TOTAL		1	2	10		

3. The weighted annual average (January 1 to December 31) SO_2 concentration is to be included in all cases where an instrument is maintained year round at one location.

4. Time and duration of annual plant turnaround.

5. Basic Monitoring Equipment

   Information should include explanation of any significant changes made with respect to the monitoring hardware and an indication of the effective on stream time for the equipment.

6. Brief exposure cylinder review - especially of those individual stations exhibiting the highest levels. Data to include:

   1. Station No., suspected source of the respective pollutant.

   2. Unusual occurrences that relate to these high levels in plant or field operations.

   3. General trend of the overall network.

   4. Lines of equal value (seasonal as minimum) if more than 16 stations are maintained.

   5. Annual average of individual stations and annual averages of network.

7. Brief review of the continuous stack emissions monitor data and the stack sampling surveys as the emission data relates to the approval. Data to include:

   i) No. of total days stack monitor was in operation

ii) No. of days 1/2 hr. limit was exceeded

iii) No. of stack surveys conducted - including the

actual dates and emission rates.

8. Brief commentary as to frequency and amount of flaring.

Data to include:

i) Total volume flared (H_2S)

ii) Commentary only as to frequency

9. Basic overall annual sulphur balance:

i) Total Gas Inlet (Annual)

ii) Total Gas Flared (Annual)

iii) Total Sulphur Produced (Annual)

iv) Total Emissions (Annual)

VII NOTIFICATION OF THE DEPARTMENT DURING NON-OFFICE HOURS

The following guidelines are to be followed:

The plant will provide the following details to TAS:

1. Plant name and operator

2. Telephone number.

3. Nature of the occurrence, ie, "Ambient" or "Stack".

Note that T.A.S. will not be responsible for receiving any

details of the occurrence other than one of the two key words "Ambient" or

"Stack".

"Ambient" Occurrences

T.A.S. has been instructed that calls regarding "Ambient"

occurrences are considered urgent, and that the Department staff member

on call is to be notified immediately. The staff member will then call

the plant for the details of the violation.

Note that "Ambient" occurrences include any violation of the Clean Air Act (Maximum Level) Regulations and any uncontrolled release of air contaminants from the plant.

"Stack" Occurrences

T.A.S. has been instructed that calls regarding "Stack" emission violations are less urgent, and that the staff member on call is to be notified when he makes his routine checks with T.A.S. The staff member on call will then contact the plant at the earliest convenient time (usually the next morning).

If any difficulties should arise in interpretation of this Directive, please contact the Air Quality Control Branch.

(T.A.S. - Telephone Answering Service - 425-1130)

ATTACHMENT A

MAP OF THE PLANT AREA

The map is to include the following details:

- Plant Location

- Location of adjacent towns or other major landmarks
  (such as rivers, etc.).

- Continuous Monitoring locations (if applicable)

- Exposure cylinder locations.

- Sulphur dustfall cylinder locations (if applicable)

- Well and battery site locations (using convential
  designations).

- Groundlevel elevation contours.

- The map coverage should extend slightly beyond the
  area covered by the exposure cylinders.

- Size: 8 1/2" x 11".

EXPOSURE CYLINDERS

This type of survey is conducted by the Department of the Environment, Pollution Control Division and the gas plant or field operators in the vicinity of all sour gas plants or oil fields. It is a continuous type of survey in that the hydrogen sulfide and total sulfation cylinders report would be considered a monthly average pollution figure as they are exposed for approximately a one month period (weather permitting) before they are replaced. This type of survey provides the Department with an invaluable source of information as it is a rough indication of the trends in any given area.

In the case of sour gas plants the Department attempts to set up the exposure stations before the plant goes on stream. In this way the increase in pollution over the previous ambient level can be determined. It is important to note that when the exposure cylinder values are studied to determine the pollution trends, only two types of valid comparisons can be made. Either each station is considered on its own or the yearly averages of all stations in the area are compared. As each area has its own unique meteorological conditions and sources and each cylinder is located in its own unique topography, the reported values are also unique. It must also be remembered that there is a general seasonal variance with the values being highest in the winter and lowest during the summer.

There is no maximum allowable concentration as such for the total sulfation or hydrogen sulfide cylinders, however, most of the reported values from the total sulfation cylinders are less than 0.3 SO_3

equivalent mg./day/100 sq. cm. and for the hydrogen sulfide cylinders are less than 0.05 SO_3 equivalent mg./day/100 sq. cm. The readings in any given month are considered to be significant when they deviate from what is considered to be norm of the station for the time considered.

