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**ATMOSPHERIC EMISSIONS MONITORING AND  
VEGETATION EFFECTS IN THE ATHABASCA  
OIL SANDS REGION**

Edited by

**Don L. Dabbs**

**DABBS ENVIRONMENTAL SERVICES**

With Contributions From  
Western Research  
Concord Scientific Corporation  
Hardy Associates (1978) Ltd.  
CASE Biomanagement

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**Synchrude Canada Ltd.**

November 1985

## FOREWORD

The following report is a consolidation of the findings of four separate monitoring research projects. The purpose of this report is to present our current understanding of atmospheric emissions in the Athabasca oil sands region and their effects on vegetation.

Syncrude's Environmental Research Monographs are published verbatim from final reports of professional environmental consultants. Only proprietary technical or budget-related information is withheld. Because Syncrude does not necessarily base decisions on just one consultant's opinion, recommendations found in the text should not be construed as commitments to action by Syncrude.

Syncrude Canada Ltd. welcomes public and scientific interest in its environmental activities. Please address any questions or comments to Environmental Affairs, Syncrude Canada Ltd., 10030 - 107 Street, EDMONTON, Alberta, T5J 3E5.

## ACKNOWLEDGEMENTS

This report is a consolidation of findings from four separate monitoring research projects. The projects were set-up at different times, had differing objectives, and the work was carried out by different consulting firms.

The research results have been summarized by the consulting firms responsible for the various components of the total monitoring program.

Chapters 1 and 4 were prepared from the work of the other consultants by the report editor, Mr. Don L. Dabbs of DABBS ENVIRONMENTAL SERVICES,

Chapter 2, section 2.1.1 **Sulphur** was prepared by Dr. Douglas Leahey and Mr. Mike Schroeder of Western Research,

Chapter 2, section 2.1.2 **Metallic Elements** was written by Mr. Philip Fellin, Dr. Claude Davis, Mr. Ron Portelli and Dr. Robert Caton of Concord Scientific Corporation,

Chapter 2, section 2.2 **Vegetation Stress Studies** plus a contribution to Chapter 3 were written by Mr. David Reid of Hardy Associates (1978) Ltd.,

Chapter 2, sections 2.3 and 2.4 on **Biomonitoring and Bioaccumulation** plus Chapter 3 were prepared by Dr. James W. Case of CASE Biomanagement.

The study was initiated by Syncrude Canada Ltd. Critical review and comments were provided by Dr. George Lesko, Mr. Al Hyndman, Mr. Sven Djurfors, Mr. Don Thompson and Mr. John Clark of the Research and Development Department of Syncrude.

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## CHAPTER 1: EXECUTIVE SUMMARY

Atmospheric emissions from oil sands plants are regulated by government. Both Syncrude Canada Ltd. and Suncor Inc. independently operate emission and air quality monitoring and reporting systems. The systems include air quality monitoring trailers and sulphation cylinder stations. In addition to the required monitoring, both Syncrude and Suncor conduct a number of voluntary monitoring research projects to enhance the understanding of regional atmospheric conditions, and the cumulative ecological effects of emissions from oil sands plants in the area. This report presents a consolidation of the findings of four individual projects sponsored by Syncrude. The study area for this report was centred over the emission sources, and extended approximately 50 km around the plants.

The additional monitoring projects included stack gas sampling, elemental analysis, and dispersion modelling. Two biological monitoring programs have also been conducted to measure vegetation stress and bioaccumulation of elements in lichens and mosses. The biological monitoring studies were initiated prior to the start-up of the Syncrude plant, and continued with repeat sampling in 1983 and 1984.

The environmental effects of oil sands development have been studied by both government and industry. The significance of these impacts and predictions of long-term changes in ecosystems, however, have been assessed based on studies of relatively short duration. This report contains some of the first results of monitoring studies that have been designed to measure subtle changes in the longer term.

Primary producers (lichens, mosses, and trees) are sensitive indicators used in this study to provide an early indication of future potential ecological effects. Physical and chemical monitoring results and dispersion modelling were used to explain some of the observed stress and bioaccumulation of elements in the vegetation. The report addresses sulphate deposition data in relation to stress symptoms in the forest canopy and metallic element deposition modelling is discussed in relation to measured element accumulation in lichens and mosses.

Sulphur deposition is monitored using sulphation cylinders. A total of eighty stations are located in the study area, and data from these stations were used to estimate annual dry sulphate deposition over the five years from 1979 to 1983. These data are representative of a period during which both Syncrude and Suncor were in operation. Sulphate deposition data collected during the growing season (June, July, and August) were analyzed to help understand stress patterns observed in forest communities. The largest estimated sulphate depositions for the summers of 1978 (pre-Syncrude), 1980, and 1983 were in areas along the Athabasca River valley, both north and south of the Suncor plant.

Dispersion modelling was conducted for both the combined sulphur emissions from the Syncrude and the Suncor plants, and for each plant separately. Maximum values of annual sulphur deposition rates for Suncor were predicted to be 2 to 3 times higher than those for Syncrude. This is primarily the result of Suncor's emission reaching a smaller effective plume height. Model estimates of the combined emissions show similarities in their deposition pattern with data derived from sulphation cylinders.

The results of both the sulphation cylinder analysis and the dispersion modelling indicate that the total annual sulphate deposition in the region should not exceed 25 kg ha<sup>-1</sup>y<sup>-1</sup>. This compares favourably with the maximum desirable objective of 40 kg

ha<sup>-1</sup>y<sup>-1</sup> of total sulphate deposition which has implied accepted by Federal and Provincial Environment Ministers. Based on this analysis, the current sulphate deposition levels should not be harmful to this region.

False Colour Infrared (FCIR) aerial photography has been used to monitor natural and man-induced stress in forest communities. Air photo coverage of a portion of the study area centred over the two oil sands plants has been ongoing, at intervals, since 1972. FCIR aerial photos taken in 1984 were compared, in detail, with photos taken in 1978, prior to the start-up of the Syncrude plant.

Within the photographed study area, the total area of stressed vegetation in 1978 was approximately 5500 ha, of which about 4020 ha, or 73%, was due to a combination of tent caterpillar, dwarf mistletoe and low degree air pollution. The total area of stressed vegetation in 1984 was approximately 10 300 ha, of which about 8390 ha, or 81%, was caused by insect, disease and low and medium degree air pollution. Large areas of stressed vegetation were located in the valleys centred near the confluence of the Athabasca and Steepbank rivers, corresponding to an area which the computer model predicted to have a high sulphate deposition.

A series of samples from Syncrude's main stack were analysed to determine the concentrations and emission rates of selected elements emitted in particulate and vapour forms. These data, along with meteorological data and other stack parameters, were used in a computer model to predict atmospheric concentrations and deposition patterns of metallic elements in the study area. These predicted deposition patterns were then compared to the measured accumulation of these elements in mosses and lichens.

The measured emission rate of total particulate matter from Syncrude's main stack was about  $35 \pm 26 \text{ g s}^{-1}$  ( $3020 \pm 2250 \text{ kg day}^{-1}$ ) at the 90% confidence level. The equivalent emission quantity varied between 0.014 and 0.092 g kg<sup>-1</sup> of stack gas. This is well below the Alberta standard of 0.2 g kg<sup>-1</sup> of stack gas.

The estimated ambient atmospheric concentrations of particulate matter and metals were, in all cases, more than 100 times lower than any Alberta or North American air quality regulatory standard or guideline. The estimated contribution of the Syncrude emissions to downwind ambient concentrations of both particulate matter and individual metals, was about 1000 times lower than corresponding concentrations in typical populated areas of Canada and the U.S.A.

The model estimated maximum concentrations and deposition rates for metallic elements from Syncrude's main stack would occur at 3 to 5 km southeast of the plant. The next greatest concentration and deposition rate would be 3 to 5 km northwest of the stack.

The sensitivity of lichens to the oxides of sulphur has been well documented in the scientific literature. Therefore, in 1976, prior to commissioning the upgrading facility, Syncrude established a lichen monitoring network of 56 permanent stations to be used as an "early warning" monitoring system.

The sites were resampled in 1983 by rephotographing the permanent quadrats and both the 1976 and 1983 photographs were analysed simultaneously. Lichen growth and vitality were found to have been depressed within a 15 km radius of the oil sands plants between 1976 and 1983. Re-examination of the 1976 baseline photos revealed that lichens in the study area were damaged prior to the start-up of the Syncrude plant.

A second aspect of the lichen and moss biomonitoring study entailed the elemental analysis of lichen and moss samples collected in 1976 and 1983/84. Tissue samples were analysed for 48 elements. Elemental accumulation (above background levels) were found to have taken place by 1976, and continued to increase in the succeeding 7 years. The rate of accumulation, however, remained nearly constant even after the second oil sands plant came on-stream.

General agreement was found between the predicted deposition rates as computed by the model, and the measured bioaccumulation of elements in lichens and mosses both close to, and at considerable distance from, the oil sands plants. There was very little agreement, however, in the Athabasca River valley and along its tributaries. This discrepancy was attributed to the fact that elemental emission rates from Suncor were not available for inclusion in the model, so predicted depositions were underestimated in these areas. It should be noted that the Suncor facility was originally approved as a coke burning plant with less particulate emission control than is required for newer plants. Recent information from Suncor indicates that retrofitted electrostatic precipitators are successfully controlling their particulate emissions.

To develop a perspective on the observed elemental bioaccumulation in the oil sands region, lichen and moss samples were collected at sites in and around the cities of Fort McMurray, Edmonton, and Calgary. While sulphur and nickel content in mosses was higher in the vicinity of the oil sands plants, lead was much higher in the urban areas.

The vascular plant study revealed the presence of stress symptoms and elemental accumulations consistent with air pollution exposure in an area within 15 km of the oil sands plants and in association with the Athabasca River valley and its tributaries. This region coincides with the zone of lichen and moss population decline.

The results presented in this report show that the predicted pattern of deposition of sulphur and metallic elements, based on modelling, generally agreed with the bioaccumulation values measured in the vegetation studies. However, incomplete emission data have limited the degree of correlation between the predicted and measured values. Measurable stress in lichen and tree species, plus the bioaccumulation of elements in sensitive species were expected in the vicinity of these complex industrial facilities.

The monitoring studies were initiated to act as an "early warning" detection system. The objective was to be able to detect changes which might lead to deterioration before any serious damage took place. The results of these research programs indicate that the early warning system is working. Sulphur and elemental accumulation is taking place with stress symptoms observed in mosses, lichens and tree species in the vicinity of the two oil sands plants. However, there is no evidence that serious deterioration of the ecosystem has taken place.

The samples from the urban areas demonstrate that similar accumulations are taking place in other regions of the province. This perspective is useful as it indicates that the oil sands region is not unique. It is essential that additional research be undertaken to address the question of ecological significance of these monitoring results.

## CHAPTER 2: MODELLING AND MONITORING RESEARCH

### 2.1 EMISSIONS

#### 2.1.1 Sulphur

##### 2.1.1.1 Introduction

Environment Canada has established maximum desirable and maximum acceptable objectives for ground-level sulphur dioxide concentrations. Desirable ground-level average hourly, daily and annual concentrations for  $\text{SO}_2$  are 0.17, 0.06 and 0.01 ppm,\* respectively. Comparable acceptable concentrations are 0.34, 0.11 and 0.02 ppm, respectively. The maximum desirable level defines the ultimate goal for air quality and provides a basis for an anti-degradation policy for the unpolluted parts of the country and for the continuing development of control technology. The maximum acceptable level is intended to provide adequate protection against adverse effects on soil, water, vegetation, materials, animals, visibility, personal comfort and well being. When this level is exceeded, control action by a regulatory agency is indicated.

Alberta Environment's air quality standards for  $\text{SO}_2$  are the same as Environment Canada's desirable objectives.

Sulphur dioxide emissions result in the deposition of sulphate. This substance may be deposited through the scavenging effects of rain (wet deposition) or through the direct uptake of materials by soils and water as a result of chemical and physical interactions (dry deposition). Wet and dry depositions are collectively known to the public as "acid rain". The acidification potential of pollution is usually defined in terms of sulphate ( $\text{SO}_4^{2-}$ ) deposition. The maximum desirable guideline for wet sulphate deposition accepted by Federal and Provincial Environment Ministers is presently  $20 \text{ kg ha}^{-1}\text{yr}^{-1}$  (Alberta Environment 1984a). This level has been suggested as being protective of all, but the most sensitive aquatic environments. As wet and dry depositions are usually considered to be of equal magnitude (Alberta Environment 1984b; Shaw 1985) this guideline appears to be equivalent to a total sulphate deposition (wet and dry) of about  $40 \text{ kg ha}^{-1}\text{yr}^{-1}$ .

Environment Canada has proposed desirable and acceptable maximum hourly average concentrations for hydrogen sulphide of 0.7 and 10.8 ppb, respectively. The proposed maximum daily average level for  $\text{H}_2\text{S}$  is 3.6 ppb. There is neither a proposed maximum desirable level for daily average concentrations nor any proposed levels for the annual average. Alberta Environment's air quality standard for hourly and daily averages for  $\text{H}_2\text{S}$  are 10 and 3 ppb, respectively.

The location of the two large extraction and upgrading plants in the Athabasca Oil Sands area operated by Suncor and Syncrude are shown in Figure 1. The Suncor plant, which currently emits, on the average, about  $220 \text{ t d}^{-1}$  of sulphur dioxide, is located in the Athabasca River valley. This valley, about 2 km wide at the plant site, has steep 40 m high banks. The Syncrude plant, which currently emits on the average about  $265 \text{ t d}^{-1}$  of sulphur dioxide, is located on the plateau about 4 km west of the valley edge.

\* It was necessary to use the units ppm,  $\text{mg m}^{-3}$ , and  $\mu\text{g m}^{-3}$  in this report as they are used throughout the scientific and regulatory literature. To aid the reader, the relationships are:  $\text{ppm SO}_2 (\text{v/v in air}) = 2.62 \text{ mg m}^{-3} = 2620 \mu\text{g m}^{-3}$  (Richardson and Nieboer 1983).

Syncrude and Suncor each maintain five air quality monitoring trailers for purposes of continuously measuring ambient ground-level concentrations of sulphur dioxide and hydrogen sulphide (H<sub>2</sub>S). Locations of Suncor (A-E) and Syncrude (1-5) are shown in Figure 1. Each company also maintains its own network of 40 sulphation cylinders which can be used for the assessment of sulphate deposition.

Information on exceedances of Alberta's SO<sub>2</sub> 1 hour ground-level air quality standard of 0.17 ppm was available from monitoring sites operated by both Syncrude and Suncor for the years 1982 and 1983. The number of exceedances is shown in Table 1. Most of the exceedances tended to occur near the Athabasca River valley at sites 5, E, B and 3.

Table 1 Number of hourly average SO<sub>2</sub> readings in excess of 0.17 ppm for the indicated year and monitoring site.

Monitoring Site*	1982	1983
1	6	4
2	5	3
3	6	19
4	11	4
5	1	49
A	4	9
B	14	22
C	2	4
D	6	3
E	16	26

\* Monitoring equipment at sites 1 to 5 is operated by Syncrude and equipment at sites A to E is operated by Suncor

Information for the monitoring sites operated by Syncrude indicated that there were only five occasions when observed ground-level SO<sub>2</sub> concentrations exceeded 0.34 ppm. These occurred at monitoring site 5 in 1983. Comparable information relating to exceedances of 0.34 ppm was not available for the Suncor sites.

There were many observed exceedances at all trailer sites of Alberta Environment's hourly average standard for H<sub>2</sub>S of 10 ppb. Maximum observed H<sub>2</sub>S concentrations, however, tended to be much less than those for SO<sub>2</sub>. This is significant because the concentrations of H<sub>2</sub>S that vegetation can tolerate are much higher than phytotoxic concentrations of SO<sub>2</sub> (Linzon 1978). Hydrogen sulphide at this very low concentration is of concern chiefly because of the nuisance associated with its odour.

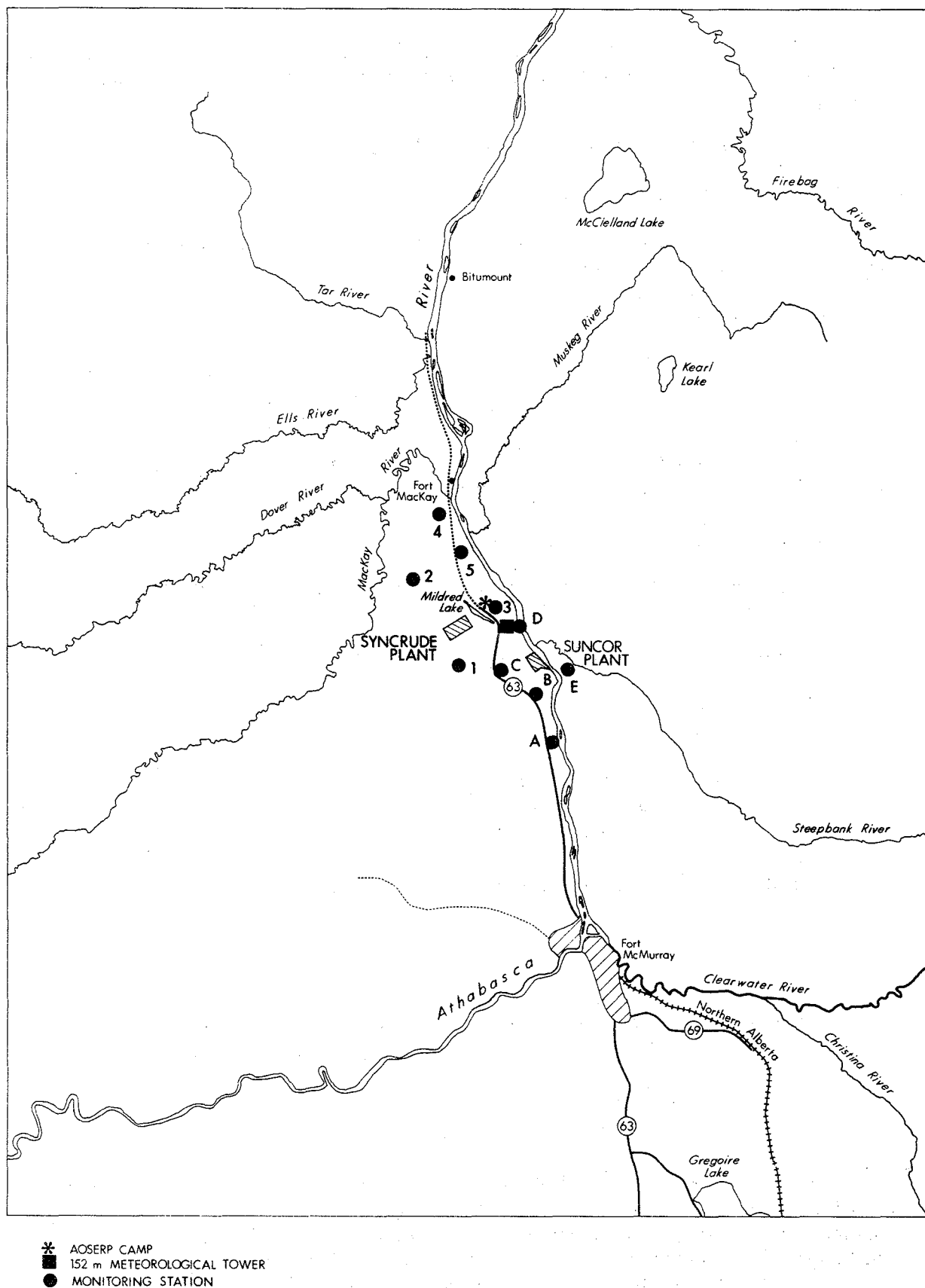


Figure 1

Map of the Athabasca Oil Sands region showing locations of oil sands plants and air quality monitoring stations.

There were no direct observations of sulphate deposition. Estimates were made both through the use of sulphation station information and through predictions using plume diffusion models.

#### 2.1.1.2 Monitoring Program for Sulphate Deposition

##### Description of Sulphation Stations

Dry sulphate deposition is measured by both companies using a network of exposure cylinders. These cylinders consist of 8 ounce glass jars having a circumference of 10 cm. Around each jar is wrapped a surgical gauze 5 cm in width to which a lead dioxide paste has been applied.

Lead dioxide reacts with  $\text{SO}_2$  and other gaseous sulphur compounds such as  $\text{H}_2\text{S}$  and mercaptans to form lead sulphate (Alberta Environment 1982). The sulphation rate depends on the lead dioxide reagent used to prepare the exposure devices. In general, the rate can be expected to increase as the specific surface area of the lead dioxide increases. Results of total sulphation obtained from chemical analyses of exposed lead dioxide cylinders may be expressed on a unit time basis in terms of  $\text{kg ha}^{-1}$  of sulphate deposition.

##### Derivation of Sulphate Deposition Estimates

Sulphation cylinder information can be used to estimate environmental sulphate deposition from a knowledge of deposition velocities (Leahey and Schroeder 1985).

Deposition velocities are defined by the equation:

$$V = \frac{D}{x} \quad (1)$$

where  $V$  = deposition velocity of gas  
 $D$  = dry deposition rate  
 $x$  = ground-level concentration of the gas

Equation (1) can be manipulated to show:

$$D_e = \frac{V_e D_c}{V_c} \quad (2)$$

where  $D_e$ ,  $D_c$  = sulphate deposition on the environmental receptor (soils, lakes, vegetation, etc.) and of sulphation cylinder, respectively

$V_e$ ,  $V_c$  = deposition velocity of the environmental receptor and sulphation cylinder, respectively.

Deposition velocities of  $\text{SO}_2$  for environmental receptors range between 0.1 and 2.5  $\text{cm s}^{-1}$  depending on the exact nature of the receptor and atmospheric turbulence levels (Sehmel 1980). Deposition velocities for sulphation cylinders, as determined by wind tunnel tests (Singh and Otto 1979), are proportional to the 0.4 power of wind speed. For a wind speed of 0.18  $\text{m s}^{-1}$ , the deposition velocity was found to be 0.72  $\text{cm s}^{-1}$ .

For this report,  $V_e$  was assumed to have a value of  $0.5 \text{ cm s}^{-1}$  which should be typical for soils and vegetation in the Athabasca Oil Sands region (Davison *et al.* 1981a, 1981b). A value for  $V_c$  was estimated by taking into account the median annual 10 m-level wind speed of about  $2 \text{ m s}^{-1}$  as observed at the Fort McMurray airport. This wind speed is  $1.7 \text{ m s}^{-1}$ , as scaled to the exposure cylinder height of 1.5 m using the wind power law of Touma (1977) for neutral atmospheric conditions. The deposition velocity for sulphation cylinders corresponding to this wind speed is  $1.8 \text{ cm s}^{-1}$ . Estimates of sulphate deposition in the environment were therefore obtained from equation (2) as:

$$\begin{aligned} D_e &= \frac{0.5 D_c}{1.8} \\ &= 0.28 D_c \end{aligned} \quad (3)$$

Equation (3) applies to sulphate deposition from sulphation cylinders which employ the Matheson type lead dioxide as recommended by Alberta Environment and used by Syncrude. Suncor uses a type of lead dioxide prepared by Fisher Scientific Limited whose properties have not been documented. Comparisons between data from Suncor and Syncrude sulphation stations in proximity to each other indicated that the Fisher type lead dioxide was less efficient than the Matheson type. On average, sulphation rates measured by Suncor were about half the value of those measured by Syncrude. For this reason, Suncor sulphation data were increased by a factor of two prior to their use in calculation of annual sulphate deposition.