As the total sulfation cylinders also react with H_2S, it is advisable, for the sake of comparing the total sulfation and hydrogen sulfide cylinder results, to report both results in the same units. The most common units are SO_3 equivalent mg./day/100 sq. cm.

There is no relationship between units of SO_3 equivalent and parts per million (ppm). Although various studies have been made it is impossible to relate these two unless the concentration of sulphur compounds is constant throughout the exposure period. This can be accomplished in the laboratory but it never occurs as an actual situation. As an example, a cylinder exposed to a low SO_2 concentration for one month can have the same final reading as a cylinder which is exposed to a relatively high concentration for five days.

The exposure cylinder survey was developed in 1932 at the Building Research Station in England. Details of the original instrument and developmental investigations are described in a booklet entitled 'The Investigation of Atmospheric Pollution', Fuel Research Station, 1948.

This type of survey is carried out by exposing strips of lead dioxide and zinc acetate to the atmosphere for a known period of time, generally one month. Sulphur dioxide and other sulphur compounds react with PbO_2 to form $PbSO_4$ while hydrogen sulfide reacts with $Zn(C_2H_3O_2)_2$ to form ZnS.

The following facts have been established concerning the reaction between lead peroxide and sulphur dioxide.[1]

1. Both the reagent (lead peroxide) and the products (lead sulfate) are insoluble in water.

2. The yield of lead sulfate is proportional to the concentration of sulphur dioxide for all concentrations up to one part per thousand.

3. When air containing a constant proportion of sulphur dioxide is blown slowly past a test surface of lead peroxide, the reaction goes at a constant rate until more than 15% of the lead peroxide has been converted. In this case the resulting reading is approximately 13 mg. SO_3/100 cm.^{2}/day.

4. The reactivity is not significantly dependent on wind speed under the following test conditions:

Conc. of SO_2 (ppm)	Wind Speed (mph)
30 - 700	.067 - .67
1 - 6	3.3 -20.1
1	.33 -17.9

5. The reactivity increases 1% for a temperature increase of 12.5°F.

6. There is no significant correlation with relative humidity.

7. The reactivity increases when the lead peroxide surface is wet.

8. Different batches of lead peroxide can have different reactivity.

Although no article discussing the reaction of hydrogen sulfide and zinc acetate could be located, the following facts were found concerning the reaction of lead acetate and hydrogen sulfide.[2] As both

chemicals are used for H_2S detections it is felt that the following
general statements may be true for each reaction:

1. The reaction rate increases significantly with increased air turbulence.

2. Variations in relative humidity between 57% and 97% have no affect
    on the rate of reaction.

3. Methyl mercaptan, dimethyl sulfide and dimethyl disulfide in
    concentrations much higher than normally present in the outdoor atmos-
    phere, had no significant effect on the rate of reaction.

References:

1. 'Measurement of Sulphur Dioxide with Lead Peroxide Instrument',
    Department of Scientific and Industrial Research, 1948.

2. E.F. Galardi and R.M. Manganelli, Laboratory Study of Lead Acetate
    Tile Method for the Quantitative Measurement at Low Concentrations
    of Hydrogen Sulfide - Journal of Air Pollution Control Assoc.
    13:305-309 (1963).

3. S.F. Liang, C.V. Sternling and T.R. Galloway, Evaluation of the
    Effectiveness of the Lead Peroxide Method for Atmospheric
    Monitoring of Sulphur Dioxide - Journal of Air Pollution Control
    Association. Vol. 23, No. 7: 605 - 607 (1973).

MONTHLY REPORT OF PLANT AND AIR MONITORING DATA

PLANT LOCATION: _____ OPERATOR: _____

MONTH OF: _____ 19_____

1. EXPOSURE CYLINDER RESULTS

	Total Sulphation	Hydrogen Sulphide		Total Sulphation	Hydrogen Sulphide
	SO_3 equiv. mg./day/100 sq. cm.			SO_3 equiv. mg./day/100 sq. cm.	
Station No. 1	_____	_____	Station No. 21	_____	_____
Station No. 2	_____	_____	Station No. 22	_____	_____
Station No. 3	_____	_____	Station No. 23	_____	_____
Station No. 4	_____	_____	Station No. 24	_____	_____
Station No. 5	_____	_____	Station No. 25	_____	_____
Station No. 6	_____	_____	Station No. 26	_____	_____
Station No. 7	_____	_____	Station No. 27	_____	_____
Station No. 8	_____	_____	Station No. 28	_____	_____
Station No. 9	_____	_____	Station No. 29	_____	_____
Station No. 10	_____	_____	Station No. 30	_____	_____
Station No. 11	_____	_____	Station No. 31	_____	_____
Station No. 12	_____	_____	Station No. 32	_____	_____
Station No. 13	_____	_____	Station No. 33	_____	_____
Station No. 14	_____	_____	Station No. 34	_____	_____
Station No. 15	_____	_____	Station No. 35	_____	_____
Station No. 16	_____	_____	Station No. 36	_____	_____
Station No. 17	_____	_____	Station No. 37	_____	_____
Station No. 18	_____	_____	Station No. 38	_____	_____
Station No. 19	_____	_____	Station No. 39	_____	_____
Station No. 20	_____	_____	Station No. 40	_____	_____

An explanation of high exposure cylinder results (such as abnormal plant or field operations, their persistence and rectification) shall be attached. For the purpose of this comparison, a high exposure cylinder reading shall be deemed a hydrogen sulphide level greater than 0.10 SO_3 equiv. mg./day/100 sq.cm. and a total sulphation level in excess of 0.50 SO_3 equiv. mg./day/100 sq. cm. (NOTE: These values are guidelines for comparison only and are not intended to serve as ambient air quality standards).

2. SULPHUR DUSTFALL CYLINDERS:

Short tons S/sq. mi./30 days   Short tons S/sq. mi./30 days

Station No. 1 _____   Station No. 7 _____

Station No. 2 _____   Station No. 8 _____

Station No. 3 _____   Station No. 9 _____

Station No. 4 _____   Station No. 10_____

Station No. 5 _____   Station No. 11_____

Station No. 6 _____   Station No. 12_____

The location of the sulphur dustfall cylinders as numbered here shall

be indicated on the attached map of the plant area.

ATTACHMENT E

DEPARTMENT OF THE ENVIRONMENT
POLLUTION CONTROL DIVISION
LABORATORY

January 14, 1972

DETERMINATION OF TOTAL SULPHUR IN DUSTFALL SAMPLES

USING LECO INDUCTION FURNACE AND SULPHUR TITRATOR

1. Principle

The analysis proceeds according to the following equation:

$$KIO_3 + 5 \ KI + 6 \ HCl = 6 \ KCl + 3 \ I_2$$

$$SO_2 + I_2 + 2 \ H_2O = H_2SO_4 + 2 \ HI$$
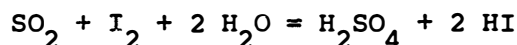
Thus, a weak HCl solution is put into a titration vessel: KI and

starch solutions are added. Then, when a very small amount of the

standard KIO_3 solution is added, free I_2 is released indicated by

the starch turning blue. An automatic buret containing the KIO_3 is

then refilled to the zero or starting point. The sample under test

is next combusted in oxygen where the sulphur in the sample goes to

SO_2 and/or SO_3 depending on the combustion conditions, though only

SO_2 is titrated with the iodometric method. SO_2 from the burning

sample is conducted to the titration vessel where it reacts with the

free iodine and ties it up as a compound, HI. Since starch turns

blue only in the presence of free iodine, and not when the iodine is

in compound form, the starch turns colorless. More KIO_3 is added to

form more free iodine and to bring the solution back to its original

color. This is repeated in a continuous manner until all the SO_2

is out of the sample and has been titrated.

2. <u>Apparatus and Equipment</u>

  Leco Induction Furnace (Fisher 12-153)

  Leco Sulphur Titrator (Fisher 12-156)

  Crucibles, Leco (Fisher 12-186-8)

  Covers, Porous, Leco (Fisher 12-187-4)

  Combustion Accelerator, Granular Tin, Metal, Leco (Fisher 12-173-5)

  Accelerator, Analyzed Iron Chip, Leco (Fisher 12-174-5)

  Scoop, Accelerator, Leco (Fisher 12-192-5)

3. <u>Reagents</u>

  (a) Dissolve 6 g. Potassium Iodide (KI) in 200 m. distilled water.

  (b) 0.25% starch - potato. Dissolve starch in 200 ml. distilled
      cold water. Bring 800 m. distilled water to boil. Add
      200 ml. starch suspension in small portions allowing time to
      dissolve, cool and add potassium iodide.

  (c) Dissolve 0.444 g. potassium iodate (KIO_3) in one liter distilled
      water.

  (d) Dissolve 15 ml. conc. HCl and 2 g. sodium azide (NaN_3) in one
      liter distilled water.

4. <u>Procedure</u>

  (a) Filter total dustfall sample or aliquot through a Gooch crucible
      using Reeve-Angel Glass Fiber filter (Fisher 9-873A).

  (b) Place into Leco crucible in the following order:

      1 scoop Sn (accelerator).
      filter containing sample,
      2 scoops Fe (accellerator,
      1 Cu ring (accelerator).