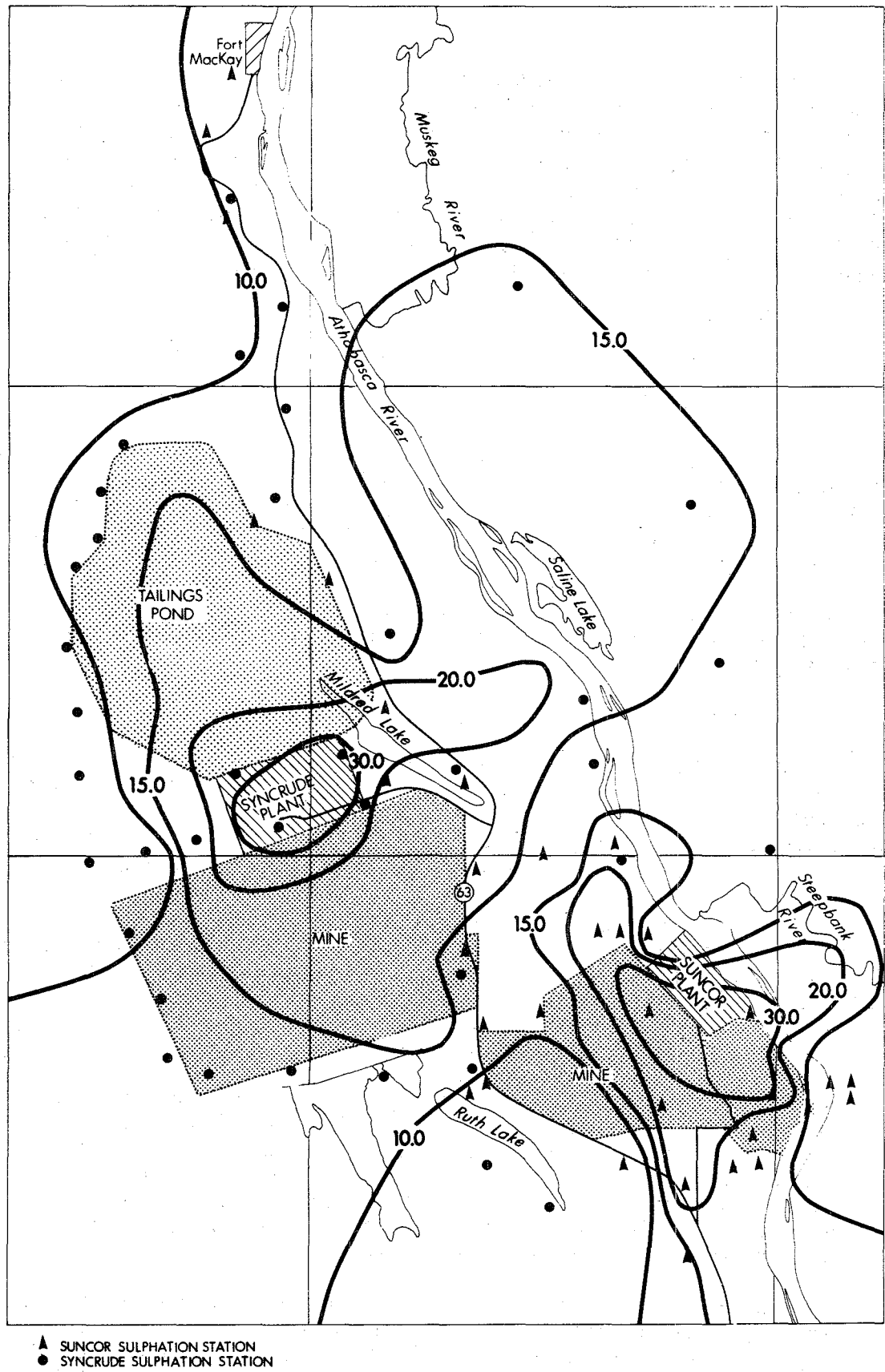
### Summary of Results

Figure 2 shows estimates of annual dry sulphate deposition on soils as derived from sulphation cylinder information collected by both Syncrude and Suncor, over the 5 year period from 1979 to 1983. The large maxima observed in the vicinity of the plants likely reflects the effects of fugitive  $\text{H}_2\text{S}$  emissions. Maxima of annual sulphate deposition at distances removed from the immediate vicinity of the plants are about  $15 \text{ kg ha}^{-1}$ .

There are seven sulphation stations located south of Suncor which are not shown on the map. They are spread along the 30 km distance between Suncor and Fort McMurray. Values of annual sulphate deposition from these stations range from  $15 \text{ kg ha}^{-1}$  in the north to about  $10 \text{ kg ha}^{-1}$  around Fort McMurray.

The sulphation cylinder information does not include wet deposition. According to Shewchuk (1985a), combined wet and dry background annual sulphate deposition for remote northern areas should not exceed  $5 \text{ kg ha}^{-1}$ . About 50 percent of this amount should be due to wet deposition (Garland 1978; Hales 1978). Annual maximum wet sulphate deposition due to stack emissions in the region is estimated to be about  $7 \text{ kg ha}^{-1}$  (see Section 2.1.1.3). It follows that maximum annual sulphate deposition values given in Figure 2 should be increased by about  $10 \text{ kg ha}^{-1}$  in order to reflect estimates of total sulphate deposition. It should be noted that, at distances removed from the plants, maximum annual sulphate deposition values do not exceed about  $25 \text{ kg ha}^{-1}$ .

Estimates of sulphate deposition were obtained for the months of June, July and August when ground-level sulphur dioxide concentrations are most likely to be harmful to actively growing vegetation. Figures 3, 4 and 5 show estimates for the summers of 1978, 1980 and 1983 when vegetation stress data were collected. The largest estimated sulphate depositions for each of the summers in areas along the Athabasca River valley, both north and south of the Suncor plant, are similar. The relatively low values recorded in 1978, in



▲ SUNCOR SULPHATION STATION  
● SYNCRUDE SULPHATION STATION

Figure 2

Estimates of average annual dry sulphate deposition (kg ha<sup>-1</sup>) derived from information obtained from Suncor and Syncrude sulphation data collected from 1979 to 1983.



Figure 3

Estimates of average June, July, August (growing season) sulphate deposition ( $\text{kg ha}^{-1}$ ) derived from information obtained from Suncor and Syncrude sulphation data collected during the summer of 1978.

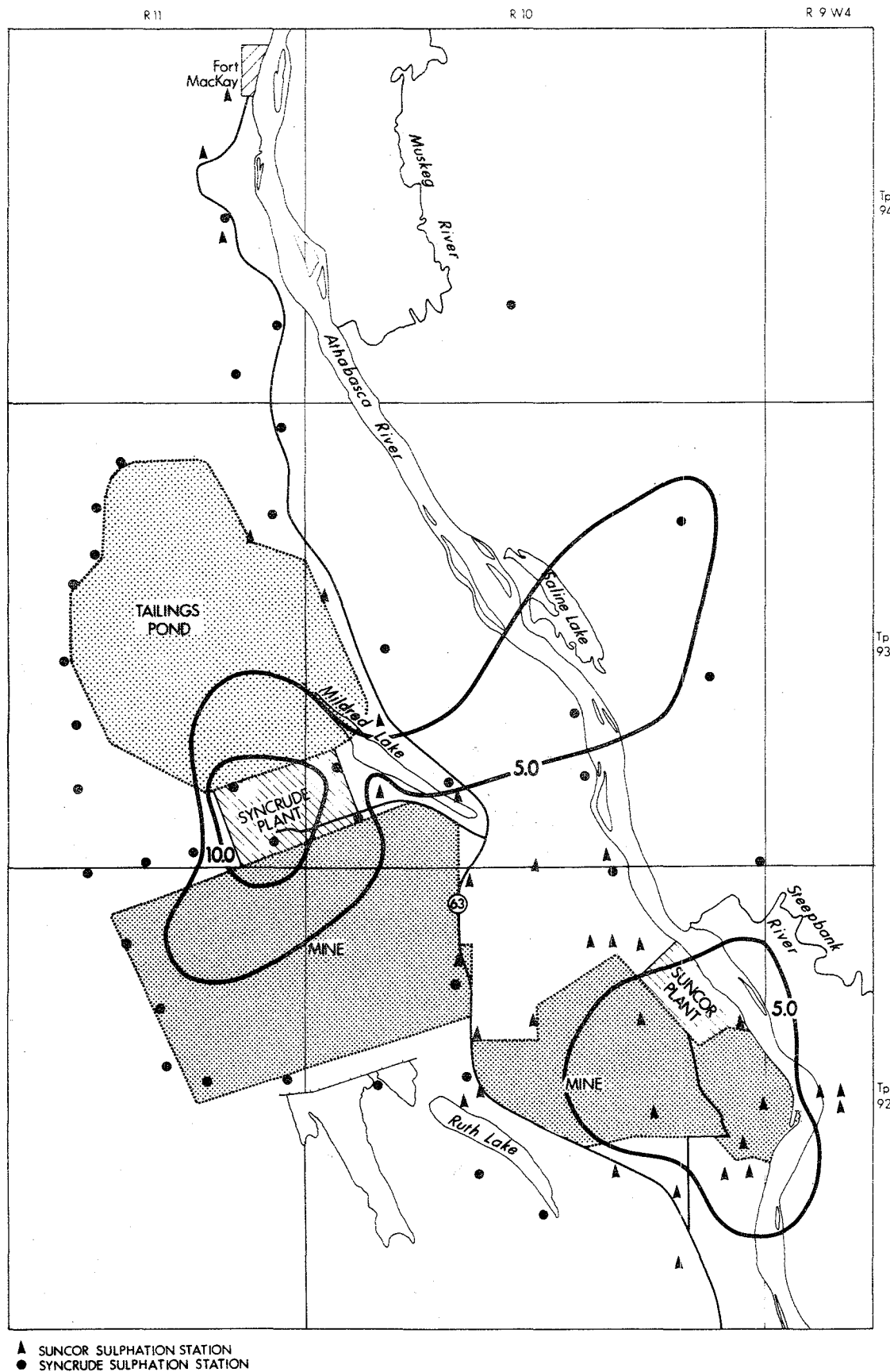


Figure 4

Estimates of average June, July, August (growing season) sulphate deposition ( $\text{kg ha}^{-1}$ ) derived from information obtained from Suncor and Syncrude sulphation data collected during the summer of 1980.

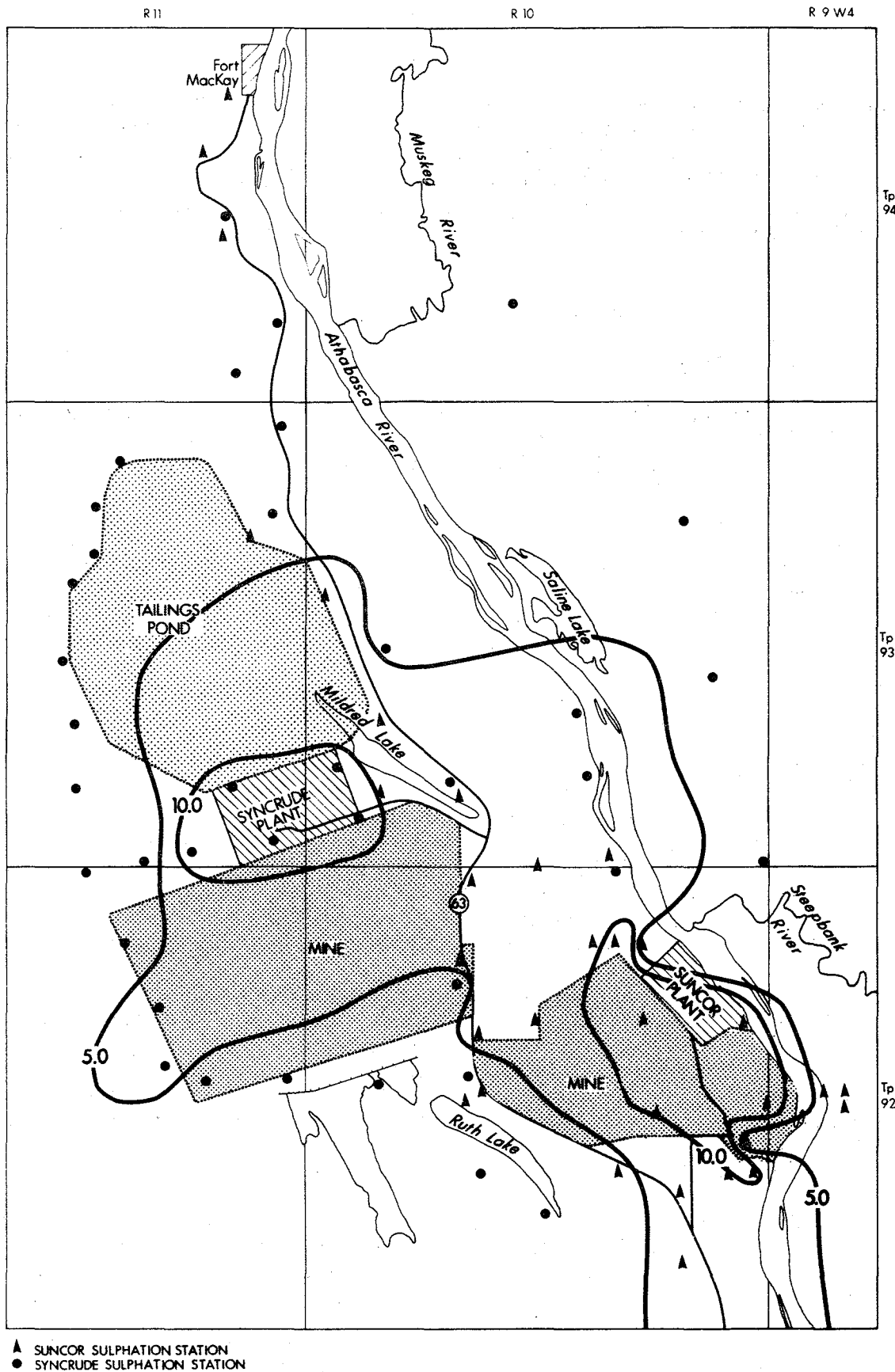


Figure 5

Estimates of average June, July, August (growing season) sulphate deposition ( $\text{kg ha}^{-1}$ ) derived from information obtained from Suncor and Syncrude sulphation data collected during the summer of 1983.

the vicinity of the Syncrude plant, reflect the fact that it did not start operations until August of that year. Estimated sulphate deposition in the vicinity of the Suncor plant was much greater for 1983 than for 1980. The differences could be explained by flared emissions. Suncor flared 1700 tonnes of SO<sub>2</sub> during the summer of 1983, but comparable information is not available for 1980. This is important, because flaring of sour gas usually results in higher ground-level H<sub>2</sub>S and SO<sub>2</sub> concentrations as compared to usual incineration processes.

#### 2.1.1.3 Model Predictions

##### Description of Models

A Gaussian diffusion model was employed for estimating sulphate deposition which might occur as a result of the total emissions from both Suncor and Syncrude. The model was developed for Alberta Environment by Intera Environmental Consultants and Western Research for flat terrain conditions. It uses hourly values of meteorological data to estimate sulphate depositions.

Plume sigmas for use within the Gaussian framework are calculated from statistical theory which uses wind speed, heat flux and boundary layer heights. Plume rise is estimated with the assumption that plume diameters increase linearly with plume rise (Briggs 1975). Model formulations allow for the effects of limiting mixing layers.

Mathematical details of the model and justifications for its assumptions have been presented by Davison *et al.* (1981a).

##### Meteorological Model Inputs

A file of hourly average values of meteorological inputs as used in the model has been prepared for the Athabasca Oil Sands area for January, April, July and October for the years 1976 through 1978 (Davison *et al.* 1981b). These inputs include hourly average values of wind, weather conditions, temperature, relative humidity, cloud cover, net radiation, snow cover and mixing depths. Values of wind for use in the file were obtained at the 400 m level from minisonde flights conducted at the AOSERP camp (Figure 1).

Figure 6 is a wind rose compiled from data obtained at the 400 m level. The total length of the "barbs" show the frequency with which wind from a given direction occurs. Portions of the "barbs" are of different thickness to indicate the frequency of given wind speed classes. For example north winds are shown as having occurred for a total of 13.5 percent of the time. North winds of between 5.1 and 15.0 km h<sup>-1</sup> occurred only about 4 percent of the time. The fact that winds are more often westerly than easterly reflects influences of the earth's rotation. The relative high frequency of north winds is probably due to channeling effects of the Birch and Muskeg Mountains (Leahey and Hansen 1982).

The AOSERP wind data do not show any obvious effects of channeling that could be due to the Athabasca River valley. These effects become more pronounced at lower elevations, at locations closer to the valley axis. Increased valley influences are shown in Figure 7, which presents a wind rose compiled from data collected from October 27, 1976 to April 30, 1979 at the 152 m level of a tall tower located on the valley floor (Figure 1). This wind rose shows the high frequencies of southerly and northerly winds which are attributable to the channeling action of the steep river valley banks.

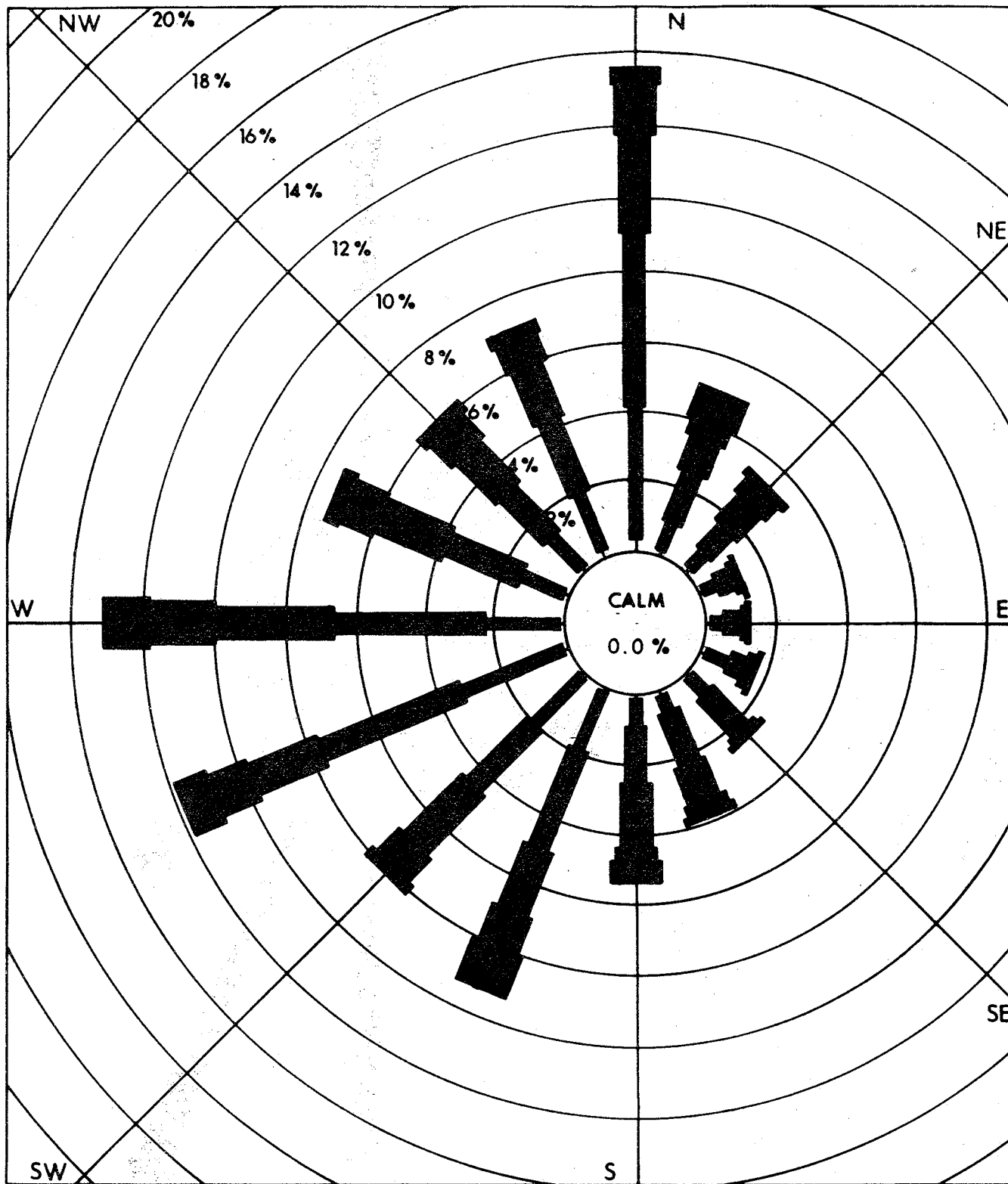
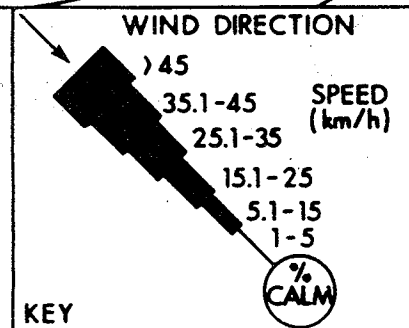


Figure 6 Direction and wind speed frequency distribution for winds observed at a 400 m height from 1976-78.



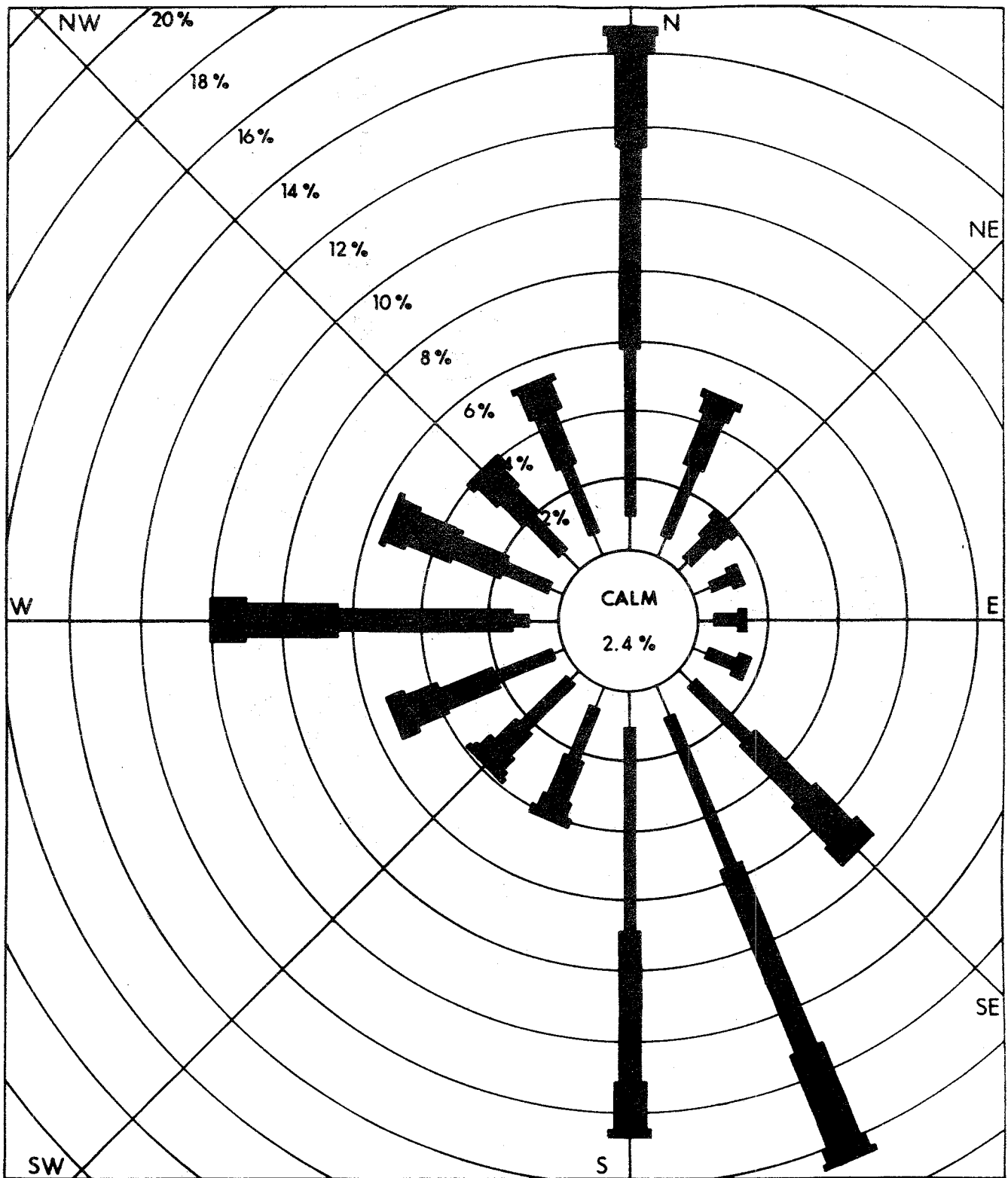
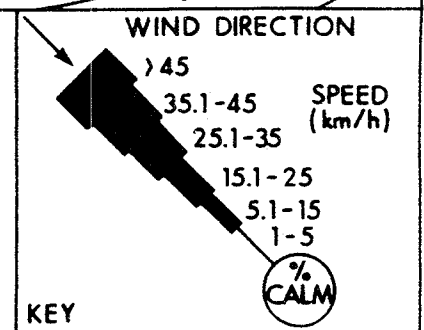


Figure 7

Direction and wind speed frequency distribution for winds observed at the 152 m tall tower from 1976-78.



Winds observed at the AOSERP camp were used to analyze the behaviour of the Syncrude plume. However, they were not considered appropriate for evaluating the behaviour of the Suncor plume which originates essentially from within the river valley. Influences of this valley on the dispersion of the Suncor plume were incorporated into the model calculations. In this case, values of wind were taken from the 152 m tall tower. Because data from this tower were available for only 2 full years (1977, 1978), model calculations for the Suncor plume did not include as large a meteorological data base as those used to evaluate the Syncrude plume. Two years of climate information was considered adequate, however, to delineate the main features of sulphate deposition patterns.

### Stack Emission Model Inputs

Table 2 presents the expected stack and emission parameters for the Syncrude and Suncor sources as used in the plume diffusion model (Syncrude 1984; Davison *et al.* 1981c). The Syncrude stack is higher with a larger exit velocity. The Suncor stack is situated near the river, and is only about 70 m higher than the nearby steep river banks.

Table 2      Stack and emission parameters.

	Syncrude Main Stack	Power Plant	Suncor Incinerator
Stack Height (m)	183	107	107
Stack Diameter (m)	7.9	5.8	1.8
Gas Exit Temperature (°C)	177	272	538
Gas Exit Speed (m/s)	28.7	17.5	17.0
Average annual SO <sub>2</sub> emission rate (t/d)*	265	190	30
Height above river (m)	70	20	20

\* Average quarterly emission rate

### Summary of Results

Figures 8 and 9 show model estimates of annual sulphate depositions due to Syncrude and Suncor. Maximum sulphate depositions attributable to Syncrude and Suncor are about 5 and 15 kg ha<sup>-1</sup>, respectively. As expected on the basis of wind rose information, maximum sulphate depositions caused by Suncor are predicted to occur along the river valley.

It is important to remember that the model predicts depositions for flat terrain conditions. Air flows over the river banks will cause higher turbulence than over flat terrain (Leahey 1974). Effects of this turbulence will appreciably increase SO<sub>2</sub> concentrations closer to the Suncor plant, especially along the valley sides. For this reason, model results will tend to underestimate deposition in the vicinity of the Suncor plant.

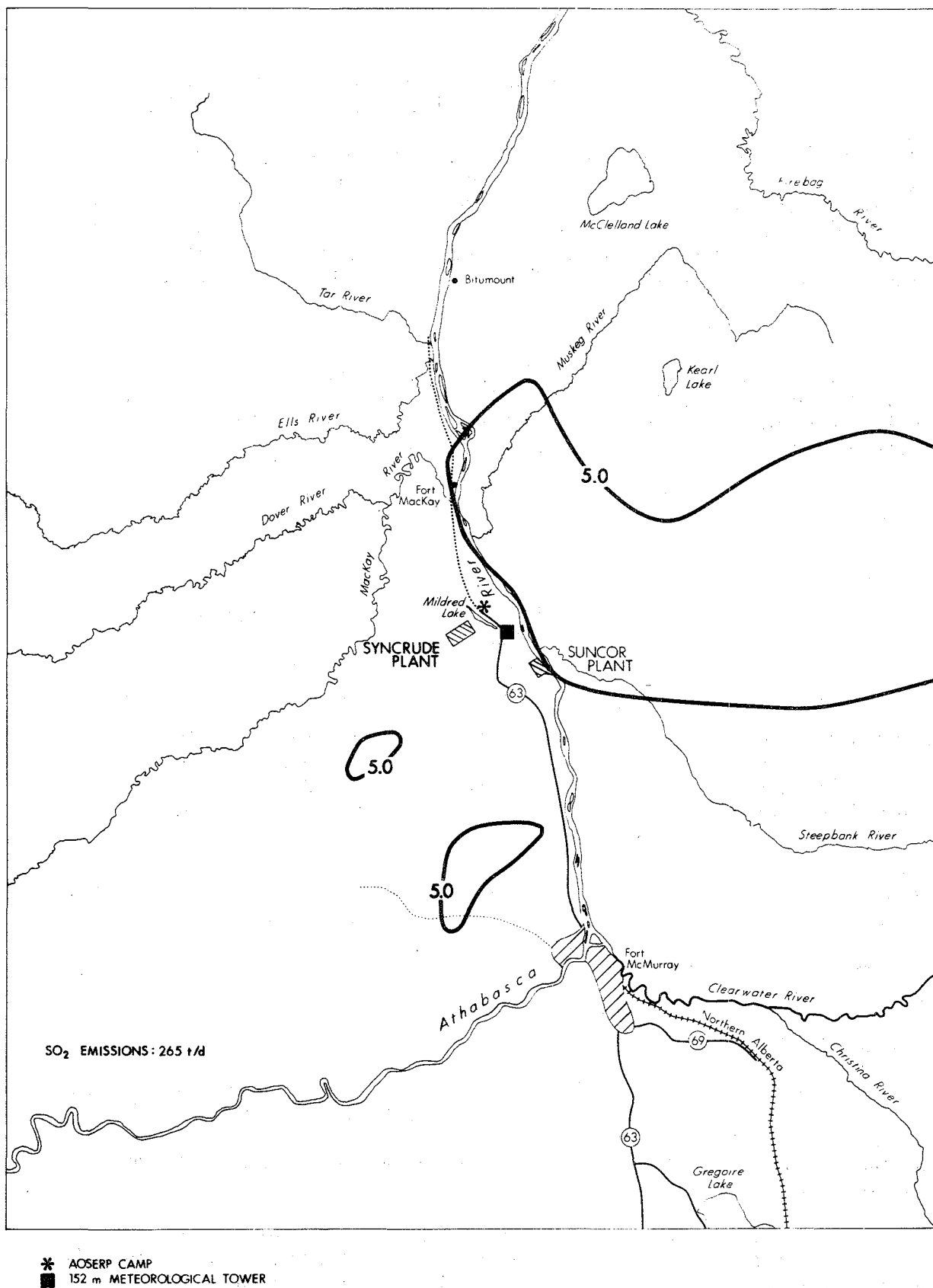


Figure 8 Model estimates of annual sulphate deposition (kg ha<sup>-1</sup>) originating from Syncrude emissions.

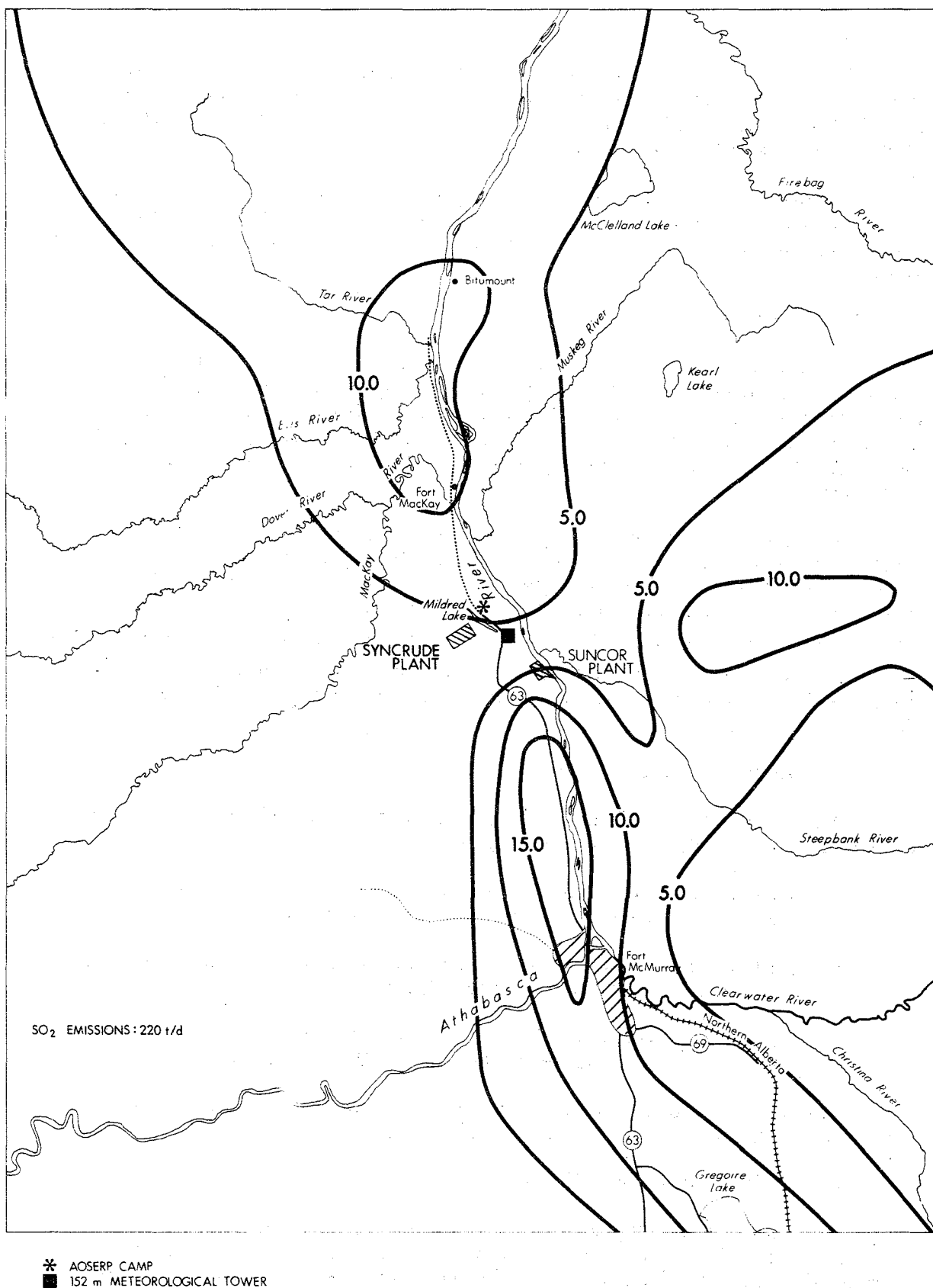


Figure 9

Model estimates of annual sulphate deposition (kg ha<sup>-1</sup>) originating from Suncor emissions.

Figure 10 shows the calculated combined effects of Suncor and Syncrude emissions. The maximum predicted deposition (wet plus dry) of about  $20 \text{ kg ha}^{-1}$  occurs in areas east of the Suncor plant and near Fort McMurray. Maximum annual wet sulphate deposition in these areas is about  $7 \text{ kg ha}^{-1}$ .

Values of sulphate deposition estimated from plume model calculations should be increased by the background value of about  $5 \text{ kg ha}^{-1}$  to reflect total deposition. Total annual sulphate deposition in the region should, therefore, not exceed values of about  $25 \text{ kg ha}^{-1}$ .

#### 2.1.1.4 Discussion

The Suncor plant is located on the floor of the Athabasca River valley, where the emissions tend to be transported along the valley by wind channeling effects. The Syncrude plant is situated about 70 m above the valley floor. Its' emissions tend to be transported cross valley by prevailing westerlies. For these reasons, sulphate deposition and air quality within the river valley are much more influenced by Suncor operations than by Syncrude's.

Sulphate deposition has been obtained by two independent methods. The first method involved the interpretation of sulphation cylinder information while the second method relied on plume diffusion modelling techniques. Results of both methods indicated that the total annual sulphate deposition in the region should not exceed values of about  $25 \text{ kg ha}^{-1}$ . This is well within the Alberta Environment implied annual guidelines of  $40 \text{ kg ha}^{-1}$ . Based on this deposition rate, there should not be any harmful soil acidification effects within the region as a result of sulphur dioxide emissions from Syncrude and Suncor.

#### 2.1.2 Metallic Elements

A study of emissions from the main stack at Syncrude's Mildred Lake plant was conducted in June of 1984 with the following goals:

- to determine the composition of stack emissions with respect to selected metallic elements and related compounds in particulate and vapour form,
- to determine the emission rates of selected metallic elements and the relationship to the size distribution of emitted particles, and
- to model the dispersion of these emissions to estimate the average annual concentrations and annual deposition within 100 km from the stack.

This study has been separately published (Concord Scientific Corporation 1984), and the following represents a summary of that document.

##### 2.1.2.1 Characterization of Emissions

The emissions from the main stack at the Syncrude plant are mainly off gases from the cokers with a limited contribution from the power plant. The particulate matter produced during combustion is mainly removed by four banks of electrostatic precipitators (99% efficiency for particle removal) and particulate levels are maintained below the standard set by Alberta Environment ( $0.2 \text{ g kg}^{-1}$  of flue gas). Prior to this study, little was

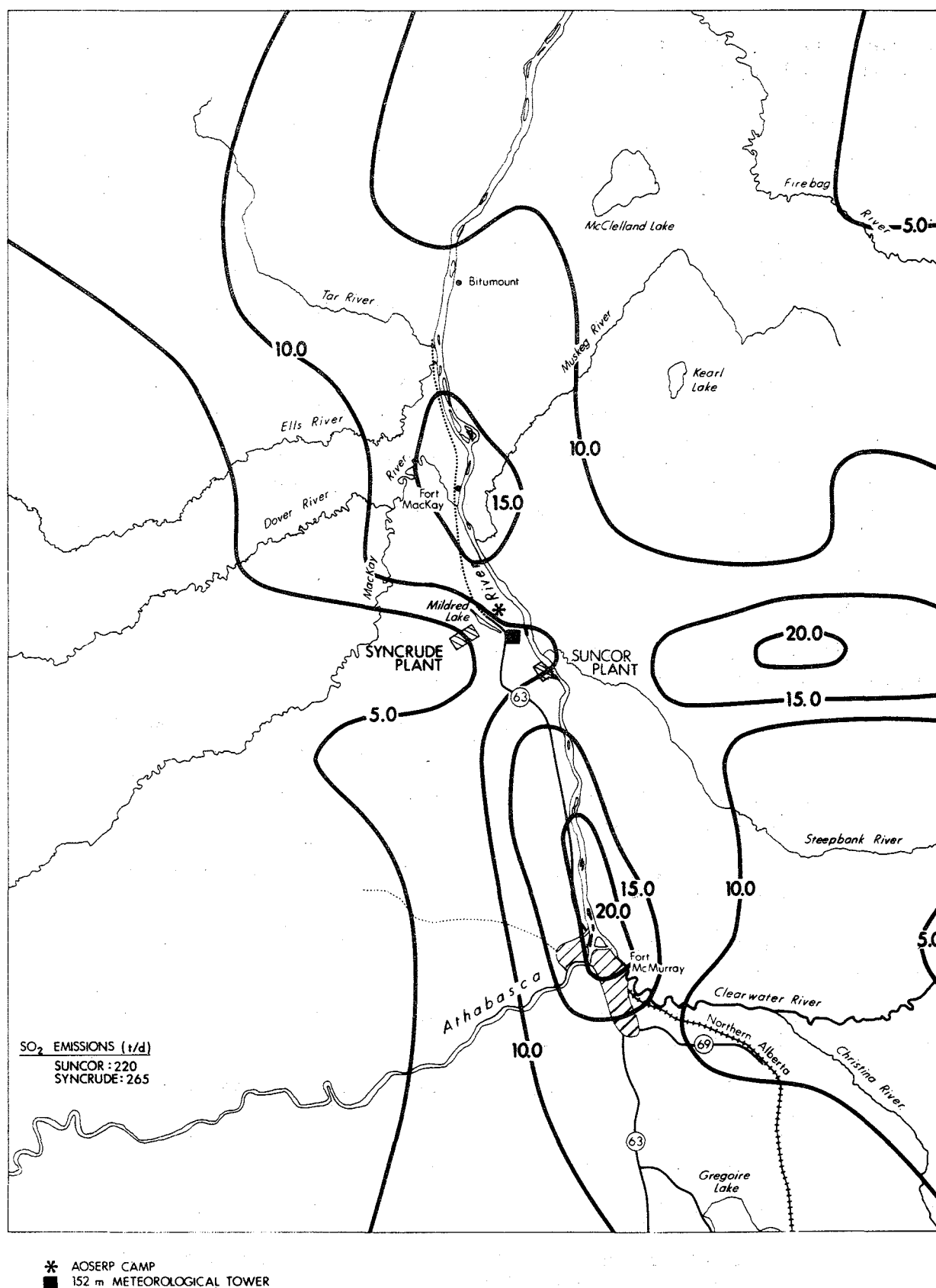


Figure 10

Model estimates of annual (wet plus dry) sulphate deposition (kg ha<sup>-1</sup>) originating from Syncrude and Suncor emissions.

known about the composition and size distribution of the remaining particulate matter released in the flue gases with respect to metallic elements..

### Study Objectives

The technical objectives of the study were to perform a series of rigorous tests on stack emissions to determine:

- the metallic composition and emission rates of particulate matter and 26 specific elements,
- the size distribution of the particulate matter and the relationship between size distribution and composition, and
- the vapour phase composition of the flue gases with respect to selected volatile metals including mercury, arsenic, selenium, cadmium and lead.

These data were then utilized as inputs, along with meteorological data and other stack parameters, to determine the air concentrations and deposition at selected distances used within the study area outlined in Figures 11 and 12.

#### 2.1.2.2 Methods

##### Sampling

The most rigorous sampling methods for determining compliance with emission regulations were used for the study. This required that:

- the sampling must be performed under process conditions representative of normal production rates and processes, excluding process upsets,
- the equipment and methods for sampling meet the specifications of the applicable source test code (see below), and
- a minimum of three valid tests must be completed after satisfactory completion of a preliminary test.

To assure that the first two criteria were met, the following process trends were monitored:

- assignable trends in a number of key process and emission parameters produced by 10-minute slices of data points,
- assignable trends in the process and emissions parameters produced by hourly average data points,
- operator's process logs, and
- manually logged electrostatic precipitator rectifier panel readings.

To satisfy the requirement for collection of particulate and vapour phase metals and to obtain size distribution information, the use of three separate sampling trains was necessary: (i) an isokinetic sampling train for sampling total particulate matter, vapour-phase Pb and Cd, (ii) an isokinetic sampling train for sampling total particulate matter,

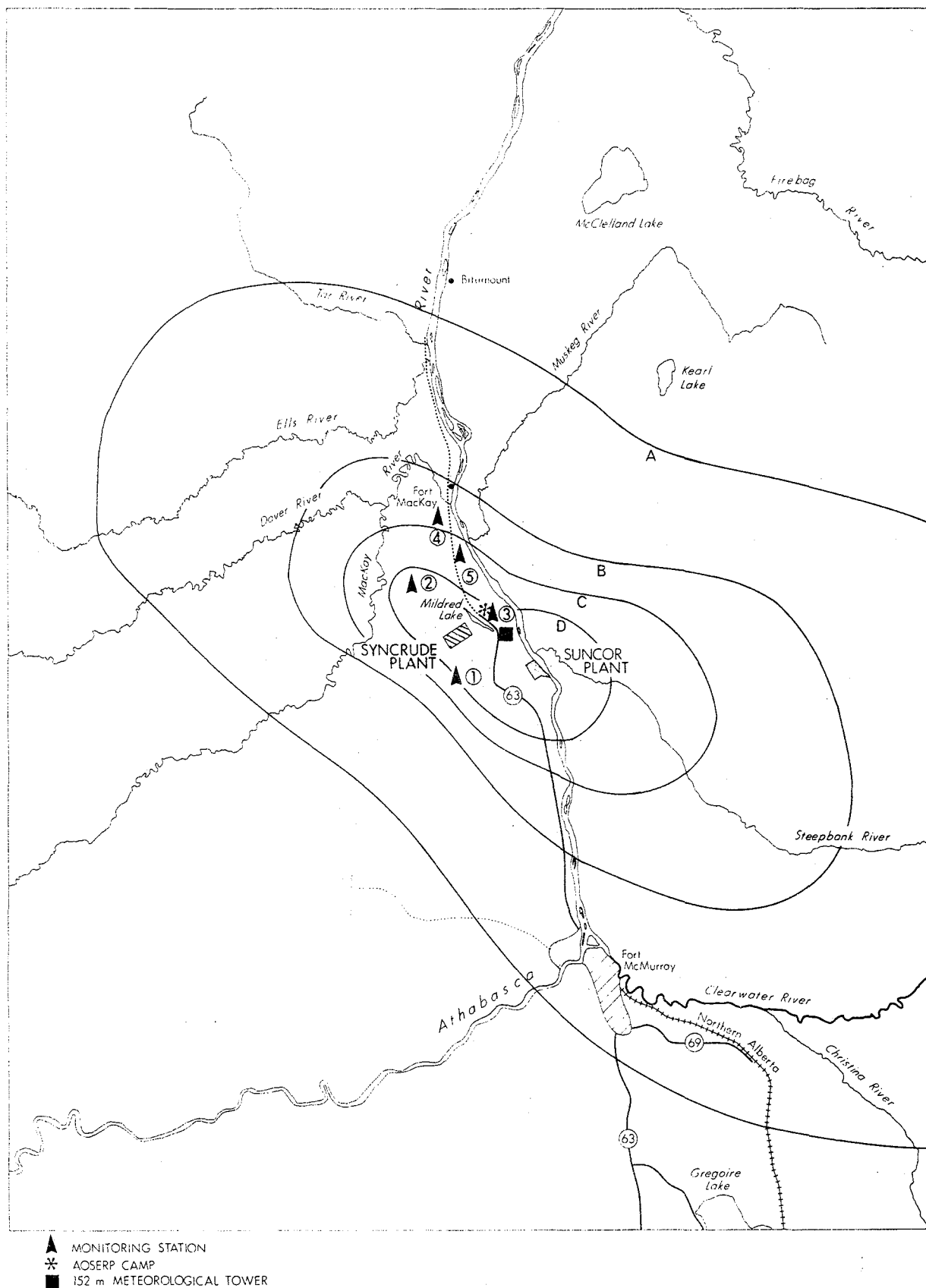


Figure 11

Generic contour plot for the concentration of  $0.1 \mu\text{m}$  particles (0-50 km). Refer to Table 7 for definition of the contour values.