(c) Fill Leco titration cell with:

    5 ml. starch solution,

    0.015 ml. KIO_3 solution from buret.

    Bring volume in cell to mesh by adding HCl/NaN_3 solution.

(d) Set the meter needle arbitrarily, with the blue color in the titration cell.

(e) Place the crucible containing the sample into the Leco furnace. Set Grid Tap switch to High and put igniter on.

(f) Titrate by hand. Titration is ended when the meter needle is brought back to its original setting.

(g) Apply a continuous stream of oxygen during the total time of analyzis at a flow rate of approximately 1 liter/minute, through the pipe provided on the sample holder of the furnace.

(h) Set up a calibration curve using sulphur of highest purity and plot milliters of used KIO_3 solution versus microgram sulphur. Place always a blank filter inthe crucible since it contains sulphur compounds as impurities.

Reference: 1. A.S.T.M. method E30-47

             2. Instruction Manual for Operation of Leco Sulphur Determinators Models 517, 518, 532. Laboratory Equipment Corporation, Saint Joseph, Michigan. Form No. 133A.

CONSTRUCTION AND MAINTENANCE OF DUSTFALL CYLINDERS

In the construction of particulate fallout stations the Department utilizes open top 48 oz. fruit juice tins fitted with open top polyethylene juice containers. The tin cylinder is fastened to a 1" diameter, 3 foot long steel pipe and this assembly is then fastened to a fence post or other support by means of steel wire strapping. The top of the dustfall container should be a least 6 to 8 feet above ground level and at least 4 feet above any other surface such as a roof. Once selected, a site should be maintained unless conditions occur to cause undue influence on the sample or to create an unsatisfactory condition. During warm weather 500 mls. of distilled water, containing at least 2 ppm by volume of a 1% solution of Dowicide 'B' or quatenary ammonia to inhibit algae growth, is added to each polyethylene cylinder. During cold weather the cylinder is exposed dry as almost any aqueous solution will freeze and other solutions may interfere with the analysis. A sampling period should be one calendar month corrected to 30 days. An allowance of plus or minus 2 days is permitted in setting out and/or collecting the polyethylene sampling cylinders. When servicing the fallout stations the exposed polyetheylene cylinder is simply replaced by a freshly prepared polyethylene cylinder. The exposed cylinders should be properly covered during transfer to avoid the possibility of extraneous material pickup during transit. Any extraneous material that may be present shall be removed by means of a chemically

inert 20 mesh screen. The presence of small insects may require the use of a screen smaller than 20 mesh. The oversize material should be examined to avoid removing material that is properly a portion of the sample. Inspections of field cylinders should be made during periods of heavy rainfall to prevent their overflow and they should be replaced if they are apt to overflow. If bird droppings become a problem, we suggest the use of a bird ring around the container to provide a perch at a distance.