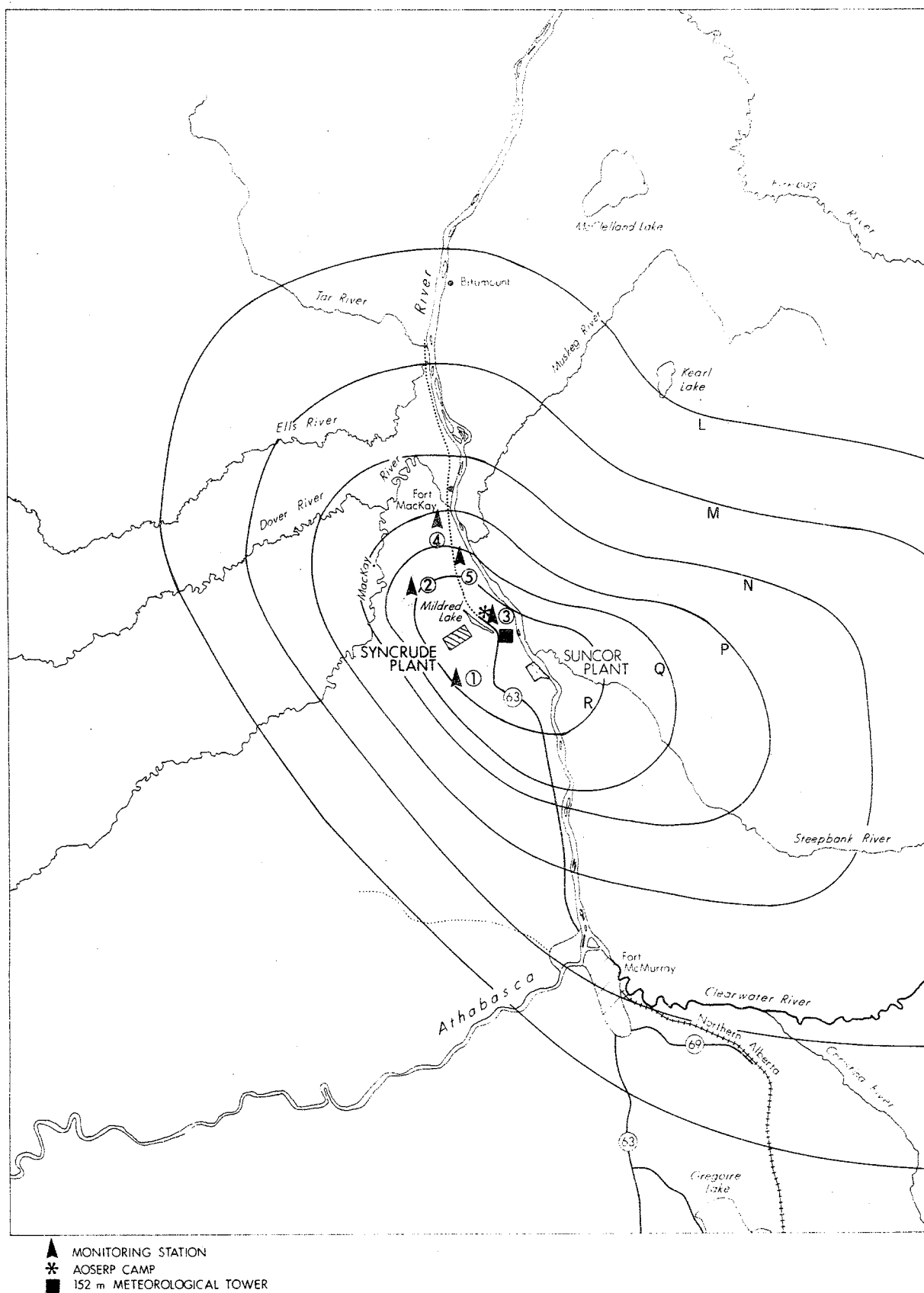


Figure 12

Generic contour plot for the deposition rate of  $10\ \mu\text{m}$  particles (0-50 km). Refer to Table 7 for definition of the contour values.

vapour-phase As, Se and Hg, and (iii) a multi-cyclone train to determine the particle size distribution. All containers, impingers, connectors and miscellaneous glassware employed in the study were cleaned by rigorous procedures prior to sampling.

Final aliquots of rinse solutions were kept for proofing purposes. Sampling protocols were executed in accordance with the Government of Canada stack sampling code, since this was considered marginally more stringent than the Alberta Government code. Samples were kept locked in containers at all times after sampling and hand delivered to the analytical laboratories. Process conditions were monitored during sampling to assure representativeness of the samples.

The reference source testing method for measurement of particulate matter from stationary sources is the Environment Canada Code: EPS 1-AP-74-1. Equipment and apparatus used had specifications equivalent to those required by the Code. There are no applicable codes for size-selective sampling or for vapour-phase metals, although reference methods exist for collection of mercury vapour from chlor-alkali plants (EPS 3-EC-81-4), lead from secondary lead smelters, (EPS 1-AP-78-31), and arsenic (EPS 1-AP-79-1).

A Flow Sensor™ particle sizer sampling train was used in-stack to collect particles in a series of five cyclones and on a back-up glass fiber filter. Cyclone D<sub>50</sub> values were 6.0, 2.6, 1.9, 0.7, and 0.4 micrometers. The Flow Sensor was selected because of the very low wall loss characteristic and the ability to collect a large amount of particulate matter in each stage without carry-over to adjacent stages. A cold box was used in series with the Flow Sensor train to determine the moisture content of the stack gas as a cross-check on the two other sampling trains. A second sampling train used a Teflon-lined probe to collect particulate matter on a glass fiber (Gelman AE) filter. This filter was followed by a series of impingers containing distilled water for collection of gaseous arsenic and selenium and a solution of 2% w/v KMnO<sub>4</sub> in 10% v/v H<sub>2</sub>SO<sub>4</sub> for collection of gaseous mercury. A third train was similar to the second train, but was followed by impingers filled with 5% v/v aqua regia for collection of gaseous cadmium and lead.

Sampling was conducted June 13, 1984 for the preliminary test and on June 14, 17 and 19 for the three compliance tests. For each of these tests the minimum sampling period was 4 hours or one hour at each of four sampling ports, with sampling at 12 positions for 5 minute intervals from each port. Analysis of process data for the sampling periods indicated that representative conditions were sampled, i.e. tests were not conducted during process upset conditions. Samples were handled by well-defined, strict procedures and were transported using strict sample custody procedures.

### Analysis

To ensure confidence in the analysis, some of the samples were divided into three fractions, with each of the fractions analyzed by a separate analytical laboratory. The laboratories used for analysis were the Ontario Research Foundation Trace Metals Laboratory (ORF) which analyzed each of the samples, Barringer Magenta Laboratories (BML) and Diagnostic Research Laboratories (DRL) which analyzed fractions of the glass fiber filter samples, impinger samples and proofing solutions. Standard solution samples containing some of the 26 metals and National Bureau of Standards urban particulate standard reference material (SRM1648) were also submitted (coded as samples) to each of the laboratories to assess accuracy and precision of analysis. As a further quality assurance measure, some of the samples were split and resubmitted for analysis to the laboratories.

Sample extraction and analytical protocols were specified for the laboratories to ensure comparability of the analysis. An aqua regia digestion was selected for extraction to minimize filter background effects. Since the sampling protocols required the use of glass fiber filters due to the rigorous conditions for sampling, and these filters are known to be contaminated with metals, a digestion procedure yielding total rather than extractive fractions for the metals would have produced potential contamination from the filter matrix. This would have been particularly problematic for lead, cadmium, arsenic, selenium and mercury which were suspected to be present at low levels in the stack particulates. For many metals, the aqua regia digestion yielded results equivalent to a total sample fusion procedure, as was shown for analysis of SRM 1648 by both digestion methods. Extraction of mercury from filter and particulate matter samples was performed on separate sample portions by a digestion procedure using nitric, sulphuric and hydrochloric acids, in addition to potassium permanganate and potassium persulphate (60°, 16 hr). The solutions were then reduced with hydroxylamine hydrochloride and diluted to volume. An aliquot was removed and further reduced with stannous chloride immediately prior to analysis by cold vapour atomic absorption spectrophotometry.

Other metals, Al, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Sn, Si, Ti, Be, V, and Zn were analyzed by DC plasma emission spectrophotometry (ORF, DRL) or inductively coupled plasma emission spectrophotometry (BML), while Pb, Cd, and Ag analyses were performed by flame atomic absorption spectrophotometry. For arsenic and selenium, aliquots of the filtered solutions were removed. Nitric acid (5 mL) and concentrated sulfuric acid (2 mL) were added and the solutions were evaporated to fumes of SO<sub>3</sub>. Deionized water (≈5 mL) and hydrochloric acid (5 mL) were added and the solutions were heated to boiling. After cooling, the samples were diluted to volume for analysis by hydride generation and atomic absorption spectrophotometry.

### Modelling

The Mixed Layer Statistics Dispersion Model (MIX) developed by the Atmospheric Environment Service, Environment Canada (Matthias 1981) was selected for modelling the dispersion of emissions from the Syncrude stack. Model outputs are based on unit emission rates.

The MIX model is a Gaussian point source dispersion model. Gaussian formulations have been tested extensively by the air quality community and are now an accepted tool for air quality assessment purposes and are considered to be accurate within a factor of two. Although the MIX model has not been validated directly against experimental data, it has been compared to existing validated models. An assessment using the MIX model was carried out in 1980 by Environment Canada and the Ontario Ministry of the Environment on the air quality impacts of the Atikokan power plant in Ontario, which had become a Canada-U.S. environmental issue. The U.S. EPA reviewed the model methodology. The results of the MIX model were found to be very similar to those produced by EPA's RAM model (a UNAMAP model) which had undergone considerable evaluation. The MIX model results were found to be an accepted basis for evaluation of air quality impacts in an international forum.

The requirements for annual estimates of deposition resulting from the emissions of the Syncrude plant also suggested that average (representative) meteorological data would provide the most realistic (i.e. least biased) results. For this reason, a four-year averaged meteorological data set was utilized in the study.

MIX uses statistical or climatological input data and includes depletion of the plume pollutants by dry deposition. Wet deposition is not considered, since this model does not employ any rainfall statistics. Incorporated in MIX are submodels describing plume rise (using the Briggs formulation), diurnal variation of surface heat flux (assumed to be sinusoidal during the day and linearly decreasing at night), surface shear stress, mixing heights (daytime and nighttime), turbulence intensity and atmospheric stability class.

The climatological data for the mixed layer consists of seasonal joint frequency distributions of maximum mixing height and mean wind speed. The mean nocturnal inversion gradient, mean ambient temperature, regional albedo and the wind direction frequency distribution are also included.

The model first calculates, for any specified downwind location, the distribution of ground level concentrations. It is assumed that the wind direction within each of nine,  $40^\circ$  sectors is distributed randomly over a period of a season or a year and that the emission is uniformly distributed in the horizontal within the sector. The mean of these ground level concentrations, for a season, is then calculated and, using the wind direction frequency, the seasonal mean ground level concentration is calculated for each sector. The seasonal deposition rate in a sector is the product of the seasonal deposition velocity, and the seasonal mean ground level concentration. The annual deposition rate, is determined by summing seasonal deposition rates.

The model inputs comprise stack parameters, meteorological parameters and data, together with pollutant parameters. These input parameters and the values used in the modelling are given in Table 3. The basis for selection of the source of these parameters is indicated below. The group I parameters are measured values provided by Syncrude. The gas exit temperature and exit velocity (speed) differ from those values given in Table 2, which were design values. The effects of the relative magnitudes of these parameters used in the different modelling tasks are expected to be counterbalancing, thus leading to consistent results. The roughness length value is based on data summarized by Simiu and Scanlan (1978).

The climatological data required by the model are derived from percentage joint frequency distribution (JFD) tables of daily mixed layer, wind speed, wind direction and maximum mixing height. These mixed layer data have been generated for the four year period 1965 to 1969 over a sparse network of radiosonde stations in Canada and northern U.S.A. (Portelli 1977). The mixed layer properties do not vary strongly with surface characteristics since they are more strongly linked to geostrophic flow. The Syncrude stack is nearly equidistant from the two closest radiosonde stations at Fort Smith and Edmonton. The climatological data for these stations are different, hence model outputs describing emission from the Syncrude stack were obtained using data for both stations.

The original formulation of the MIX model was modified to allow the seasonal dependency of the deposition velocity ( $V_d$ ) to be included. The seasonal variation of  $V_d$  arises because of the difference of surface cover in the seasons (snow in winter and spring, tall grass/muskeg in summer and fall). Deposition velocity is also a function of particle size. Theoretical studies (Slinn 1977; Sehmel and Hodgson 1978) indicate that  $V_d$  passes through a minimum at  $0.1\text{--}1.0\text{ }\mu\text{m}$ , hence significant differences in  $V_d$  with particle size occur for  $\approx 0.1\text{ }\mu\text{m}$  and  $\approx 10\text{ }\mu\text{m}$  particles. It is also assumed that the deposition velocities for the vapour phase species (Pb, Se, Cd, As and Hg) are similar to the deposition velocity for  $0.1\text{ }\mu\text{m}$  particles. The model was therefore run using two sets of values for the

Table 3 Model Inputs Used in Prediction of Metallic Element Deposition.

		<u>Values</u>	
I	Location (latitude)	57.04°	N
	Stack Height	183.0	m
	Stack Top Diameter	7.9	m
	Stack Gas Exit Velocity	21.6	m s <sup>-1</sup>
	Stack Gas Exit Temperature	230.5	C
II	Roughness Length	0.03	m
	Location of Upper Air Station	Edmonton (YEG)	
III	Metallic Element Emission Rate	1	g s <sup>-1</sup>
	Downwind Distance	as noted for each site	
	Chemical Reaction Rate	0	
IV	Deposition Velocity		
	0.1 µm particles		
	Winter and spring	0.003	m s <sup>-1</sup>
	Summer and fall	0.013	m s <sup>-1</sup>
	10 µm particles		
	Winter and spring	0.014	m s <sup>-1</sup>
	Summer and fall	0.022	m s <sup>-1</sup>

deposition velocities that correspond to 0.10  $\mu\text{m}$  and 10  $\mu\text{m}$  diameter particles. The deposition rate is directly proportional to the value of  $V_d$ .

The formulation of the MIX model does not include wet deposition. The effect of omitting wet deposition on the long-term deposition estimates is not known precisely since the total percentage of time each year that precipitation occurs is small in this region. Long-term statistics indicate precipitation occurs on an average of 30% of days, but the duration of the events on these days will result in a much smaller percentage of total time that precipitation occurs. Barrie (1980) found that the latter was about 2% during a field study period and his paper provides estimates of the total deposition in the oil sands areas.

The model output (based on unit emission rate) provides:

- the frequency distribution of concentrations that occurs in a downwind sector, arising from the statistical variation of the climatological conditions,
- the long-term average concentrations in each of the nine 40° sectors, taking into account the frequency distribution, and
- the average annual deposition rate of particles in each sector for a range of downwind distances corresponding to the biomonitoring sites.

The spatial variation of the concentration and the flux can be illustrated by means of contour plots. Concentric circles are drawn to represent the distance from the stack. The contour lines show concentrations in units of  $10^{-4} \mu\text{g m}^{-3}$ , or deposition rates in units of  $\mu\text{g m}^{-2} \text{yr}^{-1}$ . The concentration and deposition rate for individual elements (using the measured elemental emission rates rather than unit emission rates) are presented in Section 2.1.2.3. The sensitivity of the model outputs to input parameters, namely deposition velocity, roughness length and climatological data (i.e., meteorological station) was examined and optimum values were selected.

The deposition velocity values selected for use as model inputs correspond to 0.10 and 10  $\mu\text{m}$  diameter particles. Field measurements of stack particle size distribution indicate a bimodal distribution with predominance of particles with 0.30  $\mu\text{m}$  and 6.0  $\mu\text{m}$  50% cutpoint. Since the deposition velocities of particles are at a minimum in the 0.1 to 1  $\mu\text{m}$  size range, the deposition velocity for the 0-1  $\mu\text{m}$  particles is appropriate for modelling the behaviour of the smaller particles from the stack (those with  $\sim 0.3 \mu\text{m}$  cutpoints). Similarly, the deposition of the large particles emitted from the stack can be modelled by using  $V_d$  for 10  $\mu\text{m}$  particles.

The roughness length selected was 0.03 m. This value, which is acceptable for the type of terrain in the study area, yields greater concentration and flux estimates than the choice of the other value tested (0.006 m) (see Table 3). Greater roughness length would also have lead to lower estimates of concentration (and deposition). The roughness length characteristic of the surface in the region would vary from less than 0.03 m to several meters, depending upon the relative coverage of water, muskeg, tall shrub and forest.

The model input included climatological data for both Edmonton and Fort Smith since no clear choice exists between these stations. The Syncrude stack is equidistant from Edmonton and Fort Smith, so the usual criteria on which a choice can be made are inappropriate. The outputs from both stations were compared and the set estimating greatest local deposition was selected.

### 2.1.2.3 Results

Process parameters were monitored during the test intervals to ensure that all contributing processes were operational and that plant or process upsets were not affecting the results. Prior to and during the tests, process status was reported to the sampling crew. Documentation of process conditions consisted of plotting selected process trends for immediate review subsequent to test completion. If the trends indicated that process parameters were within the normal range of operation, the test was considered acceptable from the point of view of the representativeness criterion.

During the survey, Electrostatic Precipitator Rectifier Sections A2 and A4 were out of service on process line 8-1 for the course of the survey. As a result, emissions were marginally higher during the survey compared with the emissions when all sections were operational. A log of all electrostatic precipitator hopper temperatures was acquired throughout the survey. With the exception of one hopper (TAG 82TA11), which gave significantly lower temperature readings, all hoppers appeared to be functioning without problems.

The main conclusion from these data were that the compliance tests were valid, representative tests.

#### Analysis Results

The analytical results are summarized in Table 4 for the filter samples from each of the sampling trains. The Flow Sensor train was used to obtain particle size information, but these data were not suitable for determination of emission rates. The two types of sampling trains (i.e. the Flow Sensor and the particulate matter sampling trains ) do not provide directly comparable data, because the cyclone train is susceptible to variations in stack gas velocity and because it samples at in-stack temperatures. The particulate train (equivalent to an EPA Method 5 train) samples isokinetically at all times and at much lower temperatures. The composition of stack gases, in terms of condensibles, affects the comparability of the results from the two trains.

The checks on recoveries (Table 5) and other quality assurance checks on the sample analysis provided the following assessment of the analytical results.

- Co and Be recoveries were approximately 50% low for BML, however, these elements were present in very low amounts.
- Fe recoveries were low for BML and ORF by approximately 19%.
- Si recoveries were uniformly poor, however, this was expected because of the digestion procedure specified.
- Mg recoveries were low by 26 to 21%.
- Al recoveries were low by a factor of 2.5 in the three laboratories.
- V and Ni data also demonstrated low recoveries, except for DRL where a nickel recovery factor of 90% was found.
- Cr and Ti values were approximately three to four times lower than certified values.

Table 4 Filter analysis (between laboratory precision [ $\mu\text{g}$ ])

	Run 2A		Run 2B		Run 4A		Run 4B		Run 5A		Run 5B	
	$\bar{x}$	$\pm\text{SD}$	$\bar{x}$	$\pm\text{SD}$	$\bar{x}$	$\pm\text{SD}$	$\bar{x}$	$\pm\text{SD}$	$\bar{x}$	$\pm\text{SD}$	$\bar{x}$	$\pm\text{SD}$
Fe	4800	$\pm 260$	3690	$\pm 1000$	1290	$\pm 120$	1660	$\pm 270$	1070	$\pm 200$	1200	$\pm 270$
Al	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Si	--	--	--	--	--	--	--	--	--	--	--	--
Ca	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Na	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
V	400	$\pm 27$	300	$\pm 85$	114	$\pm 17$	168	$\pm 46$	106	$\pm 19$	124	$\pm 28$
Mg	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Ti	330	$\pm 16$	232	$\pm 80$	77	$\pm 10$	104	$\pm 24$	72	$\pm 13$	79	$\pm 18$
Mn	128	$\pm 7$	99	$\pm 21$	33	$\pm 7$	47	$\pm 5.8$	31	$\pm 6.4$	32	$\pm 7.6$
P	70	$\pm 10^*$	95	$38^*$	50	$\pm 27^*$	83	$\pm 21^*$	BDL	--	BDL	--
Ni	140	$\pm 7.9$	87	$\pm 32$	24	$\pm 18$	66	$\pm 13$	39	$\pm 10$	63	$\pm 9.3$
Zn	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Pb	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Cr	10	$\pm 5.5$	5.8	$\pm 3.2$	3.6	$\pm 1.2$	BDL	--	BDL	--	BDL	--
Cu	3.2	$\pm 1^*$	2.5	$\pm 1^*$	2.5	$\pm 1^*$	BDL	--	BDL	--	BDL	--
Ba	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Cd	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Mo	22	$\pm 8$	17	$\pm 9.4$	BDL	--	BDL	--	BDL	--	BDL	--
Co	8	$\pm 4.7$	4.2	$\pm 1.5$	BDL	--	BDL	--	BDL	--	BDL	--
Se	5.6	$\pm 2.3$	6.9	$\pm 2.3$	7.0	$\pm 2.3$	5.8	$\pm 2.4$	4.5	$\pm 2.6$	3.2	$\pm 2.0$
Zr	7.8	$\pm 4$	3.2	$\pm 2.6$	BDL	--	BDL	--	BDL	--	BDL	--
Sn	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
As	3.1	$\pm 1$	3.0	$\pm 1.4$	1.5	$\pm 0.4$	1.6	$\pm 0.7$	1.5	$\pm 0.3$	1.3	$\pm 0.4$
Ag	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Hg	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--
Be	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--	BDL	--

\* Some laboratories reported results at or below the blank value. The blank value was therefore used for comparison.

BDL = below detection limit

Table 5 Average recoveries based on NBS-SRM 1648

Element	BML (%)	DRL (%)	ORF Aqua Regia (%)	Mean Recovery (%)	ORF Total Digestion (%)
Fe	81	98	81	87 ±10	99
Al	39	39	36	38 ±2	90
Si*	1	0.1	16	6 ±9	--
Ca	100	88	91	93 ±6	--
Na	47	40	73	53 ±18	75
V	62	66	74	67 ±6	72
Mg	74	79	77	77 ±2	95
Ti	14	23	30	22 ±8	92
Mn	81	104	85	90 ±12	91
P*	105	95	98	99 ±5	--
Ni	76	93	62	77 ±16	65
Zn	96	95	92	94 ±2	91
Pb	102	98	80	93 ±12	88
Cr	18	26	28	24 ±5	69
Cu	94	94	92	93 ±1	103
Ba	21	35	68	41 ±24	96
Cd	89	97	103	96 ±7	93
Mo*	29	52	49	43 ±12	--
Co	53	111	114	92 ±34	111
Se	79	130	62	90 ±35	--
Zr*	3	2	8	4 ±3	--
Sn*	121	75	127	108 ±28	--
As	154	113	97	121 ±29	--
Ag	100	133	112	115 ±17	--
Hg	--	--	--	--	--
Be*	47	89	100	79 ±28	--

\* Relative to total digestion performed by ORF, since no certified values are quoted.

- BML reported low recoveries on Cd by AA but acceptable results using ICAP emission spectrometry (the latter are the results reported).
- BML also reported high recoveries for As.
- BML and ORF reported low recoveries of Se.

The low recoveries on the Fe, Cu, Al, Cr and Ti were expected because these elements are usually found in non-extractable forms in particulate matter. Recovery is usually 100% efficient only by a fusion extraction method. This method would have been unsuitable for use with the glass fiber filter, however, since large amounts of contaminants would have been released from the filter matrix to interfere with quantification of the elements. Many of these features arose because of the small quantities of material and attendant detection limits.

The total digestion method using HF and Na<sub>2</sub>CO<sub>3</sub> fusion conducted by ORF on particulate matter samples, showed markedly improved recoveries for Si, Fe, Mg, Al, Mo, Cr, Ba, Ti and Zr and demonstrated similar recoveries of other elements.

On the basis of this one sample, it was not justifiable to adjust the data for the recoveries found since this standard sample is a composite of urban particulate matter which contains a variety of matrices and particle types including particles from combustion sources, windblown dust, etc. These do not accurately reflect the composition of a single source such as the Syncrude stack. Secondly, analysis for metallic elements from previous studies of Syncrude emissions were comparable with current data, indicating adjustments were not warranted.

For most elements, the elemental composition was similar between samples. Most elements were present at very low levels, or near the detection limits of the analytical methods. Total particulate matter catches varied from day to day and sample to sample (a mean value of  $530 \pm 110$  mg was observed).

One sampling anomaly detected, was the consistent enhancement of concentrations of nickel in Train B particle probe catches, but not on the corresponding filter. A possible source of this contamination could result from disassembly of the probes after each test. This could have dislodged metal from the Train B probe fittings, resulting in nickel contamination from stainless steel particles.

### Emission Rates

The total emission rate of particulate matter ( $35 \pm 7$  g s<sup>-1</sup> or  $3060 \pm 622$  kg day<sup>-1</sup>) and emission rates for each parameter were calculated on the basis of the mean values of six measurements obtained for each of three test days. These rates are shown in Table 6. For the data flagged by an asterisk in Table 6, the Train B results only were averaged, since these were consistently higher, and, therefore provide more conservative (i.e., positively biased) estimates for these metals. Train A data only were used for Ni, since Train B data were suspected to be biased by contamination.

Emissions for all elements except for Fe, Al, Mg, Ca, Si were very low. In general, the emission rates for other elements eg., Be, Cr, As, and Hg were less than 1.0 mg s<sup>-1</sup> (0.09 kg/day), except for Se, Cd and Pb which were 0.1, 0.13 and 0.33 kg day<sup>-1</sup>, respectively. The factors contributing to the emission rate and the variability in this rate are the variability in the composition of the raw materials used in the process, and variations in

the process controls, including emission control devices such as the electrostatic precipitators. The estimation of the emission rates includes these sources of variation in addition to the variation contributed by the measurement process, i.e., the sampling, extraction and analytical protocols. An additional source of variation, which is more difficult to assess in the context of this study, is the representativeness of these emission estimates for process operations when upset conditions exist or other non-routine events occur. The overall variation in the estimates for the emission rates ranges from  $\pm 122\%$  (one standard deviation) for Mg to  $\pm 22\%$  (one standard deviation) for Al.

To place these emission rates in context, the Pb emission rate, for example, corresponds to about  $14 \text{ g hr}^{-1}$  and is of the same order as Pb emission rates reported for selected Alberta sour gas plants by ERCB (Gnyp *et al.* 1983).

#### 2.1.2.4 Modelling Predictions

Modelling results describing annual mean concentration and deposition rate estimates based on unit emission rates are shown as contour plots in Figures 11 and 12. These extend to about 50 km from the stack. The major factors affecting the interpretation of the modelling estimates of the concentration and deposition rate data include:

- the influence of the selection of the climatological station on the model results,
- the distance from the stack at which maximum concentrations or rates occur,
- the downwind directions where the greatest impacts occur,
- the effect of particle size, and
- the most cautious estimates of potential impact of plant emissions.

The sector-independent concentrations as a function of downwind distance, for climatological data for Edmonton and Fort Smith were used for modelling the dispersion from the Syncrude stack. These sector-independent concentrations correspond to the hypothetical case in which the wind direction is constant, i.e., the wind blows from only one sector all the time. The use of the Edmonton data resulted in higher concentrations at all distances. The concentrations for the 0.1 and 10  $\mu\text{m}$  particles are similar (but not identical). Modelling results for the sector ( $105^\circ$ - $145^\circ$ , i.e. southeast of the Syncrude stack) with the highest concentration and deposition rate for 0.1  $\mu\text{m}$  particles shows higher values result when the Edmonton data are used. The highest concentrations occur between 3 and 5 km from the stack. In general, similar directional patterns of the dispersion from the Syncrude stack are shown regardless of the climatological data set used (viz., Fort Smith or Edmonton). This pattern shows that:

- the sector lying between  $105^\circ$  and  $145^\circ$ , and the adjacent sectors (approximately southeast of the Syncrude stack) had the highest concentrations and deposition rates, and
- the direction with the second highest concentration and, deposition levels occurs in the sector between  $305^\circ$ - $345^\circ$ , and adjacent sectors or approximately northwest of the Syncrude stack.

In view of these results, the model predictions obtained through use of Edmonton climatological data were used to avoid underestimating impact.

The smaller particles, which have the lower deposition velocities, have concentrations that are slightly higher than those for the large particles in the study area, especially at downwind distances of 5 km or more. At increasingly greater distances, the difference between the modelled concentrations for the 0.10  $\mu\text{m}$  and 10  $\mu\text{m}$  particles increases. This is to be expected since the heavier particles are deposited more rapidly and are depleted from the plume to a greater extent. The difference in the deposition velocities of the 0.1 and 10  $\mu\text{m}$  particles result in a deposition rate for 10  $\mu\text{m}$  particles of about twice the magnitude of that for 0.1  $\mu\text{m}$  particles.

### Concentration Estimates

The modelling results which reflect the higher estimates of concentration and deposition rate were used to illustrate the total suspended particulate concentration and the concentration of specific elements. Since the use of data characteristic of 0.10  $\mu\text{m}$  particles yields the higher estimates for the concentration of particulate matter, these data were used. The mean total stack emission rate measured in the field sampling program was 3060 kg day<sup>-1</sup>. The maximum concentration of total particulate matter (assuming 0.1  $\mu\text{m}$  particles) was about 0.06  $\mu\text{g m}^{-3}$  at a distance of 3 to 5 km in the sector lying southeast of the plant. The total emission rates for elements are presented in Table 6. These emission rates result in the highest concentration in the southeast sector ranging from 540  $\text{pg m}^{-3}$  for Fe to 0.010  $\text{pg m}^{-3}$  for Be. These concentrations are directly attributable to the Syncrude stack emissions only.

The concentration contour plots for each element are illustrated in Figure 11 in conjunction with Table 7. The concentration contour plots are generically labelled and refer to model results for 0.1  $\mu\text{m}$  particles using climatological data from Edmonton.

### Deposition of Total Particulate Matter and Metals

The most conservative modelling results (i.e. biased toward over-predicting) for deposition rate are obtained by using 10  $\mu\text{m}$  particles. The maximum deposition rate of total particulate matter would therefore be about  $3.5 \times 10^4 \mu\text{g m}^{-2} \text{yr}^{-1}$  at 3 to 5 km from the stack in the sector southeast of the stack. The rates for total particulate matter and for individual elements are summarized in Figure 12. In conjunction with these plots, Table 8 shows the numerical values to be attached to the contour for both total particulate matter and individual metals. The estimated annual average deposition rate of each element at a site may be obtained by interpolating the values between the contours and multiplying the rate for total particulate matter by the relative composition of the emitted particulate matter for that element.

#### **2.1.3 Emissions and Deposition - Overview**

In order to place the estimates for concentration and deposition of metallic elements into perspective, several sets of multi-element concentration and deposition data are summarized. For populated areas the National Air Pollution Surveillance network (NAPS) in Canada and the National Air Surveillance Network (NASN) in the U.S.A., Tables 9, 10, and 11, provide comparative data.

The estimated contribution (i.e., increment above background and other source contributions) of the Syncrude emissions to downwind ambient concentrations of both total particulate matter and individual metals is about 1000 times lower than corresponding concentrations in typical populated areas of Canada and the U.S.A.

Table 6 Metal Emission Rates ( $\mu\text{g s}^{-1}$ )

Element	Flow Sensor Run 2	Run 2A	Run 2B	Flow Sensor Run 4	Run 4A	Run 4B	Flow Sensor Run 5	Run 5A	Run 5B	Mean	Std. Dev.	Mean (kg day <sup>-1</sup> )	Std. Dev. (kg day <sup>-1</sup> )
Particle													
Total (g s <sup>-1</sup> )	(18.1)	40.6	33.3	(13.5)	42.5	40.7	(17.5)	24.1	30.9	35.4	7.2	3060	622
Fe	290,000	489,000	580,000	151,000	219,000	260,000	342,000	160,000	197,000	318,000	174,000	27	15
Al	182,000	114,000	150,000	130,000	126,000	105,000	169,000	71,400	111,000	112,900	25,8000	9.8	2.2
Si	225,000	95,400	231,000	137,000	74,000	87,400	166,000	55,700	110,000	109,000	62,600	9.4	5.4
Ca	32,100	26,600	279,000	28,400	30,900	95,400	31,400	12,200	79,700	87,300	99,400	7.5	8.6
Na	380,000	29,200	57,300	270,000	121,000	28,900	241,000	30,600	25,900	48,800	37,200	4.2	3.2
V	27,500	44,800	48,400	18,600	25,200	33,000	22,400	18,300	24,200	32,300	12,100	2.8	1.0
Mg	13,800	9,700	48,700	10,500	100,000	11,400	12,700	5,030	9,500	30,700	37,500	2.6	3.2
Ti	39,800	39,500	58,000	23,000	23,400	9,410	26,000	16,300	22,100	28,100	17,700	2.4	1.5
Mn	11,600	15,400	23,200	8,900	7,060	7,660	53,700	4,350	5,240	10,500	7,400	0.90	0.64
P	3,340	6,290	15,100	1,800	3,560	19,600	2,200	1,090	12,800	9,740	7,200	0.84	0.62
Ni**	11,700	15,600	208,000	7,800	7,500	292,000	35,000	4,900	190,000	9,300	5,600	0.8	0.5
Zn	1,640	3,110	14,500	2,600	2,560	2,550	2,000	1,220	1,630	4,260	5,060	0.40	0.40
Pb*	390	390	6,400	<170	390	2,220	690	200	2,590	3,750	2,310	0.32	0.20
Cr*	2,400	840	8,200	2,400	600	1,340	38,200	540	880	3,500	4,100	0.3	0.35
Cu*	2,100	390	2,100	1,000	400	2,080	4,600	270	1,090	1,760	580	0.15	0.05
Ba	1,230	400	1,510	830	870	2,020	1,000	750	3,680	1,540	1,200	0.13	0.10
Cd*	<60	40	1,910	<60	30	1,610	<140	<60	1,020	1,510	450	0.13	0.04
Mo	2,100	910	1,970	2,211	940	940	1,500	610	820	1,030	480	0.09	0.04
Co	1,000	520	1,700	660	400	600	1,300	200	480	650	540	0.06	0.05
Se	180	550	660	140	690	740	100	660	120	570	230	0.05	0.02
Zr	1,150	1,300	790	760	460	310	1,500	200	350	570	410	0.05	0.04
Sn	390	190	460	540	270	270	530	200	340	290	100	0.02	0.009
As	180	240	320	170	190	260	140	170	180	230	58	0.02	0.005
Ag	300	40	<70	<200	40	<40	<200	<40	90	28	35	0.002	0.003
Hg	9	10	7	4	30	30	3	10	8	20	10	0.002	0.001
Be	<60	10	30	<100	<6	<6	<70	<6	<6	6	11	0.0005	0.0009
<u>Vapour</u>													
Se	--	630	--	--	500	--	--	440	--	520	97	0.045	0.008
Pb	--	--	<60	--	--	<60	--	--	<60	<60	0	<0.005	0.000
Cd	--	--	20	--	--	10	--	--	110	50	56	0.004	0.005
Hg	--	20	--	--	10	--	--	20	--	20	6	0.002	0.0005
As	--	20	--	--	<5	--	--	<5	--	6	11	0.0005	0.001
<u>Total</u>													
Pb	--	--	6,400	--	--	2,280	--	--	2,650	3,800	2,310	0.330	0.200
Cd	--	--	1,930	--	--	1,620	--	--	1,130	1,560	400	0.13	0.03
Se	--	1,180	--	--	1,190	--	--	1,100	--	1,160	49	0.10	0.004
As	--	260	--	--	190	--	--	170	--	210	47	0.02	0.004
Hg	--	30	--	--	40	--	--	30	--	40	6	0.003	0.0006

\* Run 2B, 4B, and 5B values only were used to calculate mean emission rates.

\*\* Run 2A, 4A, and 5A values only were used to calculate emission rates.

Table 7 Key to the concentration contour plots (0-50 km) shown in Figure 11

Emission Rate $\mu\text{g s}^{-1}$		Value for Contour Label in $\text{pg m}^{-3}$				
		A	B	C	D	Max†
X1*	1°	100	200	300	500	1,700
X2**	35.4°	3540	7,080	10,620	17,700	60,000
Fe	318,000	31.8	63.6	95.4	159	540
Al	112,900	11.3	22.6	33.9	56.4	190
Si	109,000	10.9	21.80	32.7	54.5	185
Ca	87,300	8.73	17.5	26.2	43.6	150
Na	48,800	4.88	9.76	14.6	24.4	80
V	32,300	3.23	6.46	9.69	16.2	55
Mg	30,700	3.07	6.14	9.21	15.4	50
Ti	28,100	2.81	5.62	8.43	14.0	48
Mn	10,500	1.95	2.10	3.15	5.25	18
P	9,740	0.97	1.95	2.92	4.87	17
Ni	9,300	0.93	1.86	2.79	4.65	16
Zn	4,260	0.43	0.85	1.28	2.13	7
Pb	3,750	0.38	0.75	1.13	1.88	6
Cr	3,500	0.35	0.70	1.05	1.75	6
Cu	1,760	0.18	0.35	0.53	0.88	3
Ba	1,540	0.15	0.31	0.46	0.77	3
Cd	1,510	0.15	0.30	0.45	0.76	3
Mo	1,030	0.10	0.21	0.31	0.52	2
Co	650	0.07	0.13	0.20	0.32	1
Se	570	0.06	0.11	0.17	0.28	1
Zr	570	0.06	0.11	0.17	0.28	1
Sn	290	0.03	0.06	0.09	0.14	0.5
As	230	0.025	0.05	0.07	0.12	0.4
Ag	28	0.003	0.006	0.01	0.01	0.05
Hg	20	0.002	0.004	0.006	0.010	0.03
Be	6	<0.001	0.001	0.002	0.003	0.01
Vapour						
Se	520	0.104	0.052	0.156	0.260	
Pb	<60	<0.01	<0.005	<0.02	<0.03	
Cd	50	0.01	0.005	0.02	0.02	
Hg	20	0.004	0.002	0.006	0.010	
As	6	0.001	<0.001	0.0018	0.0030	
Total						
Pb	3,800	0.76	0.38	1.14	1.90	
Cd	1,560	0.31	0.16	0.47	0.78	
Se	1,160	0.232	0.12	0.348	0.580	
As	210	0.042	0.02	0.063	0.105	
Hg	40	0.008	0.04	0.012	0.020	

\* Unit emission rate

\*\* Total particle emission rate

° Units of  $\text{g s}^{-1}$ 

† Approximate value at maximum concentration (3 to 5 km from stack)

Table 8

Key to the deposition rate contour plots (0-50 km) shown in Figure 12

	Emission Rate	Value for Contour Label in $\text{ng m}^{-2} \text{yr}^{-1}$					
	$\mu\text{g s}^{-1}$	L	M	N	P	Q	R
X1*	1°	50,000	70,000	100,000	150,000	200,000	300,000
X2**	35.4°	1,770,000	2,480,000	3,540,000	5,310,000	7,080,000	10,620,000
Fe	318,000	15,900	22,260	31,800	47,700	63,600	95,400
Al	112,900	5,650	7,900	11,300	16,900	22,600	33,900
Si	109,000	5,450	7,630	10,900	16,340	21,800	32,700
Ca	87,300	4,370	6,110	8,730	13,100	17,500	26,200
Na	48,800	2,440	3,420	4,880	7,320	9,760	14,600
V	32,300	1,620	2,260	3,230	4,850	6,460	9,690
Mg	30,700	1,540	2,150	3,070	4,610	6,140	9,210
Ti	28,100	1,410	1,970	2,810	4,200	5,620	8,430
Mn	10,500	525	735	1,050	1,580	2,100	3,150
P	9,740	487	682	974	1,460	1,950	2,920
Ni	9,300	465	651	930	1,400	1,860	2,790
Zn	4,260	213	298	426	639	852	1,280
Pb	3,750	188	263	375	562	750	1,130
Cr	3,500	175	245	350	525	700	1,050
Cu	1,760	88	123	176	264	352	528
Ba	1,540	77.0	108	154	231	308	462
Cd	1,510	75.5	106	151	226	302	453
Mo	1,030	51.5	72.1	103	154	206	309
Co	650	32.5	45.5	65.0	97.5	130	195
Se	570	28.5	39.9	57.0	85.5	114	171
Zr	570	28.5	39.9	57.0	85.5	114	171
Sn	290	14.5	20.3	29.0	43.5	58.0	87.0
As	230	11.5	16.1	23.0	34.5	46.0	69.0
Ag	28	1.4	2.0	2.8	4.2	5.6	8.4
Hg	20	1.0	1.4	2.0	3.0	4.0	6.0
Be	6	0.3	0.4	0.6	0.9	1.2	1.8
Vapour							
Se	520	26.0	36.4	52.0	78.0	104	156
Pb	<60	<3.0	<4.2	<6.0	<9.0	<12	<18
Cd	50	2.5	3.5	5.0	7.5	10	15
Hg	20	1.0	1.4	2.0	3.0	4.0	6.0
As	6	0.3	0.4	0.6	0.9	1.2	1.8
Total							
Pb	3,800	190	266	380	570	760	1,140
Cd	1,560	78	109	156	234	312	468
Se	1,160	58	81	116	174	232	348
As	210	10.5	14.7	21.0	31.5	42.0	63.0
Hg	40	2.0	2.8	4.0	6.0	8.0	12.0

\* Unit emission rate

\*\* Total particle emission rate

• Units of  $\text{g s}^{-1}$

Table 9 NAPS air quality data for TSP and lead (1978-1981) for selected Canadian cities\*

	1978				1979				1980				1981			
	TSP <sup>a</sup>		Lead <sup>b</sup>		TSP <sup>a</sup>		Lead <sup>b</sup>		TSP <sup>a</sup>		Lead <sup>b</sup>		TSP <sup>a</sup>		Lead <sup>b</sup>	
Edmonton																
127 St. & 133 Ave.	65	(2.0)	0.26	(2.35)	81	(1.9)	NA		82	(1.7)	NA		64	(1.6)	NA	
146 St. & 92 Ave.	41	(1.6)	0.21	(2.20)		NA	NA			NA	NA			NA	NA	
175 St. & 105 Ave.	59	(2.4)	0.20	(2.41)	73	(2.2)	NA		72	(2.1)	NA		66	(1.8)	NA	
Calgary																
Bonny Brk & 18A St. S.E.	96	(1.5)	0.24	(2.54)	139	(1.8)	NA		152	(1.7)	NA		136	(1.7)	NA	
39 St. & 29 Ave. N.W.	49	(1.7)	0.11	(3.31)	56	(1.6)	NA		70	(2.0)	NA		65	(1.7)	NA	
Red Deer																
4747 50th St.	53	(2.1)	0.21	(2.36)	61	(2.1)	NA		70	(2.2)	NA		61	(1.8)	NA	
Vancouver																
250 West 70th Ave.**	82	(1.5)	0.75	(2.10)	86	(1.6)	0.72	(2.17)	72	(1.6)	0.56	(2.10)		NA		NA
970 Burrard †	67	(1.5)	0.80	(1.60)	62	(1.6)	0.75	(1.77)	70	(1.5)	0.73	(2.30)	66	(1.6)	0.88	(1.71)
Toronto																
Sherbourne & Wilton**	140	(1.7)		NA	129	(1.7)	0.88	(1.94)	131	(1.6)	0.60	(2.39)	113	(1.7)	0.56	(1.78)
Evans & Arnold†	71	(1.5)	0.99	(2.87)	84	(1.4)	0.75	(1.85)	91	(1.5)	0.87	(1.97)	96	(1.5)	1.1	(1.86)

\* For comparison, Syncrude 1984 contributions (modelled) were 0.06  $\mu\text{gm}^{-3}$  for TSP and  $6 \times 10^{-6}$   $\mu\text{gm}^{-3}$  for lead.

\*\* generally, higher TSP readings occur at these stations for the respective city

† similarly, for lead

a TSP,  $\mu\text{g m}^{-3}$  annual geometric mean (and geometric deviation)

b lead,  $\mu\text{g m}^{-3}$  annual geometric mean (and geometric deviation)

NA Not available or insufficient data (1979, 1980 & 1981 Alberta lead not reported).

National Ambient Air Quality Objective for TSP = 60  $\mu\text{g m}^{-3}$  annual geometric mean (Acceptable = 70  $\mu\text{g m}^{-3}$ )

Source: Environmental Protection Service, 1981

Table 10 U.S. air quality data for metals (ng m<sup>-3</sup>)\* compared to modelled Syncrude contribution to the oil sands region airshed

	1977		1978		1979		Syncrude 1984 (modelled)
<hr/>							
<u>Urban</u>							
Be**	45.1	(70.2)	74.9	(89.5)	53.8	(75.8)	0.01
Ba	31.6	(63.1)	26.5	(82.7)	4.8	(68.1)	0.003
Cd	2.2	(7.3)	2.4	(8.3)	1.9	(5.1)	0.003
Cu	208	(242)	201	(211)	259	(179)	0.003
Fe	1,308	(1,191)	1,273	(1,272)	1,018	(1,049)	0.54
Pb	889	(759)	765	(688)	584	(560)	0.006
Mn	43	(68)	42	(52)	38	(62)	0.018
Mo	2.2	(5.6)	2.1	(4.9)	1.5	(6.5)	0.002
Ni	10.0	(20.9)	11.0	(23.2)	9.6	(12.8)	0.016
V	16.5	(27.4)	19.1	(33.5)	20.8	(35.2)	0.055
Zn	161	(260)	164	(303)	26.3	(238)	0.007
 <u>Non-Urban</u>							
Be**	38.9	(38.7)	47.4	(37.9)	38.6	(19.9)	0.01
Ba	8.9	(9.4)	5.7	(11.8)	11.8	(70.0)	0.003
Cd	0.8	(1.6)	0.8	(1.0)	0.8	(5.1)	0.003
Cu	193	(219)	266	(290)	142	(290)	0.003
Fe	218	(326)	307	(433)	162	(230)	0.54
Pb	92.0	(104)	84.3	(110)	84.2	(102)	0.006
Mn	22	(13)	21	(5)	21	(3)	0.018
Mo	1.1	(1.1)	1.1	(1.3)	0.8	(0.4)	0.002
Ni	4.8	(14.3)	3.9	(3.5)	3.2	(1.9)	0.016
V	6.9	(8.2)	8.5	(10.4)	7.9	(8.5)	0.055
Zn	46.6	(232)	42.4	(110)	13.4	(46.2)	0.007

\* arithmetic mean (and S.D.)

\*\* data for Be are in pg m<sup>-3</sup>

Urban: n = 4, 648 for 1977; 3,614 for 1978; 2,507 for 1979  
where n = # of valid 24 hour samples

Non-Urban: n = 709 for 1977, 458 for 1978, 235 for 1979  
ICAP analysis

Source: EPA-660/S4-83-053

Air Quality Data for Metals: 1977 through 1979 from the  
National Air Surveillance Network, USEPA 1984.