DUSTFALL STATION

48 ounce plastic juice dispenser

48 ounce juice can

3/4 inch galvanized anchor strap

1/2 inch steel pipe

3/4 inch galvanized anchor strap

Post

Ground Level

6'
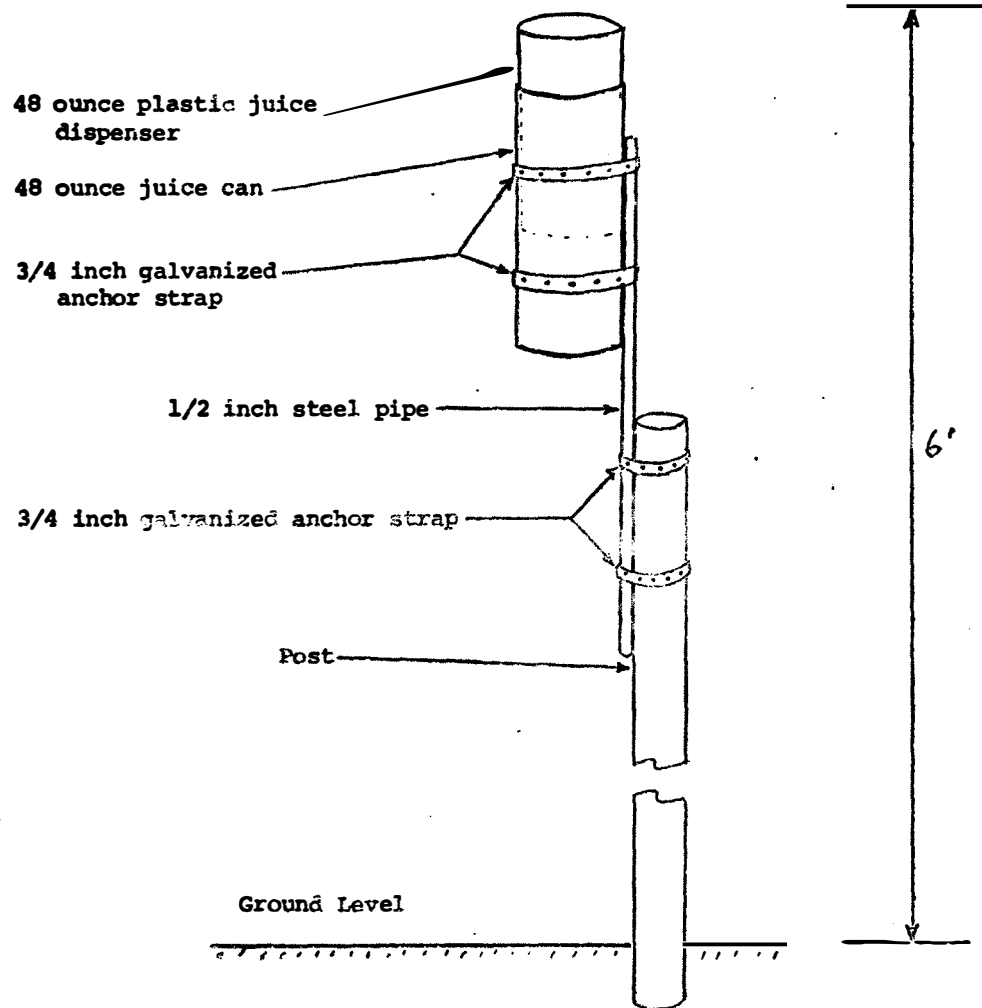
AIR MONITORING INSTRUMENTATION DATA

MONTH of _____ 19 ____

SULPHUR DIOXIDE:

1. Make and Model of instrument used: _____

2. Minimal Detectable limit and precision of instrument _____

_____

3. Hours that instrument was operational _____ hours _____ %

4. Instrument was calibrated on _____ 19 _____

    by the _____ method.

5. Instrumentation difficulties, if any:

HYDROGEN SULPHIDE:

1. Make and model of instrument used: _____

2. Hours that instrument was operational _____ hours _____ %

3. Instrumentation difficulties, if any:

WIND SPEED AND DIRECTION:

1. Make and model of instrument used: _____

2. Hours that instrument was operational _____

    Direction _____ hours _____ %

    Speed _____ hours _____ %

3. Instrumentation difficulties, if any:

SUMMARY TABLE

LOCATION: _____ PERIOD: _____

_____ miles _____ plant site.

WINDS:

Most Frequent	Direction	Percentage	Velocity (mph)
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____

Average wind speed: _____ mph.

HYDROGEN SULPHIDE:

Sampler Operating _____ hrs. _____ %

H_2s Detected _____ hrs. _____ %

Max. 1/2 hr. average _____ ppm on _____ 19 __; _____ - _____ hrs; wind _____.

Max. 1 hr. average _____ ppm on _____ 19 __; _____ - _____ hrs; wind _____.

Max. 24 hr. average _____ ppm on _____ 19 __; _____ - _____ hrs; wind _____.

MAJOR WIND CORRELATIONS:

_____ % of readings recorded with _____ winds.

_____ % of readings recorded with _____ winds.

_____ % of _____ Winds resulted in readings.

_____ % of _____ winds resulted in readings.

SULPHUR DIOXIDE:

Sampler Operating _____ hrs. _____ %

SO_2 Detected _____ hrs. _____ %

Max. 1/2 hr. average _____ ppm on _____19 __; _____ - _____ hrs; wind _____

Max. 1 hr. average _____ ppm on _____19 __; _____ - _____ hrs; wind _____

Max. 24 hr. average _____ ppm on _____19 __; _____ - _____ hrs; wind _____

MAJOR WIND CORRELATIONS:

_____ % of readings recorded with _____ winds.

_____ % of readings recorded with _____ winds.

_____ % of _____ winds resulted in readings.

_____ % of _____ winds resulted in readings.

ATTACHMENT G – 3

WIND ROSE

PERIOD _____

LOCATION _____
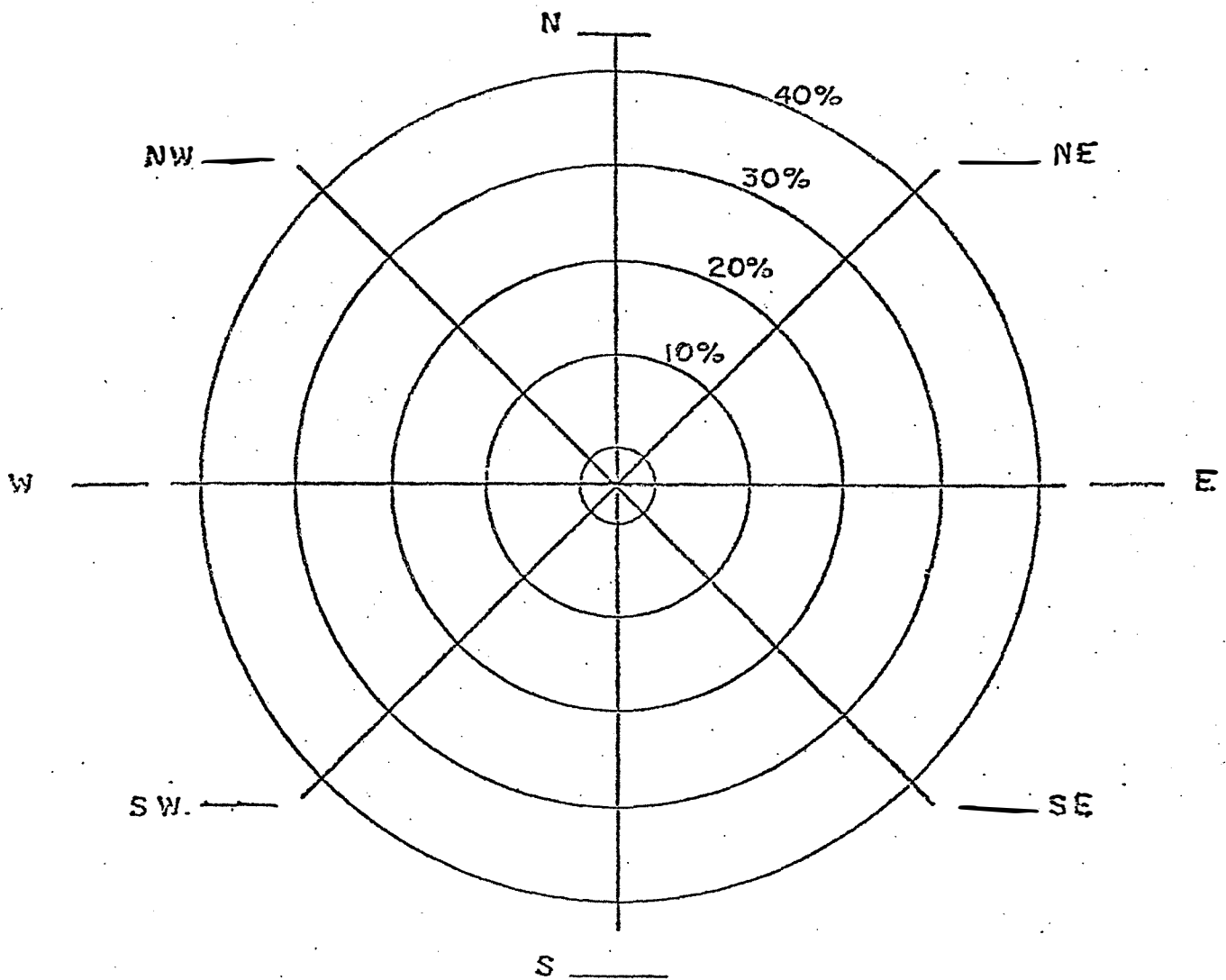
Calm or Light Variable _____ %

Average Wind Speed _____ mph

Average Wind Speed mph is shown at the Outer Circle.

ATTACHMENT G – 4

SULPHUR DIOXIDE IN PPM

LOCATION: _____ PERIOD _____ 19___ TO _____ 19 ___

PEAK CONCENTRATIONS EXCEEDING 0.10 ppm and AVERAGE CONCENTRATIONS EXCEEDING 0.05 ppm FOR
15 MINUTES

DAY	DATE MO	YR.	TIME INTERVAL FROM	TO	DURATION MINUTES	PEAK	AVE.	WIND VEL.	DIR.
15	1	72	1740	1743	3	0.100	0.050	6	SW
					(example)				

SAMPLE RANGE PPM	TOTAL TIME OF RECORD	FREQUENCY OF OCCURRENCE	CUM FREQUENCY OF OCCURRENCE
.000	1361	92.96	92.96
.000 – .029	102	6.97	99.93
.030 – .059	0	0.00	99.93
.060 – .099	1	0.07	100.00
.100 – .169	0	0.00	100.00
.170 – .199	0	0.00	100.00
.200 – .499	0	0.00	100.00
.500 – .999	0	0.00	100.00
1.0 +			