Table 11 Coarse/fine particulate and selected trace metal data - 7 canadian cities 1980†

		Edmonton (10255-104th St.)	Halifax (N.S. Tech. Coll.)	Montreal (Peel & deMaisonneuve)	Ottawa (88 Slater)	Toronto (67 College)	Winnipeg (65 Ellen)	Vancouver (2294 W 10th Ave.)
Mass	$\mu\text{g m}^{-3}$							
	Coarse*	43.8 $\pm$ 33.6	17.7 $\pm$ 6.4	29.1 $\pm$ 18.0	17.4 $\pm$ 8.9	21.7 $\pm$ 9.7	30.4 $\pm$ 15.6	48.8 $\pm$ 33.6
	Fine**	24.9 $\pm$ 11.6	21.7 $\pm$ 8.9	28.6 $\pm$ 19.3	20.7 $\pm$ 11.6	22.4 $\pm$ 11.8	17.2 $\pm$ 8.8	24.9 $\pm$ 11.6
	Total	73.6 $\pm$ 36.1	39.3 $\pm$ 13.4	57.5 $\pm$ 24.2	38.1 $\pm$ 17.4	44.0 $\pm$ 17.6	47.6 $\pm$ 18.6	46.7 $\pm$ 20.7
Metals	$\text{ng m}^{-3}$							
	Arsenic							
	Coarse	4.3 $\pm$ 1.4	6.3 $\pm$ 2.0	4.2 $\pm$ 1.9	3.1 $\pm$ 1.7	3.0 $\pm$ 1.5	13.7 $\pm$ 37.8	4.5 $\pm$ 2.2
	Fine	3.5 $\pm$ 1.1	6.1 $\pm$ 2.4	5.5 $\pm$ 2.3	5.1 $\pm$ 3.1	5.8 $\pm$ 2.4	5.4 $\pm$ 4.0	6.0 $\pm$ 2.9
	Total	7.7 $\pm$ 1.0	12.4 $\pm$ 3.7	9.6 $\pm$ 3.9	8.2 $\pm$ 3.7	8.8 $\pm$ 3.7	19.1 $\pm$ 41.5	10.5 $\pm$ 3.3
Chromium	Coarse	12.6 $\pm$ 8.6	3.9 $\pm$ 3.3	9.9 $\pm$ 10.2	4.4 $\pm$ 2.3	7.3 $\pm$ 5.0	6.6 $\pm$ 8.0	5.7 $\pm$ 4.1
	Fine	11.3 $\pm$ 9.6	6.2 $\pm$ 4.8	13.6 $\pm$ 11.9	5.6 $\pm$ 4.0	7.6 $\pm$ 4.7	8.3 $\pm$ 11.6	18.6 $\pm$ 17.4
	Total	23.9 $\pm$ 17.0	10.1 $\pm$ 5.5	23.5 $\pm$ 20.8	9.0 $\pm$ 5.1	14.9 $\pm$ 8.0	14.9 $\pm$ 11.9	24.4 $\pm$ 16.4
Lead	Coarse	189.0 $\pm$ 76.0	66.7 $\pm$ 30.1	189.0 $\pm$ 99.1	138.0 $\pm$ 84.9	87.1 $\pm$ 71.5	149.0 $\pm$ 87.3	184.0 $\pm$ 95.4
	Fine	556.0 $\pm$ 290.0	174.0 $\pm$ 81.3	676.0 $\pm$ 235	402.0 $\pm$ 157.0	290.0 $\pm$ 134.0	315.0 $\pm$ 172.0	693.0 $\pm$ 365
	Total	745.0 $\pm$ 356.0	241.0 $\pm$ 91.8	865.0 $\pm$ 270.0	538.0 $\pm$ 188.0	377.0 $\pm$ 145.0	478.0 $\pm$ 249.0	877.0 $\pm$ 446

\*  $d < 2.5 \mu\text{m}$ ; \*\*  $2.5 < d < 15 \mu\text{m}$ † For comparison, Syncrude 1984 contributions were  $0.06 \mu\text{gm}^{-3}$  (total mass);  $0.0004 \text{ ngm}^{-3}$  (arsenic);  $0.006 \text{ ngm}^{-3}$  (lead).

Source: Concord Scientific Corporation report 110.27/110.30. Determination of Concentrations of Selected Fine Particulate Air Contaminants in Seven Canadian Cities, for EPS, March 1981. All stations are NAPS stations.

Table 12 illustrates particulate metals concentrations measured 10 km downwind (predominantly) and 20 km upwind of the Suncor plant in 1976 and 1977 (prior to start-up of the Syncrude plant). The upwind concentrations (at Birch Mountain) under the conditions of measurement represent clean, background levels. The Syncrude emissions are estimated to increase these background levels by only about 10 percent.

The relative impact on local soil can be assessed by examining the deposition to these soils over a reasonable operating period. Table 13 summarizes soil concentrations of the 26 metals for which emission data were produced, and estimates of the impact of a 20-year operating period for Syncrude's plant. The deposition increment in percent (column G) compared to the surface soil concentration (column D) results in much less than a 10th of one percent for all metals except V (0.11%), Se (0.55%), Cd (0.15%), and Hg (0.10%).

The impact of the Syncrude emissions, relative to the concentrations measured downwind of the Suncor plant, can be assessed by comparing the relative emission source strengths (at the time of measurement), the relative release (stack) height and the time-averaging basis, as follows. According to Barrie (1980), the Suncor parameters were  $27 \text{ t d}^{-1}$  total particulate emission at a stack height of 107 m, compared with the Syncrude values of  $3 \text{ t d}^{-1}$  at a height of 183 m. The measurements at Mildred Lake in Table 13 are three-day average concentration at sites which were directly impacted by the Suncor plume (samples A and B); whereas, the estimates of Syncrude's plume impact are annual averages.

Taking these factors into account, the data yield comparable annual average concentrations for the Suncor plant to the estimates based on the Syncrude emissions provided in this report, namely, concentrations of less than  $100 \text{ ng m}^{-3}$  total particulate at the point of maximum concentration and less than  $1 \text{ ng m}^{-3}$  for the most concentrated elements. That is, the current estimates of deposition for Syncrude emissions are consistent with previous measurements in the oil sands area.

The relative importance of dry and wet deposition processes is unclear. Since only a few studies have been performed in this region, the predominant mechanisms for deposition of material from the stack have not been established. It has been suggested that wet deposition processes may be relatively more efficient near a point source and some indication of this has been reported by Barrie (1980) in the oil sands area. Barrie, however, also indicated that precipitation occurred only for 2% of the time during his field studies. The relative importance of all deposition in the area can therefore be assessed by evaluating a total deposition scenario in a limited area around the Syncrude stack. This will provide an upper limit to the deposition and will therefore be indicative of worst case conditions. A reasonable upper limit estimate of deposition of the Syncrude emissions into the predominant southeast sector within 25 km of the stack, is  $45 \text{ mg m}^{-2} \text{ yr}^{-1}$  for total particulate matter and proportionately less for individual elements.

A comparison of data provided by Barrie (1980) in a study conducted in 1977 can also be made using V as an elemental tracer for an oil sands plant and normalizing the data to compensate for the different emission source strengths. Vanadium was the only element identified in the current study, by factor analysis of biomonitoring data, as being directly traceable to source emissions.

Barrie (1980) reported that 58% (i.e. 28.4 tonnes) of the vanadium released over a 70 day period ( $49 \pm 7$  tonnes) was deposited within 25 km of the Suncor stack. This

Table 12 Atmospheric concentration ( $\text{ng m}^{-3}$ ) of various elements in suspended particles at Mildred Lake and Birch Mountain

Element*	June 1977 - Mildred Lake			March 1976 - Birch Mountain		
	A (16th-19th)	Period B (19th-22nd)	C (22nd-25th)	1 (3rd-7th)	Period 2 (7th-13th)	3 (13th-17th)
Al	1,500	2,300	1,500	41	56	70
As	0.7	0.9	0.4	0.4	1.1	0.4
Ba	--	38	--	--	--	--
Ca	2,200	2,800	2,700	19	41	40
Fe	3,000	2,400	890	--	--	--
Mg	260	870	780	31	23	26
Mn	28	49	38	0.7	0.9	7.0
Na	--	--	--	130	76	67
Ti	110	210	82	--	6.7	7.9
V	80	110	4.2	0.5	4.5	4.7
Zn	--	23	--	--	~6	--

\* INAA analysis

Note: Samples taken at Birch Mountain were true background (no wind-blown dust or anthropogenic component from GCOS) Samples taken at Mildred Lake, A and B contain a larger proportion of anthropogenic particles since there were directly affected by GCOS emissions.

Source: Barrie (1980)

Table 13 Comparative deposition estimates and relative deposition increment attributable to the Syncrude source only.

Element	A Terrestrial Abundance (mg kg <sup>-1</sup> )	B SCL Soil Sample (mg kg <sup>-1</sup> )	C SCL Stack Particulate (mg kg <sup>-1</sup> )	D SCL Soil Surface* Concentration (kg ha <sup>-1</sup> )	E Deposition** (kg/ha/y)	F 20-Year** Deposition (kg ha <sup>-1</sup> )	G Relative Deposition† Increment (Percent)
Iron (Fe)	50,000	11,100	8,820	2,220.0	3.1 (-3)	0.062	0.0028
Aluminum (Al)	81,300	1,900	3,200	380.0	1.1 (-3)	0.022	0.0058
Silicon (Si)	277,200	670	3,070	130.0	1.1 (-3)	0.022	0.017
Calcium (Ca)	36,300	13,000	2,450	2,600.0	8.6 (-4)	0.017	0.00065
Sodium (Na)	28,300	250	1,370	50.0	4.8 (-4)	9.6 (-3)	0.02
Vanadium (v)	150	30	920	6.0	3.2 (-4)	6.4 (-3)	0.11
Magnesium (Mg)	20,900	4,050	850	810.0	3.0 (-4)	6.0 (-3)	0.00074
Titanium (Ti)	4,400	87	780	17.0	2.7 (-4)	5.4 (-3)	0.032
Manganese (Mn)	1,000	150	290	30.0	1.0 (-4)	2.0 (-3)	0.0067
Phosphorus (P)	1,180	140	270	28.0	9.4 (-5)	1.9 (-3)	0.0067
Nickel (Ni)	80	17	260	3.4	9.1 (-5)	1.8 (-3)	0.053
Zinc (Zn)	132	42	130	8.4	4.6 (-5)	9.2 (-4)	0.011
Lead (Pb)	16	12	104	2.4	3.6 (-5)	7.2 (-4)	0.030
Chromium (Cr)	200	12	98	2.4	3.4 (-5)	6.8 (-4)	0.028
Copper	70	9.6	49	1.9	1.7 (-5)	3.4 (-4)	0.018
Barium (Ba)	250	24	42	4.8	1.5 (-5)	3.0 (-4)	0.0063
Cadmium (Cd)	0.15	1.1	42	0.22	1.5 (-5)	3.0 (-4)	0.14
Molybdenum (Mo)	15	12	29	2.4	1.0 (-5)	2.0 (-4)	0.0083
Cobalt (Co)	23	3.8	20	0.76	7.0 (-6)	1.4 (-4)	0.018
Selenium (Se)	0.09	0.2	16	0.04	5.6 (-6)	1.1 (-4)	0.28
Zirconium (Zr)	220	3.7	16	0.74	5.6 (-6)	1.1 (-4)	0.015
Tin (Sn)	40	6	6.5	1.2	2.3 (-6)	4.6 (-5)	0.0038
Arsenic (As)	5	1.8	6.5	0.36	2.3 (-6)	4.6 (-5)	0.013
Silver (Ag)	0.10	<1	0.6	<0.2	2.1 (-7)	4.2 (-6)	>0.0021
Mercury (Hg)	0.50	0.04	0.6	0.008	2.1 (-7)	4.2 (-6)	0.052
Beryllium (Be)	6	0.2	0.2	0.04	6.0 (-8)	1.2 (-6)	0.003

\* Assuming 1 cm depth and density = 2 g cm<sup>-3</sup>\*\* Number in parentheses is power of ten by which number is to be multiplied, e.g. 9.8 (-3) = 9.8 x 10<sup>-3</sup>

° Column E values calculated for maximum value of deposition of total particulate matter (0.35 kg/ha/y at 3 to 5 km from stack)

† Column F/Column D x 100

corresponds to an average of  $75 \text{ mg m}^{-2} \text{ yr}^{-1}$ . If all the particulate vanadium emissions from the Syncrude stack were deposited in a 25 km radius from the stack, the vanadium flux would be only  $513 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$ . The model estimates of the present study indicate that the highest flux of V would be  $10 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$  for  $0.1 \text{ } \mu\text{m}$  particles, or  $19 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$  for  $10 \text{ } \mu\text{m}$  particles. It should be noted that the stack emissions of V that gave rise to the fluxes derived from Barrie's data were about 250 times greater than those measured in this study: in contrast, the V fluxes within 25 km radius from the stack as measured by Barrie are about 150 times greater than those estimated by the model.

Measured deposition rates (Fanaki *et al.* 1979) for vanadium at fifteen stations in the vicinity of the Suncor stack ranged from  $600$  to  $8100 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$ . These values may be compared with the current model estimates for the sector with the highest fluxes in which the values ranged from about  $600 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$  at 3 to 5 km to  $30 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$  at 100 km from the stack. Again the lower V emission rates of the Syncrude stack (by a factor of about 250) as well as other differences such as stack height, temperature etc. must be borne in mind.

The important findings of the study of metallic elements are that:

- The measured emission rate of total particulate matter from Syncrude's main process stack is about  $35 \pm 26$  grams per second ( $3020 \pm 2250 \text{ kg d}^{-1}$ ) at the 90% confidence level. The emission rate, therefore, would be expected to vary between  $9$  and  $61 \text{ g s}^{-1}$  ( $770$  to  $5270 \text{ kg d}^{-1}$ ) at the 90% confidence level. Similarly, the equivalent emission quantity would vary between  $0.014$  and  $0.092 \text{ g kg}^{-1}$  of stack gas. This result is well below the Alberta standard of  $0.2 \text{ g kg}^{-1}$  of stack gas.
- The range of emission rates for individual metallic constituents of the stack gas (including both particulate and vapour-phase forms) ranged from  $320 \text{ mg s}^{-1}$  ( $27.6 \text{ kg d}^{-1}$ ) for Fe to  $6 \text{ } \mu\text{g s}^{-1}$  ( $0.0005 \text{ kg d}^{-1}$ ) for Be. Table 6 summarizes these results.
- Emissions for Pb, Cd, Se, As, Hg and Be are very low. The selected metals comprised about 10% of the total particulate matter. The remainder would be predominantly C (about 85%) and S (about 5%), based on previous data.
- The particle size distribution in all three tests was characterized as a bimodal distribution with 50 to 70% of the mass in a size fraction with effective particle diameters greater than 6 micrometers, while most of the remainder was in the fraction with effective diameters less than 0.4 micrometers. Very little of the particle mass was found in the four size fractions sampled between these values. Both, the major elements (Si, Fe, Al, Ca), and trace metals were found predominantly in the coarser of the two relatively fine fractions above.
- The corresponding ground level concentrations of particulate matter and metals in the area around the stack, as determined by the model calculations, were found to reach a maximum at 3 to 5 km from the Syncrude stack. The maximum ground level concentration (annual average) at this distance is estimated at  $0.06 \text{ } \mu\text{g m}^{-3}$  for total particulate matter (assumed to be  $0.1 \text{ } \mu\text{m}$  in diameter). The corresponding range for metals was from  $540 \text{ pg m}^{-3}$  for Fe to  $0.01 \text{ pg m}^{-3}$  for Be. These concentrations are summarized in Figure 11, which is to be used in conjunction with Table 7.

- The Syncrude contribution to average annual ground level concentrations of total particulate matter and its constituent metals at the point of maximum concentration (3 to 5 km) are, at most, about 10% above typical natural and man-made background levels in the region. Further away from the stack, the contribution of Syncrude's emissions is expected to be less than this amount. These conclusions are based on previous measurements in the region (mainly under AOSERP; Barrie 1980).
- The model output also included dry deposition rates of total particulate matter and metals. The maximum deposition also occurs at a distance of 3 to 5 km from the stack. The annual average deposition of total particulate matter (assumed to be 10  $\mu\text{m}$  diameter) (Sehmel 1980; Concord Scientific 1983) at this distance is 0.35  $\text{kg ha}^{-1} \text{yr}^{-1}$ . Similarly, for individual metals, the annual deposition ranges from  $3 \times 10^{-3} \text{ kg ha}^{-1} \text{yr}^{-1}$  for Fe to  $6 \times 10^{-8} \text{ kg ha}^{-1} \text{yr}^{-1}$  for Be. These values are summarized in Figure 12, to be used in conjunction with Table 8.
- The model used considered only dry deposition. Previous studies at an oil sands plant (Barrie 1980; Fanaki *et al.* 1979) suggest that wet deposition may be important in removing particles, especially in winter. An upper estimate of the total (wet and dry) deposition from the Syncrude stack may be obtained in a scenario in which all the stack emissions are deposited in only two sectors within 25 km from the stack. The sectors to the southeast and northwest receive deposition in approximately 2.4:1 ratio. If all particulate emissions were deposited in these sectors in this ratio, and within 25 km, the rates would be 0.45  $\text{kg ha}^{-1} \text{yr}^{-1}$  in the southeast sector and 0.19  $\text{kg ha}^{-1} \text{yr}^{-1}$  in the northwest. For metals, the range for the sector of maximum deposition would be from about  $4 \times 10^{-3} \text{ kg ha}^{-1} \text{yr}^{-1}$  for Fe to about  $8 \times 10^{-8} \text{ kg ha}^{-1} \text{yr}^{-1}$  for Be. This would represent the maximum amount of deposition attributable to the Syncrude stack. These concentrations and deposition estimates are those attributable to the Syncrude stack, since other influences were not evaluated (i.e., other stacks, emission sources or wind blown dust).
- The metallic composition of the particulate matter emitted from the Syncrude stack is similar to that from coal-fired power plants, to which the same 0.2 g particulate matter per kg of stack gas standard applies.

In summary, the estimated maximum concentrations and deposition rates occur at 3 to 5 km southeast of the stack. The next greatest concentration and deposition amounts occur at the same downwind distance, but to the northwest of the stack. The estimated ambient levels of particulate matter and metals are in all cases more than 100 times lower than any published air quality standards or guidelines and Syncrude's contribution represent, at most, only 10% of these levels. In all cases, where choice or uncertainty pertained in interpreting the data produced by the study, the conclusions reported are based on those data that reflect greater, rather than lesser, impact on the environment.

## 2.2 VEGETATION STRESS STUDIES

### 2.2.1 Introduction

Atmospheric emissions from oil sands upgrading facilities contain sulphur and nitrogen oxides. Sulphur, although an essential plant nutrient in small amounts, has, in larger amounts, or certain forms ( $\text{SO}_2$  and  $\text{H}_2\text{S}$ ), the potential to cause injury to vegetation.

It is often assumed that there has been no injury to vegetation until visible symptoms of phytotoxicity such as dead, defoliated, malformed or discoloured leaves, needles, or branches develop. This can be misleading, since, in greenhouse and laboratory studies, sulphur dioxide has been shown to reduce the growth and yield before any visible symptoms of damage appeared (Malhotra and Hocking 1976). Initial injury is believed to take place at the biochemical level (interference with photosynthesis or respiration), and progresses to the ultrastructural level (disorganization of cellular membranes), then the cellular level (cell wall, mesophyll and nuclei breakdown). Finally, visible symptoms develop, such as chlorosis and necrosis of foliar tissue (Dreisinger and McGovern 1970). These visible symptoms are the most important for distinguishing vegetation stress in the field or on air photos.

As part of their environmental monitoring program, Syncrude conducts on-going vegetation stress surveys using false colour infrared aerial photography. Baseline photography was taken in 1972, 1973, 1974, 1977 and 1978, prior to and during the construction phase, to document the existing natural and man-made causes of vegetation stress prior to commencement of Syncrude operations; and to provide data against which to monitor any future changes. Interpretation of this photography showed several areas of vegetation stress where suspected causes of damage included beaver activity, fluctuating water levels, insects, disease, frost, land clearing and test hole-drilling (The Sibbald Group 1973, 1977).

The 1978 survey indicated both declines and increases in damage and stress of various types in the area compared to 1974, however, the random pattern, suggested that the changes were not likely due to air pollution (The Sibbald Group 1979), and no evidence of soil pollution was noted in 1978.

On the basis of annual visual observations Loman (1981) documented a plume impingement zone between 3 and 6 km southeast and east of Suncor's plant site, in mature aspen stands. Annual observations showed variability in the severity of foliar stress and the size of the areas involved.

Concern about the potential of fly ash on vegetation and soils prompted Suncor to initiate field studies in 1977 which were monitored again in 1983 (Hardy Associates (1978) Ltd. 1983). The study concluded that uptake of elements, particularly heavy metals, from fly ash by native vegetation 7 years after the application, has declined from potentially toxic levels in 1978 to very low levels comparable to that of normal (control) soils in 1983. This was confirmed by a lack of visible health problems or effect of the fly ash treatments on plant cover in 1983.

Trace element analysis in the sapwood of white spruce in the vicinity of Syncrude and Suncor plants has shown no effects due to air emissions in the area (Pauls *et al.* 1985). The analysis was conducted in white spruce at five locations ranging up to 67 km from the plant sites and from 3 age classes; before either oil sands plant, after Suncor and after both plants began operating.

The study area was re-photographed in July, 1984. The air photos were analysed and ground truthing of the interpretation was completed late in August of 1984. The work was reported by Reid and Sherstabetoff (1985), and the following has been extracted from their report.

### 2.2.2 Study Objectives

The major objective of the study was to identify and document any industrial causes of vegetation stress associated with the previous 6 years (1978 to 1984). The specific objectives were:

- to interpret the 1984 false colour infrared (FCIR) photos for evidence of vegetation stress, and to review previous stress interpretations made from the 1978 photography,
- to conduct a field reconnaissance to briefly examine stressed vegetation in order to determine the probable cause,
- to tabulate the areas stressed or damaged according to cause and degree for the period 1978 to 1984,
- to prepare a map of stressed vegetation which could be easily updated with data from future biomonitoring surveys, and
- to relate areas of vegetation stress to sulphur dioxide emission and sulphur deposition data.

### 2.2.3 Methods

Several techniques for detecting stress in vascular plants can be used. Suncor (Loman 1981) used visual aerial inspection and ground truthing. Aerial photographic techniques have the advantage of providing a permanent record for systematic, repeat and multi-observer analysis.

False colour infrared aerial photography extends the monitoring capability to sense changes in reflectance, caused by stress, into the near-infrared band of electromagnetic spectrum, thus enhancing the sensitivity of the monitoring project. These techniques are in common use for the detection of damage in forest communities (Gimbarzevski 1984).

Syncrude elected to use aerial colour and FCIR photographic techniques to establish a record which can be repeated in subsequent years and reanalyzed as scientific advances in this field take place.

#### 2.2.3.1 Colour Air Photo Interpretation

Colour and FCIR photography of the study area were taken on July 25, 1984 at a scale of 1:10 000. The photography covered a relatively small area of approximately 29 500 ha, with flight lines centered at the Syncrude and Suncor plant sites and extending about 30 km north-south and east-west directions. The colour photography was received in time to carry out preliminary interpretation for stressed vegetation prior to the field reconnaissance. Boundaries of typical stressed areas were marked on the photographs, potential ground truthing sample sites, representative of the visible types of stress were

selected on the basis of access by truck, helicopter and foot, and a brief field reconnaissance was conducted from August 29 to 31, 1984.

#### 2.2.3.2 Field Reconnaissance

The air photo interpretation identified seven major causes of stress. A total of 14 sites located within homogeneous vegetation types were selected for field sampling as representatives of typical damage types. The appearance of the site on the air photo, in terms of vegetation stress, was compared to the ground appearance of the vegetation.

A specimen of a stressed tree was cut down in order to examine the upper branches and foliage. Notes on the health and vigor of the foliage, defoliation, needle and leaf retention, needle growth and site of tree most affected were made (Malhotra and Blauel 1980). Representative branches or twigs with attached needles or leaves were photographed then placed in plastic bags, labelled and stored in a freezer for later examination in the laboratory. Notes on the general site condition including soil type, topography and drainage, along with observations on past water table changes, presence of dust, charcoal or oil were made. To the extent possible, the cause of stress at each site was determined and recorded.

#### 2.2.3.3 False Colour Infrared Air Photo Interpretation

The 1984 false colour infrared (FCIR) photos were received following the field survey. The preliminary interpretation on the colour photos was transferred to the FCIR photos, with checking and corrections as necessary based on the field observations.

The degree of stress was estimated on the photos as the portion of the stand affected in terms of the amount of dead, defoliated or discoloured vegetation. Three classes were used to indicate the degree of stress as follows:

- High (H) - greater than 75% of the stand affected,
- Medium (M) - 25% to 75% of the stand affected, and
- Low (L) - less than 25% of the stand affected.

The 1978 FCIR photos interpreted by The Sibbald Group (1979) were re-examined and the stress areas annotated according to the legend developed in 1984. Identification of the cause of stress in 1978 cannot be definitive as field checking was not possible. In some cases several smaller areas of stress, less than 1 ha in size, were grouped together into larger units for mapping purposes.

#### 2.2.3.4. Map Preparation

The areas of stress and annotations for 1978 and 1984 were transferred to 1:20 000 base mosaics of the study area. The smallest map unit shown was about 0.5 ha in size. The base mosaics were reduced to 1:50 000 and the type lines traced separately onto a mylar copy of the 1:50 000 topographic map, one for 1978 and one for 1984. Due to the fact that stress sometimes appeared in isolated areas within a stand too small to be mapped separately, a certain amount of grouping of stressed areas was necessary for mapping purposes. The result of the grouping is that the area of stress may be an overestimate. The locations of the 1984 sample sites were marked on the 1984 map. The areas in which air pollution is believed to be a partial cause of stress, along with disease and insects, were then grouped into low and medium zones for each year, and the maps further reduced to page size for presentation. The other causes of stress, such as flooding due to beaver or human activities and fire, are not related to air emissions and are not shown on the maps.

The 1978 and 1984 airphoto coverage did not match exactly. Therefore, measurements of stressed vegetation were confined to the area of common air photo coverage. The area of each stressed map unit was measured separately for 1978 and 1984 on the 1:50 000 scale maps using a computerized digitizer.

## 2.2.4 Summary of Results

### 2.2.4.1 Causes of Vegetation Stress

The major causes of vegetation stress in the oil sands area are disease, insects, air emissions, changes in water levels, and fire; while minor natural causes such as drought, early frost, and animal browsing, covered areas too small to map on the air photos. The following is a description of the visible symptoms and air photo appearance (FCIR) of each cause.

#### Air Emissions

Emissions harmful to vegetation consist primarily of sulphur dioxide, nitrogen oxides and some particulates containing heavy metals (Malhotra and Blauel 1980). Vegetation in the field develop symptoms in response to total air emissions and not to individual pollutants in isolation, although symptoms typical of sulphur dioxide predominate.

In conifers, sulphur dioxide produces generally similar symptoms on all species. Visible symptoms on forest species depend on the sulphur dioxide impingement pattern and species sensitivity. In mixed stands, both black and white spruce, which are relatively tolerant of sulphur dioxide, will often remain unaffected even though jack pine will show foliar discolouration (Malhotra and Blauel 1980). Visible symptoms of air pollution stress in conifers are:

- discolouration of needles beginning at the tip, progressing toward the base,
- mature needles dropping prematurely,
- some needles having stunted growth due to fumigation events, and
- that portion of the crown exposed to directional fumigation developing more intense injury symptoms than the rest of the crown.

Stressed conifer crowns on air photos, particularly the more sensitive jack pine, show partial to complete needle drop. The affected pine are discoloured on FCIR from the normal magenta and blue magenta, to green and blue-green.

Of the deciduous species present, aspen and balsam poplar are moderately sensitive, and white birch and tamarack are highly sensitive to sulphur dioxide stress (Malhotra and Blauel, 1980). Major visible symptoms of air pollution stress in deciduous species include:

- a wet or water-soaked appearance,
- chlorosis and browning around the edges and between the veins,
- extensive discolouration, leaf curling and shriveling, and
- reduced leaf retention.

On air photos, stressed areas in deciduous species are evident from death, defoliation, and discolouration. The normal magenta appearance (FCIR) of foliage changes to a white or mauve colour and defoliated branches appear green to blue-green.

Symptoms on deciduous species in 1984 were not as distinctive of air emission damage as on coniferous species, perhaps due to the lack of high ground level concentrations of sulphur dioxide during the growing season. One of the more evident symptoms of sulphur dioxide damage is that trees on the side of the stand facing the source showed more stress than those in the middle or on the opposite side. In addition, older mature trees, of both balsam poplar and aspen, appeared to be more severely affected than younger trees.

The overall pattern of vegetation stress due to atmospheric emissions definitely followed the Athabasca River valley and its tributaries. Thus, the location of the affected areas is related to the direction of the prevailing winds, topography, and mosaic of forest edges.

### Tent Caterpillar

Tent caterpillars are capable of causing injury to aspen trees ranging from partly chewed leaves to complete defoliation (Hildahl and Campbell 1975). The attack by tent caterpillars early in the season, appeared to be at a low level, however, the observed stress areas may also have included other leaf eating insects, neither of which were present in late August, 1984. In addition, diseases which reduce the growth and vigor of aspen, such as *Hypoxylon* canker, *Armillaria* root rot and tinder conk (*Fomes*), were also present in low amounts.

Symptoms of tent caterpillar attack usually include partial to complete defoliation and considerable discolouration. The normal FCIR magenta colour of deciduous foliage appears as white, mauve, and yellow on stressed trees. Since the foliar symptoms of these insects on air photos are similar to those produced by airborne pollutants (Malhotra and Blauel, 1980), they are combined on the stress maps.

### Dwarf Mistletoe

Dwarf mistletoe is one of the major damaging agents of pine in Alberta (Baranyay 1970), and was found throughout the jack pine stands in the study area. Other agents which may be present, but damage jack pine to a much lesser extent, include root rot and needle-miners.

The most conspicuous symptom of dwarf mistletoe infection on the host is the "witches' broom". The sizes and shapes vary depending on the stage of the disease, but on pine they tend to be large and open. The deformed branches which make up the broom are often distorted, but not swollen. The aerial shoots of the dwarf mistletoe are also an important diagnostic sign.

Dwarf mistletoe infection is clearly evident on air photos in the form of infection centres in younger trees around larger living and dead infected residual trees. Defoliation, malformation of stems, reduced height and dead trees are often visible. The normal magenta and dark-blue magenta of pine foliage on FCIR photography changes to green, blue-green and blue on stressed trees. The symptoms of mistletoe infection on air photos are often similar to air pollution injury, hence these two causes are combined on the stress maps.

### Flood - Beaver

The dam building activities of beaver along many of the small streams throughout the study area have damaged many small stands of aspen and spruce. The visual symptoms include partially logged stands with fallen trees, dams, dead trees, defoliation and discolouration. The normal magenta and blue magenta of aspen and spruce foliage on FCIR change to green, blue and black and on stems where the bark has fallen off, to silvery-green.

### Flood - Man

As a result of man's activities in the oil sand area, several stands of aspen and spruce have been stressed by rising water tables. The symptoms are identical to the beaver caused floods in terms of dead trees, defoliation and discolouration. Man-made floods are most often associated with facilities such as roads and ditches. In some areas, however, the effects of a road may have combined with several beaver dams to raise the local water table and damage the surrounding forest.

### Fire

Recent forest fires are rare in the study area. The symptoms generally include dead, and defoliated trees and understory. The magenta and blue-magenta FCIR colour of the normal foliage is replaced by dark blue and green, with some silvery-green where bark has fallen off branches and trunks.

### Birch Dieback

Birch dieback is a catchall for a large number of possible damaging agents which operate alone or in combination to injure birch trees. Common causes of birch dieback include leaf miners, root rot, old age and drought (Murtha 1972; Malhotra and Blauel 1980). The typical symptom of dieback is that the top portion of the crown is often dead or defoliated with some discoloured leaves. On air photos, the stands appear very open with much of the understory visible. The normal magenta colour of foliage on FCIR photography is changed to white and mauve with silvery-grey colours from defoliated branches of stressed trees. Since the symptoms of dieback are similar to air emissions, the causes are shown as a combination on the stress maps.

#### 2.2.4.2 Stress in 1978

In 1978, the total area of stressed vegetation was approximately 5500 ha, of which about 4020 ha, or 73%, was due to low degree of tent caterpillar, dwarf mistletoe and air pollution (Table 14). The affected areas were found scattered in small stands along both sides of the Athabasca River valley and along the Steepbank and Muskeg River valleys (Figure 13). The symptoms on air photos, which include discolouration of foliage with some defoliation, occur mainly in aspen, jack pine and white birch stands. There were small areas of medium degree air pollution stress at the mouth of the Steepbank River and near Ruth Lake.

Stress caused by flooding made up the bulk of the remaining stress affected areas (25%). Flooding caused by beaver dam building activities was found throughout the area along small to medium sized creeks. Man-made and the combination of man and beaver caused flooding stress, occurred primarily along the southwest portion of the Syncrude west interceptor ditch. Aspen, white spruce and willow were the most common species involved, with dead and defoliated trees the typical symptoms.

Table 14 Areas of vegetation stress 1978-1984

Cause	Areas of Vegetation Stress					
	1978		1984		Change 1978-1984	
	ha	%	ha	%	ha	%
<u>Air Pollution, Insects and Disease</u>						
Low	4018.7	73.1	4222.2	40.9	203.5	6.3
Medium	19.8	0.5	4165.3	40.4	4145.5	86.1
Total Air Pollution, Insects and Disease	4038.5	73.6	8387.5	81.4	4349.0	90.2
<u>Flooding</u>						
Beaver						
Low	59.7	1.1	67.7	0.6	8.0	0.1
Medium	348.7	6.3	127.2	1.2	-221.5	-4.6
High	152.4	2.8	292.7	2.9	140.3	3.0
Subtotal	560.8	10.2	487.6	4.7	-73.2	-1.5
Man						
Low	364.7	6.6	354.7	3.4	-10.0	-0.2
Medium	90.2	1.6	121.8	1.2	31.6	0.7
High	62.2	1.2	36.0	0.4	-26.2	0.4
Subtotal	517.1	9.4	512.5	5.0	-4.6	-0.1
Man and Beaver						
Low	97.6	1.7	791.0	7.8	693.4	14.3
Medium	199.0	3.6	23.7	0.1	-175.3	-3.6
High	11.5	0.3	0	0	-11.5	-0.2
Subtotal	308.1	5.6	814.7	7.9	506.6	10.5
Total Flooding	1386.0	25.2	1814.8	17.6	428.8	8.9
<u>Fire</u>						
Medium	0	0	4.0	0.1	4.0	0.1
High	65.0	1.2	102.9	1.1	37.9	0.8
Subtotal	65.0	1.2	106.9	1.0	41.9	0.9
Total Vegetation Stress	5489.5	100.0	10309.2	100.0	4819.7	100.0

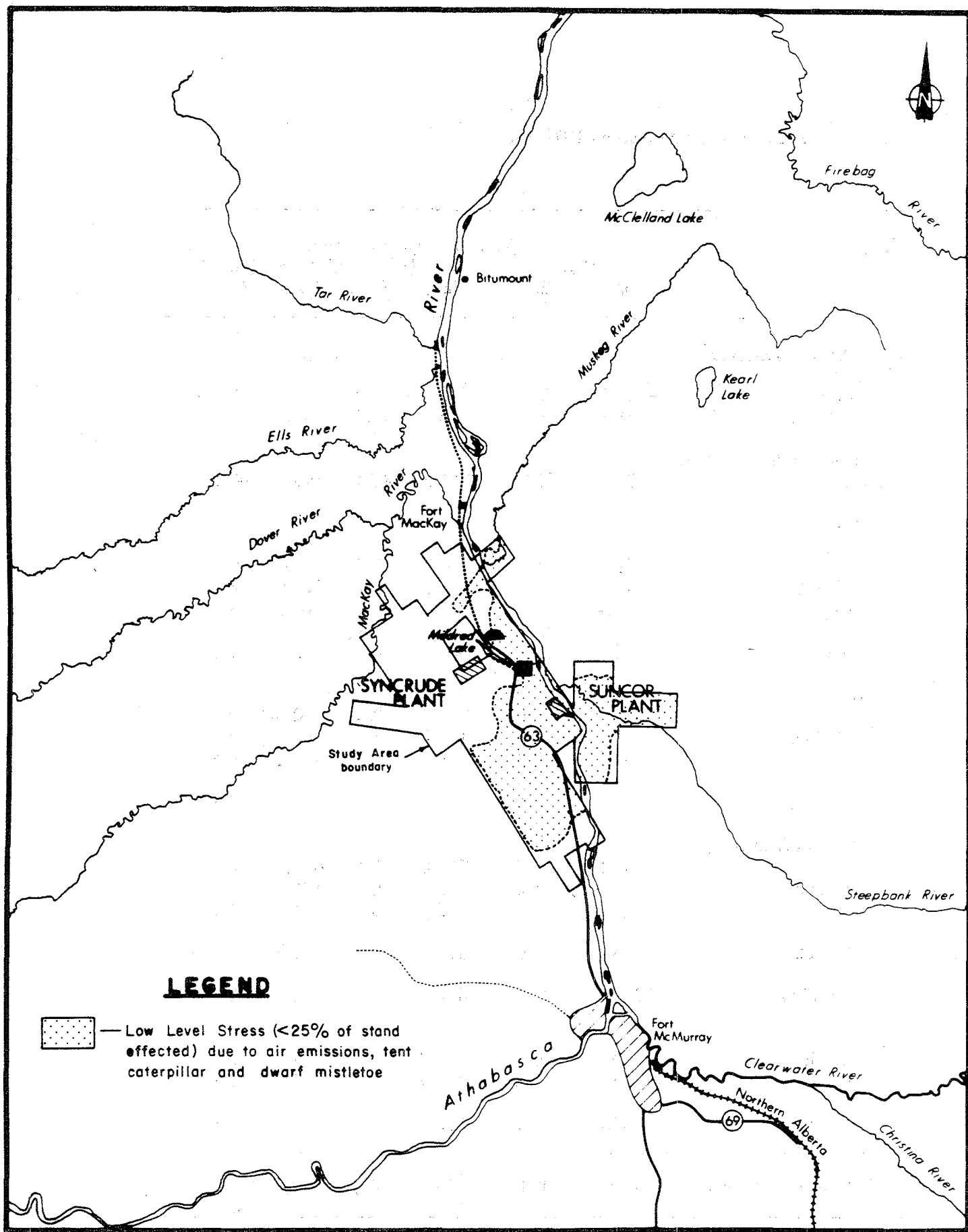


Figure 13

Vegetation stress in the oil sands region mapped in 1978.

Small areas of fires made up the remaining 1% of the stressed vegetation.

#### 2.2.4.3 Stress in 1984

The total area of stressed vegetation in 1984 was approximately 10 300 ha (Table 14) of which about 8390 ha, or 81%, were caused by low and medium degree combined dwarf mistletoe, tent caterpillar and air pollution. Large areas of medium combined, dwarf mistletoe, tent caterpillar, air pollution and/or birch dieback stress were located along the Athabasca River valley, particularly east of the Suncor plant and along the Steepbank River valley (Figure 14). Other areas of medium stress included the Poplar River valley and the Ruth Lake - Beaver Creek Reservoir areas. Areas of low degree combined disease, insect, and air pollution stress were found along the Athabasca River valley and near Ruth Lake. In the stressed areas, balsam poplar, aspen, white birch and occasionally white spruce showed symptoms such as dead tops, defoliated branches and discolouration.

Stress due to beaver caused flooding was found throughout in the stream valleys and lowlands covering 4.7% of the affected area. Man and combined man-beaver caused flooding was found primarily along the Syncrude west interceptor ditch, and Highway 63 between the two oil sands plants, covering 13% of the affected area. Aspen, white spruce, black spruce, and tamarack made up the majority of species affected, where the primary symptoms were dead and defoliated trees.

Fires made up a very small proportion of the area of vegetation stress.

#### 2.2.4.4 Changes in Vegetation Stress from 1978 to 1984.

Medium degree combined dwarf mistletoe, tent caterpillar and air pollution caused stress showed the largest increase from 1978 to 1984 (Table 14). This reflects the change of large areas of low degree stress in 1978 to medium degree stress in 1984, coupled with an overall increase in 1984 of low intensity stress. Flooding showed a slight increase, while the area of fires had a minor increase (Table 14). The average size of the affected areas increased from 27 ha/stand in 1978, to 44 ha/stand in 1984.

The study was limited by the very small area of air photo coverage, hence stress could not be related to regional patterns of major insect and disease stress. The amount of ground checking, while confirming the air photo interpretation, was not extensive enough to check every area of stress, nor to document the proportion of stress due to disease, insects, and air pollution. Follow up studies on the chemical composition of the plant tissue would be required to verify air pollution stress to the vegetation.

### 2.3 BIOMONITORING: LICHEN NETWORK

#### 2.3.1 Introduction

Previous scientific research has clearly demonstrated that lichen vitality and growth are very sensitive to sulphur dioxide; more sensitive than most vascular plant species (Case 1978, 1980, 1984; Anderson and Treshow 1984; Martin and Coughtrey 1982; Addison and Puckett 1976; Ferry *et al.* 1973; Loman 1978). The Syncrude lichen network was designed to take advantage of this sensitivity and permit identification of the areas of potential impact before overt damage to higher plants occurred.

Re-examination of lichens in permanent quadrats at intervals should permit the detection of changes in lichen vitality and growth. It was assumed that growth of the

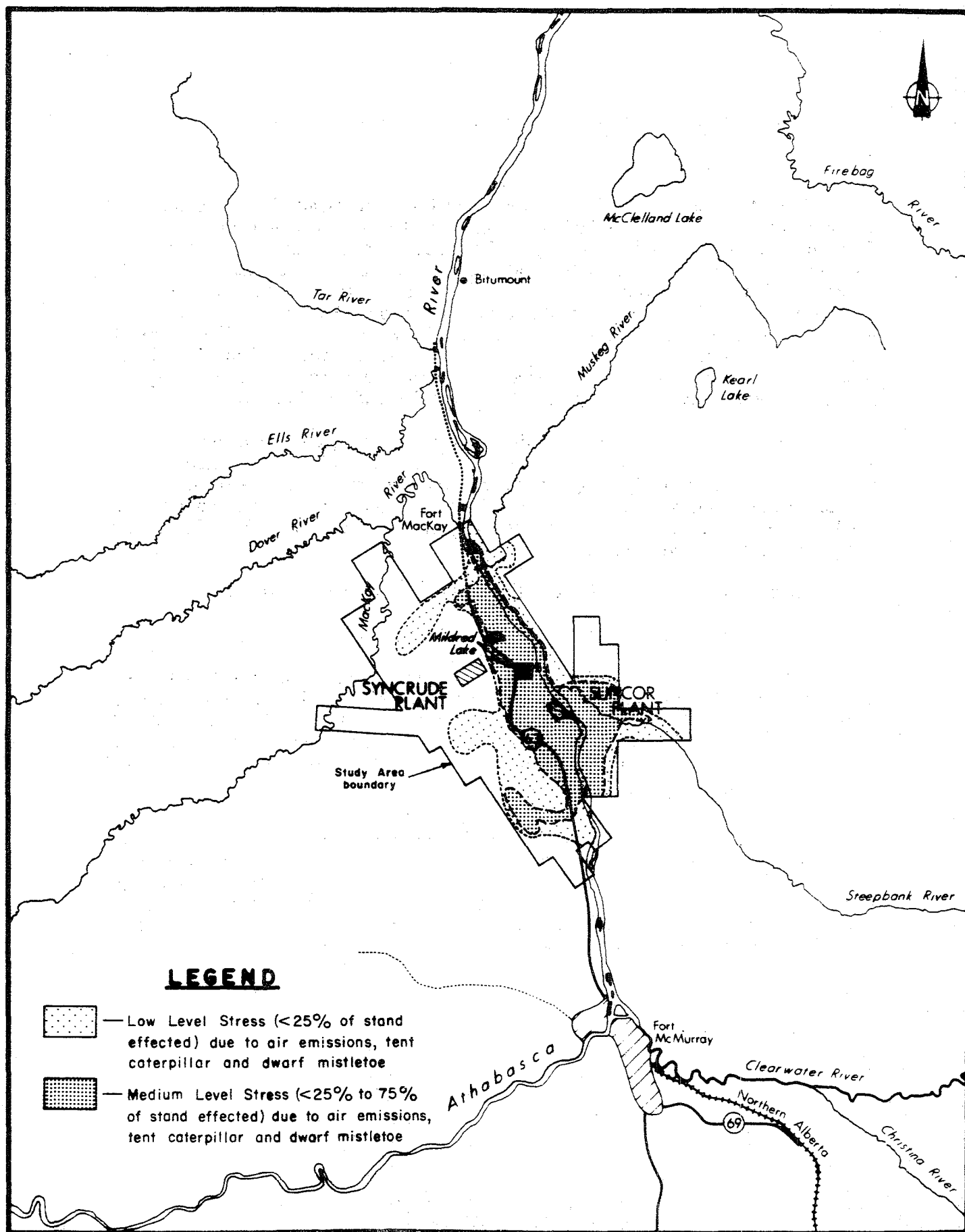


Figure 14 Vegetation stress in the oil sands region mapped in 1984.

lichens in the permanent quadrats during the interval between surveys would result in an increase in the amount of the quadrat which the lichens covered. Any decrease in lichen vitality and growth would be due to the emissions from the oil sand plants since they are the only major sources of sulphur dioxide in the area.

The following hypotheses were to be tested in this study:

- lichen vitality is uniform throughout the study area
- lichen growth has been uniform throughout the study area.
- lichen vitality has not changed from 1976 to 1983.
- lichen growth has not changed from 1976 to 1983.
- lichen growth is independent of the proximity of the oil sand processing plants.

It was assumed that exposure to increasing amounts of air pollution (principally  $\text{SO}_2$ ) would result in decreased epiphytic lichen growth and increased incidents of visible injury. In addition, it was also assumed that the concentration of air pollutants would decrease as the distance from the oil sands plants increased.

Important parameters to be taken into consideration in any multiple regression model of lichen size and vitality change would include distance and direction from the emission source(s), elevation, slope and aspect.

This study has been more fully reported in Case *et al.* (1985). The following is a summary of that report.

### 2.3.2 Objectives

The general objective of the present study was to detect and measure changes in lichen growth that occurred between 1976 and 1983 in permanent quadrats in a delimited study area in the Athabasca oil sands region, and to determine whether this could be related to plant emissions.

The two primary objectives of the present study were:

A) To resurvey the network of lichen plots:

- to make observations of the condition of trees and lichens in each plot,
- to determine whether there had been any significant change in lichen vitality from 1976 to 1983, and
- to determine whether there had been any significant change in lichen size at the network plots between 1976 and 1983.