Example

ATTACHMENT G - 5

HYDROGEN SULPHIDE IN PPM

LOCATION: _____ PERIOD _____19 ___ TO _____ 19 ___

VALUES LISTED ARE THOSE GREATER THAN 0.003

DAY	DATE MO.	YR.	TIME INTERVAL FROM	TO	CONC. PPM	WIND VEL.	DIR.
15	7	73	1200	1230	0.020	6	SW

example

PLANT LOCATION _____   MONTH OF _____ 19 _____

1/2 HOUR AVERAGE SO2 CONCENTRATIONS (PPM)

Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	DAILY AVERAGE
1																									
2																									
3																									
4																									
5																									
6																									
7																									
8																									
9																									
10																									
11																									
12																									
13																									
14																									
15																									
16																									
17																									
18																									
19																									
20																									
21																									
22																									
23																									
24																									
25																									
26																									
27																									
28																									
29																									
30																									
31																									
Mean Conc.																									

THE INDUSTRY-GOVERNMENT SOUR GAS

ENVIRONMENTAL COMMITTEE

by

J. G. Gainer, Gulf Oil Canada Limited, Calgary

Abstract

This committee provides a forum for candid discussion of criteria and guidelines for certain environmental impacts of sour gas plants. It is chaired by the assistant deputy minister of the Alberta Department of the Environment and includes representatives of that department and of the Energy Resources Conservation Board. There are 8 representatives of the industry; resource people are occasionally invited.

Objectives include:

1. minimize SO_2 emissions.

2. gain public acceptance of the industry.

3. meet ambient air quality standards.

4. review design flexibility and technical feasibility.

5. review the economics and the total resource budget.

(Editor)

BRIEF OUTLINE OF THE WHITECOURT AREA ENVIRONMENTAL STUDY GROUP

by

E. M. Baraniuk, Amoco Canada Petroleum Company Limited, Calgary

Abstract

The Whitecourt area includes 12 sour gas processing plants,
together emitting 2200 long tons of Sulfur per day, or 1/3 of the total
for Alberta. Increasing concern for environmental impacts led the
plant operators to pool resources in a cooperative study group. Sur-
veillance and research are contracted to a consulting firm with fifty
percent funding from government. The principle questions investigated
are cross-influences among the plants, cumulative effects on the area
as a whole, and possible pre-conditioning to other environmental stresses.

(Editor)

FUTURE FINANCING OF SULFUR GAS RESEARCH

by

S. B. Smith, Research Secretariat,
Alberta Department of Environment,
Edmonton

Abstract

Sulfur gas research in Alberta is heavily funded through direct grants by the Research Secretariat of the Alberta Department of the Environment. Other projects are funded by the Alberta Environmental Research Trust, which is administered partly through the Research Secretariat.

The general purposes of the Research Secretariat are to promote investigations of man-induced change in environmental systems, through funding and coordination. It does no in-house research.

(Editor)

SUMMARY OF CLOSING DISCUSSION

Following some technical discussion among small groups of participants, a general discussion led to consensus on the following points.

1. Useful contacts had been initiated among agencies.

2. Individuals with closely related projects were glad of the opportunity to exchange views and results.

3. Individuals with very different projects, but related to the same problem area, were glad to meet, listen to and discuss with each other.

4. Participants welcomed the offices of the Alberta Department of Environment, Research Secretariat, in funding research and in building towards a clearing house for environmental research projects.

5. The meeting noted the kind offer of Professor Gordon Hodgson to host a further meeting in approximately one year's time, or as required; and requested Dr. Stu Smith to act on it according to his perception of the needs of researchers.

6. Dr. Frank Webb informed participants of a forthcoming National Research Council publication with the following proposed chapter headings.

    1) Total Canadian sulfur balance

    2) Effects of sulfur on plants in Canada

    3) Effects of sulfur on soils in Canada

    4) Sulfur in plants and soils in Alberta

    5) Effects of sulfur on water and fish

    6) Effects of sulfur on human health

    7) Effects of sulfur on animals

    8) Effects of sulfur on building materials

    9) Meteorological considerations

    10) Criteria digest

PARTICIPANTS' NAMES & ADDRESSES

Dr. Kalid Aziz

Faculty of Engineering
Department of Chemical Engineering
University of Calgary
Calgary, Alberta

Dr. J. Baker

Canadian Forestry Service
Northern Forest Research Centre, 5320-122 St.
Edmonton, Alberta T6H 3S5

Mr. E.M. Baraniuk

Chairman, Whitecourt Environmental Study Group
Amoco Canada Petroleum Company Limited
Bentall Building
444 - 7th Avenue, S.W.
Calgary, Alberta

Dr. Charles Bird

Department of Biology
University of Calgary
Calgary, Alberta

Mr. R.A. Blauel

Canadian Forestry Service
Northern Forest Research Centre, 5320-122 St.
Edmonton, Alberta T6H 3S5

Mr. V.E. Bohme

Energy Resources Conservation Board
603 - 6th Avenue, S.W.
Calgary, Alberta

Mr. F.E. Burbidge

Acting Officer-in-Charge
Arctic Weather Central
Canada Atmospheric Environment Service
Box 9860
Edmonton, Alberta

Mr. G.W. Cameron

General Manager
Independent Petroleum Assoc. of Canada
Room 436, 700 - 6th Avenue, S.W.
Calgary, Alberta T2P OT8

Mr. J.W. Case

Department of Biology
University of Calgary
Calgary, Alberta

Mr. Gerry Gainer

c/o Gulf Oil Canada Ltd.
707 - 7th Avenue, S.W.
Calgary, Alberta

Dr. Paul Gorham

Chairman, Department of Botany
University of Alberta
Edmonton, Alberta

Dr. Drake Hocking   Canadian Forestry Service
Northern Forest Research Centre, 5320-122 St.
Edmonton, Alberta   T6H 3S5

Prof. Gordon Hodgson   Director
Environmental Sciences Centre
University of Calgary
Calgary, Alberta

Dr. J.B. Hyne   Dean, Faculty of Arts and Science
Department of Chemistry
University of Calgary
Calgary, Alberta

Mr. Julian Kinisky   Environment Conservation Authority
8th Floor, 9912 - 107 Street
Edmonton, Alberta

Dr. Roger Klemm   Research Council of Alberta
11315 - 87 Avenue
Edmonton, Alberta

Prof. Roy Krouse   Department of Physics
University of Calgary
Calgary, Alberta

Mr. Jerry Lack   Pollution Control Division
Alberta Department of the Environment
10040 - 104 Street
Edmonton, Alberta

Dr. Alan Legge   Environmental Sciences Centre
University of Calgary
Calgary, Alberta

Dr. A.A. Loman   Research Scientist
E.R.A. Sciences Ltd.
P.O. Box 3444, Station B
Calgary, Alberta

Mr. J.A. Love   McKinnon, Allan & Associates
631 - 42nd Ave., S.E.
Calgary, Alberta

Mr. G.H. Maduram   Alberta Forest Service
Land Use Branch
Natural Resources Building
Edmonton, Alberta

Dr. M.F. Mohtadi   Faculty of Engineering
Department of Chemical Engineering
University of Calgary
Calgary, Alberta

Mr. James Nalbach	Chairman, Athabasca Tar Sands Environmental Study Group c/o Syncrude Canada Ltd. 807 Baker Centre Edmonton, Alberta
Dr. M. Nyborg	Department of Soil Science University of Alberta Edmonton, Alberta
Mr. Michael Raymont	Department of Chemistry University of Calgary Calgary, Alberta
Mr. Joe Lukacs, Mr. R.P. Rankine and Dr. Douglas Leahey	Western Research & Development Ltd. 932, 700 - 6th Ave. S.W. Calgary, Alberta T2P OT8
Dr. W.J. Rennie	Department of Chemistry University of Calgary Calgary, Alberta
Dr. Richard Rowe	Department of Chemical Engineering University of Calgary Calgary, Alberta
Dr. H.S. Sandhu	Department of Chemistry University of Alberta Edmonton, Alberta
Dr. S.B. Smith	Research Secretariat Alberta Department of the Environment Edmonton, Alberta
Dr. D.H. Vitt	Department of Botany University of Alberta Edmonton, Alberta

Observers:

Dr. W.G. Bowen	Assistant Deputy Minister Department of Mines, Resources and Environmental Management Government of Manitoba Winnipeg, Manitoba
Dr. D.R. Muir	Sulphur Development Institute, Canada 830 Bow Valley Square, 202 - 6th Ave., S.W. Calgary, Alberta

Mr. R.R. Sentis

Director
Air Pollution Control Branch
Department of Environment
Government of Saskatchewan
Regina, Saskatchewan

Mr. D.R. Shaw

Chief Chemist
Energy Resources Conservation Board
Department of Mines and Minerals
University of Alberta
Edmonton, Alberta

Mr. Hennie Veldhuizen
        and
Mr. Asit Hazra

Environmental Protection Service
Environment Canada
10025 - Jasper Avenue
Edmonton, Alberta

Dr. F.E. Webb

Senior Staff Officer
Canadian Forestry Service
Ottawa, Ontario