B) To collect samples of *Cladina mitis*, *Hylocomium splendens*, *Peltigera aphthosa* and *Pleurozium schreberi* from each of the plots to determine if there had been any significant change of elemental concentration in lichen and/or moss tissues from 1976 to 1984.

### 2.3.3 1976 Survey

In 1976, fifty-six sampling sites were established along eight transects radiating from the periphery of the Syncrude plant site (Peterson and Douglas 1977). Seven sites at distances of approximately 1, 2, 6, 12, 20, 30 and 40 km from the stack were established on each 45° transect. Each site was located on an air photograph.

Sampling was conducted in 1976 at each plot by establishing 20 permanent 10 x 20 cm quadrats on the trees. Most of the quadrats were established on white spruce or black spruce although balsam fir, larch, trembling aspen, and jack pine were used occasionally. In addition, most of the quadrats were established on the north-facing sides of the tree near breast height, although quadrats were located on all sides of the trees from ground level to over 2 m up on the trunk. The most common lichen in the quadrats was *Parmelia sulcata*, followed by *Hypogymnia physodes*; although, on rare occasions, *Parmelia flaventior* or one of several species of *Physcia* were used.

Each quadrat was marked with a 6 cm metal circular identification tag. The corners of each quadrat were marked with aluminum nails. (These were left in the tree to aid exact replacement of the quadrat frame during resampling in the future.) A 500 cm long sheet metal shadow box was nailed over the quadrat. The quadrats were photographed in duplicate through a small opening in the end of the shadow box by hand holding a 35 mm SLR camera. Uniform lighting was achieved for each photograph by the use of electronic flash units. The film used was Kodachrome ASA 25 exposed for 1/60 second at f 16.

The percent cover of each species in each quadrat was determined by projecting the Kodachrome slides with a carousel projector onto a dot pattern composed of Letratone (Lt 113). The quadrat image was enlarged 3 times and the number of dots that each lichen species covered was counted and divided by the total (23 220) and multiplied by 100 to obtain the percent cover.

One year later, a survey of lichen diversity and vitality was conducted for Suncor within the boundaries of the Syncrude network (Loman 1978). As the results of their work are very relevant to this report, the Suncor study has been extensively referenced.

#### 2.3.4 1979 Partial Resurvey

In 1979, a partial resurvey was conducted to rephotograph a subset ( $\approx 20\%$ ) of the permanent lichen quadrats; to determine if there had been any detectable change in lichen cover and/or vitality in quadrats at a selection of the original 56 network sites; and to collect samples of moss and lichen species for future analysis (Lulman 1980). The 1979 survey was also conducted in order to satisfy the following methodological objectives: to test the practicality of resurveying the lichen plots; to test the practicality of measuring changes in lichen area; to test statistically the data obtained and to recommend improvements in the project methodology.

At that time, no clear relationship could be detected between lichen area changes and the proximity of a hypothetical sulphur dioxide emission source half way between the Syncrude and Suncor plants. However, significant differences in lichen area were detected between the 1979 results and the 1976 baseline data. It was suggested that factors other than sulphurous emissions, such as microclimatic changes, were contributing to habitat changes, and thus to the changes detected in lichen areas.

#### 2.3.5 1983 Complete Resurvey

In 1983, a complete resurvey of the lichen biomonitoring network was conducted.

##### 2.3.5.1 Objectives

The primary objectives of the 1983 study were: to rephotograph the lichen quadrats at as many of the original plots as possible; to make observations of plot conditions, tree conditions, and lichen conditions; to determine from each of the quadrat photographs the mean change in size of *Parmelia sulcata*; to detect any significant trends in the change in

lichen size or condition; to collect samples of *Cladina mitis*, *Hylocomium splendens*, *Parmelia sulcata*, *Peltigera aphthosa* and *Pleurozium schreberi* for future analysis; to collect bark samples for pH analysis; and to recommend improvements in the project methodology.

#### 2.3.5.2 Methods

Thirty-eight of the original study sites were resurveyed. The other 18 sites had been destroyed, damaged, or could not be relocated.

The photographic technique employed in 1983 was compatible with the technique used by Peterson and Douglas (1977) and Lulman (1980), but incorporated significant technical improvements.

The photographic methods utilized in 1976 and 1979 attempted to maintain uniformity of exposure and magnification by using an aluminum sheet metal shadow box and a ring flash or flash unit as a light source. The shadow box was frequently suspended on the trees by means of iron nails driven into the tree above the quadrat and the quadrat was identified by a numbered tag nailed to the tree above the quadrat. This was observed to result in the development of rusty sap tracks which ran through the quadrat, sometimes destroying lichens. A coat or jacket, stuffed around the corners was utilized as a light curtain to prevent light from entering the shadow box. The camera was hand-held and the quadrat was photographed through an opening in the end of the shadow box.

Hand-holding the camera, as in the 1976 and 1979 surveys, introduces the potential for serious error in the determination of lichen cover, since the film plane is not necessarily parallel with the subject plane. Parallax distortion of the photographic images may be one or more orders of magnitude greater than the anticipated growth of some lichens over a three year period. Thus, the comparability of hand-held photographs of the same plot over a series of years is questionable.

In 1983, an improved shadow box system was used which locked the camera lens in a clamp attached to a supporting frame. Once set to the correct focus for the length of the shadow box, the lens (50mm Zeiss f1.4) remained in exactly the same position for every photograph.

The shadow box was covered by a light-weight black cloth. Illumination for each photograph was provided by an electronic strobe unit mounted inside the shadow box which was controlled by a microprocessor in the camera to give exactly the right amount of light for the correct exposure.

Two Contax RTS™ cameras were used to photograph each quadrat. Since the shadow box was rigidly attached to the tree with straps, and the lens was immobilized, the camera bodies could be swapped between pictures. Backup pictures reduced the possibility of losing a series of photographs due to film damage or other accidents.

Kodachrome film (ASA 25) was used to maintain consistency with the 1976 baseline study and the 1979 partial resurvey. It was important to use the same emulsion and process chemistry since a change in film would result in a change in colour rendition of the same lichen, all other factors remaining constant, making the interpretation of lichen colour changes associated with injury even more difficult or impossible. The film was processed at two different times to protect against processor malfunction. All film was sent to and from the Kodak Lab by bonded courier to protect against loss.

A general description report of each study site and each quadrat photographed was dictated in the field. Included in these notes are identifications of lichens in the permanent quadrats and qualitative vitality assessments. Additional notes regarding insect damage, site disturbances, and host conditions were also made.

### 2.3.5.3 Analytical Procedures

#### Analysis of Photography

Previous studies attempted to quantify lichen thallus area by using a slide projector to project the image on a uniform matrix of dots and then counting the dots "covered" by the lichens. Counting the dots turned out to be not only tedious, but also resulted in inaccuracies because of the poor match between quadrat frame and dot grid. This was exacerbated by subjectivity in assessing whether or not dots were "in" or "out" of the lichen thallus margin, and visual problems due to masking of the lichen picture by the dot grid itself. When the 1976 dot grid coverage was recounted for the 1979 partial resurvey, it was found that the cover estimates were not reproducible and that the differences between 1976 and 1979 could be as high as 20 to 30 percent.

The original technique used in 1976 to photograph the lichens and subsequently project their image on a dot grid for counting, introduced additional parallax distortions due to even slight misalignments of the projector. The techniques used in the analysis of the photographs from the partial resurvey of 1979 were an improvement, but suffered from new errors introduced by the projection and tracing technique. The latter was also very time consuming and labour intensive.

Two species of lichens, *Parmelia sulcata* and *Hypogymnia physodes*, were chosen in 1976 for area estimates, primarily because of their wide distribution and flat growth form. These same species were measured in 1979. Examination of the data available at that time revealed that *Parmelia sulcata* contributed 99% of the area measurements. The inclusion of *Hypogymnia physodes* doubled the data analysis steps yet contributed little additional useful information.

The present study utilized the following improved technique which was considered essential for accurate area determinations. The percent coverage of the five largest *Parmelia sulcata* thalli in each of the 1976 and 1983 photographs of the quadrats were determined by projecting the colour positive image onto a Bausch & Lomb HIPAD™ digitizer tablet. The slide was mounted in a photographic darkroom enlarger to ensure the projection did not introduce parallax error and to permit accurate adjustment of the scale of each slide. Fine adjustment was handled via the digitizer tablet software. Scale adjustment was necessary with the 1976 slides because the camera had not been set at the fixed distances from the subject plane, and the 1983 pictures were taken with a 50 mm camera lens rather than a 55 mm lens as in 1976.

The digitizer tablet software incorporated an automatic calibration procedure based on the location of the quadrat marker nails and the distance between upper and lower marker nails. It was recognized that the horizontal distance between marker nails could increase significantly over a few years if the trees were rapidly growing, but the vertical distance between nails was not likely to change since little vertical growth occurs in the area of the trunk base.

The *Parmelia sulcata* thalli were traced using the cross-hair attachment of the digitizing tablet. Consistency was maintained by utilizing only one operator for analysis in all photographs. Differences between repeat measurements, even within different operators, were <1%. The lichen area was calculated in mm<sup>2</sup> using an Apple ///

microcomputer. As each lichen in the quadrat was traced, its outline was displayed on the screen so that no thallus was inadvertently omitted from consideration. The areas were accumulated in data files for future computations. Hard copy images could also be produced if desired for demonstration or additional analysis.

The original slides from 1976 were reanalyzed using the above methods. This was done to ensure data were collected on a consistent basis.

### Selection of Criteria to Monitor Changes in Lichen Size

Before any attempt can be made to determine whether or not there has been any significant change in lichen thallus size, some basic biological principles must be taken into consideration. In addition, certain design problems incorporated into the original plot network design must be dealt with so as to make the systems as consistent as possible.

Mature lichens increase in diameter with nearly the same increment each year, therefore, the best measure of lichen growth is radius increase not area increase (Lock *et al.* 1980). Under normal conditions, this rate is so constant that lichenometric dating of glacial moraines and other surfaces is based on measuring lichen diameter or radius. Change in lichen radius is also a more meaningful expression of lichen growth than is change in area since the latter is size dependent. In some instances, change in area can actually be misleading; for example, if a lichen thallus with an area of 300 mm<sup>2</sup> increases to 400 mm<sup>2</sup> this represents a radial increase of 1.5 mm. On the other hand, if a 30 mm<sup>2</sup> lichen thallus of the same species increases to 130 mm<sup>2</sup> over the same time period this represent a radial increase of 3.3 mm. Thus both have increased by 100 mm<sup>2</sup>, but the second has more than twice the radial increment of the other. It is, therefore, not surprising that Lulman (1980) found, during the partial resurvey of 1979, that the square root of the 1976 area provided the best fit in the linear regression on absolute value of change in the initial 1976 lichen area.

In order to provide the best assessment of lichen change from 1976 to 1983, an equivalent radius [ $r = (A\pi^{-1})^{0.5}$ ] was calculated for each lichen area measured (A), (Hale 1974). Changes in lichen size were therefore expressed in terms of equivalent radius (mm) rather than area (mm<sup>2</sup>).

### Elimination of Excess Variability

The area of up to five mature lichens was measured for each quadrat from both 1976 and 1983 photographs. The largest lichens were selected for measurement since they were the most likely to be in their linear growth phase.

One of the fundamental principles of any scientific investigation of cause and effect is the elimination of as many sources of variability as possible. Three serious problems had to be taken into consideration before any meaningful data analysis could be attempted.

First, the quadrats, which were set up in 1976, were established on a variety of tree species, presumably to provide comparison of response in different plant communities rather than with monitoring of uniform quadrats in mind. Unfortunately, the bark characteristics of the species chosen are sufficiently dissimilar as to invalidate intercomparison of data. The bark of coniferous trees such as white spruce, black spruce, jack pine and balsam fir tends to be acidic, whereas the bark of trembling aspen and balsam poplar is neutral to basic and actually buffers the pH of stem-flow water. Since substrate pH is one of the principal factors controlling establishment, composition and survival of lichen communities, one would expect the deciduous trees to have a unique lichen flora,

and for the lichens present to react differently to exposure to acidifying air pollutants because of the nature of the bark they are growing on.

Another problem associated with the variety of tree species originally used has to do with bark loss. Black spruce and larch are generally slower growing and, as a result, slough bark at a different rate than jack pine or white spruce. The latter two species tend to have more radial growth and subsequently slough more bark. Associated with this is the loss of lichen thalli. The factor of differing growth rate can be reduced by considering only those trees which are in the same diameter class. Balsam fir does not slough bark at all so there is no consequent lichen loss due to bark loss.

The third and fourth problems are related to quadrat placement. The height above ground at which the quadrats were centred and the direction they faced was recorded in the field in 1983. The majority of the quadrats were located between 0.66 and 1.33 metres above ground level and between 315 to 360 degrees and between 0 and 45 degrees; in other words, on the north quarter of the tree near breast height.

Lichen seres are associated with microhabitats found in different places on the tree. These seres form according to the prevailing microhabitat. A lichen growing on the north side of a tree would not be expected to grow at the same rate as one on the south facing side of the same tree. Further, the growth rates of lichens near the ground normally differ substantially from those growing at higher and drier elevations on the same tree.

In order to eliminate as much variability as possible from the data due to differences in bark characteristics and microhabitat, analysis was restricted to data from quadrats on spruce species. White and black spruce dominated all of the sites resurveyed. Further, based on previous biomonitoring design experience, it was known that variations in lichen growth rate could be reduced by restricting the quadrat placement to the same side of the tree at approximately the same height above ground. Therefore, analysis was further restricted to data for the zone of most frequent quadrat placement; i.e., between 0.66 and 1.33 m above the ground on the north quarter of the trees. In addition, instances where the thalli had completely disappeared by 1983 were excluded.

### 2.3.6 Summary of Results

#### Change in Lichen Size

##### Paired t-tests

To test the hypothesis that there was no difference between average lichen radius in 1976 (in north facing quadrats near breast height on white spruce) and average lichen radius in the same quadrats in 1983, a paired t-test was conducted. A paired t-test was selected as these pairs constitute matched observations. It was assumed that the differences, if any, were attributable to air pollution exposure; partially due to increased emissions when Syncrude came on line and partially due to continued emissions from Suncor.

The mean difference between radius scores from 1976 and 1983 was only -0.098 mm. The two tailed probability for this test was 0.21, thus, there was insufficient evidence to reject the null hypothesis that the 1976 and 1983 lichens had similar mean radii. The positive correlation of 0.914 indicated that most of the variability of the mean difference was accounted for, however, this does not mean that lichen size had not changed significantly at the individual sites. Paired t-tests of thalli at individual sites for 1976 and 1983 indicated that significant changes of lichen size had occurred at many of the sites resurveyed. Thus, while average lichen size in the study area as a whole had not changed significantly, real increases and decreases did occur at individual sites.

### Linear Regression

Correlation analysis was utilized to measure the intensity of the association observed between average changes in lichen radius and a variety of environmental parameters, including distance from emission source, elevation above sea level (as an indication of topographic influence), angle from emission source (as an indication of prevailing wind importance), tree bark pH in 1983, sulphur content of *Pleurozium schreberi* in 1983 and in 1976, and the log of distance (since this is a dispersion system). Results of the linear regression analysis revealed that none of these parameters individually accounted for a significant portion of the variability in change of lichen radius.

### Multiple Linear Regression

Multiple linear regression analysis using the same parameters, revealed that 68 percent of the average change in lichen radius from 1976 to 1983 was predicted by the average pH of the bark in 1983, vitality of the lichen, angle from the emission source, the log of distance from the emission source, and elevation above sea level. The remaining variability is most likely due to topographic and meteorological influences affecting plume dispersal.

### Growth Patterns from 1976 to 1983

The average lichen radius changes are presented graphically in a three dimensional perspective plot in Figure 15, which is a view of the study area from the southwest. It is apparent that there are two depressions in the central area of the plot. These are associated with the zones of negative radial increment. There is a depression associated with the Athabasca River bank and its tributaries. Immediately to the west is a more pronounced depression which is associated with the location of the two oil sand plants. Southwest of the oil sand plant sites there is a region of reduced radial growth associated with the Thickwood Hills. There is also a region of reduced thallus radial increase in the Ells River area. It should be noted that lichen growth is not necessarily associated with a positive increase in area. Lichens grow out at the edge while the inner central portions in the oldest areas die and disintegrate or are eaten by invertebrates. Frequently, growth more or less equals replacement.

Figure 16 presents the data on changes in lichen radius in a traditional two dimensional contour map. The contours  $>0.0$  are associated with positive radial increments. This contour map indicates that the most positive growth increments were restricted to remote areas to the west, north, and south. There was a major zone of negative growth increment in the area west of the plants. There were two secondary zones of negative growth increment to the northeast, east and southeast which seem to be associated with topographic heights-of-land downwind of the emission source.

### Lichen Vitality

A subjective assessment of lichen vitality in each quadrat examined in 1983 was made on the basis of both field observations and examination of the quadrat photographs. An average vitality rating was assigned to each site on a scale of 0-3, where 0 indicated absence, 1 indicated morbidity, 2 indicated visible injury, and 3 indicated the lack of visible injury.

It was found that the general vitality of the lichens examined in the field in 1983 improved as the distance from the oil sand plants increased (Figure 17). An examination of the lichens in the 1976 slides revealed that a similar trend existed in 1976, but that the

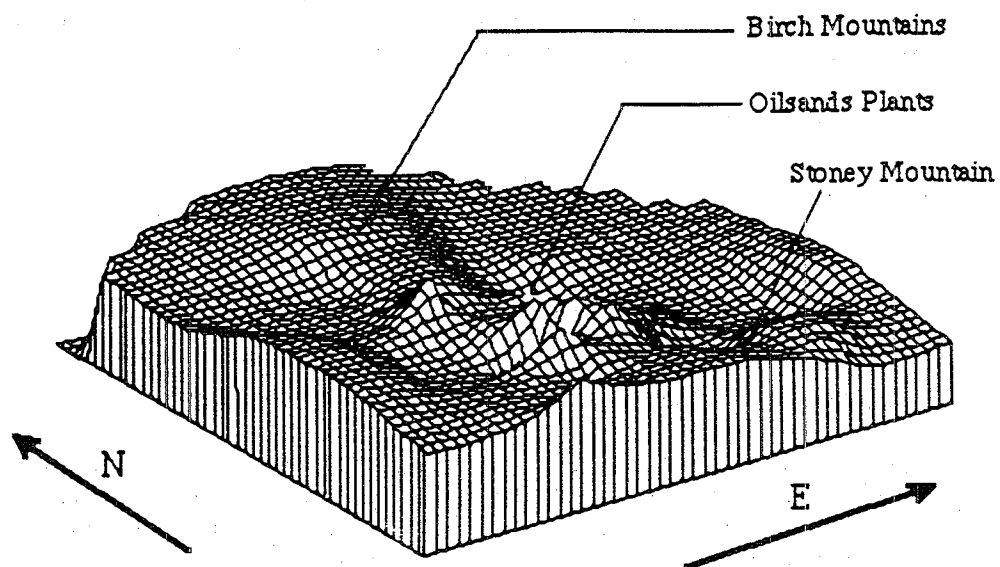


Figure 15

Three dimensional surface of lichen growth patterns for 1976-83. Peaks correspond to greater growth at the following sites: 4, 5, 7, 8, 9, 11, 12, 13, 14, 18, 21, 24, 25, 26, 27, 29, 30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 43, 44, 45, 48, 49, 51, 52, 53,, 54, 55, 56 [see Figure 18]. Hollows correspond to areas of depressed growth.

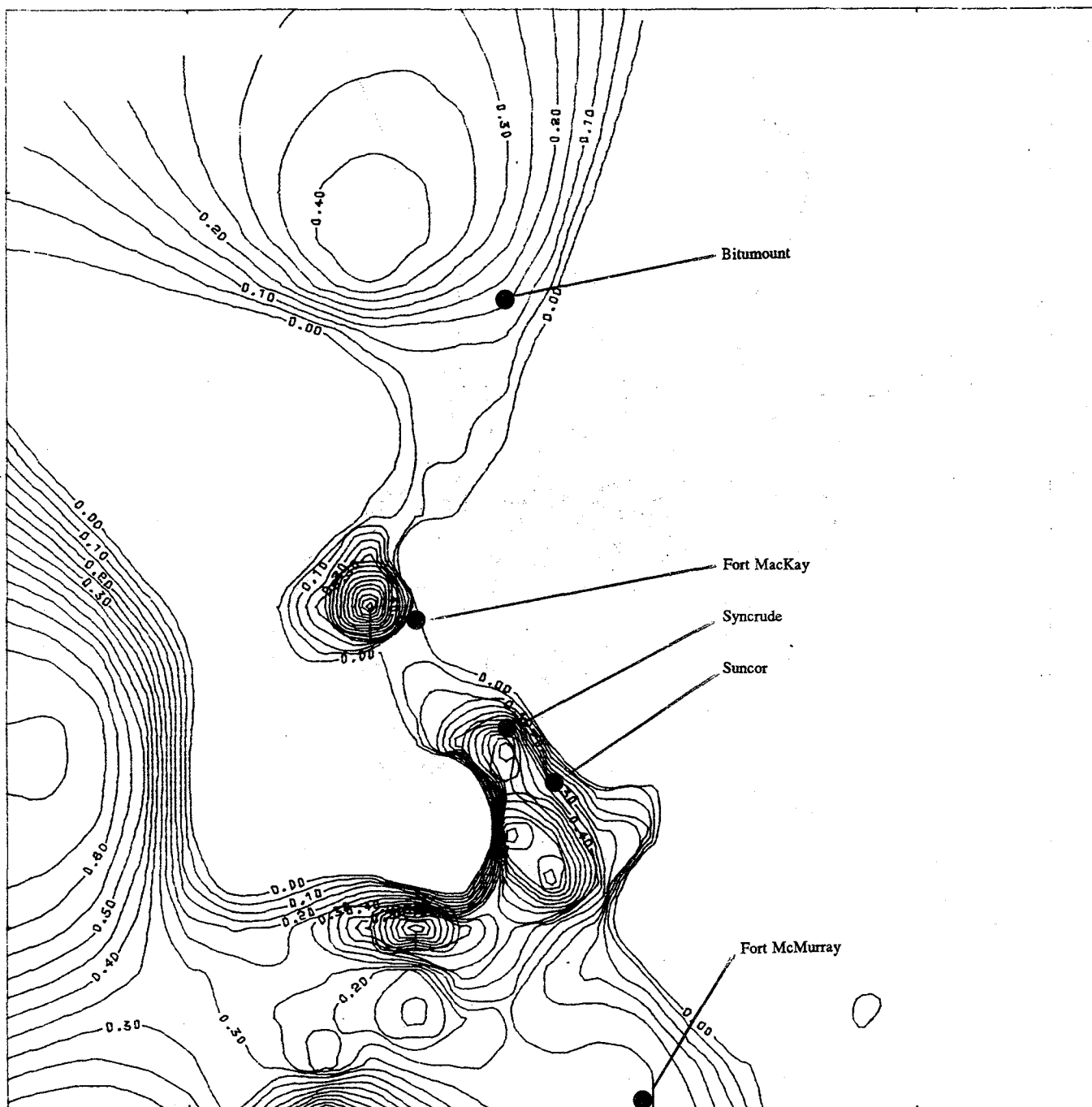


Figure 16

Lichen growth patterns from 1976 to 1983. Contour intervals represent average mm change in *Parmelia sulcata* radius at the following sites: 4, 5, 7, 8, 9, 11, 12, 13, 14, 18, 21, 24, 25, 26, 27, 29, 30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 43, 44, 45, 48, 49, 51, 52, 53, 54, 55, 56 [see Figure 18].

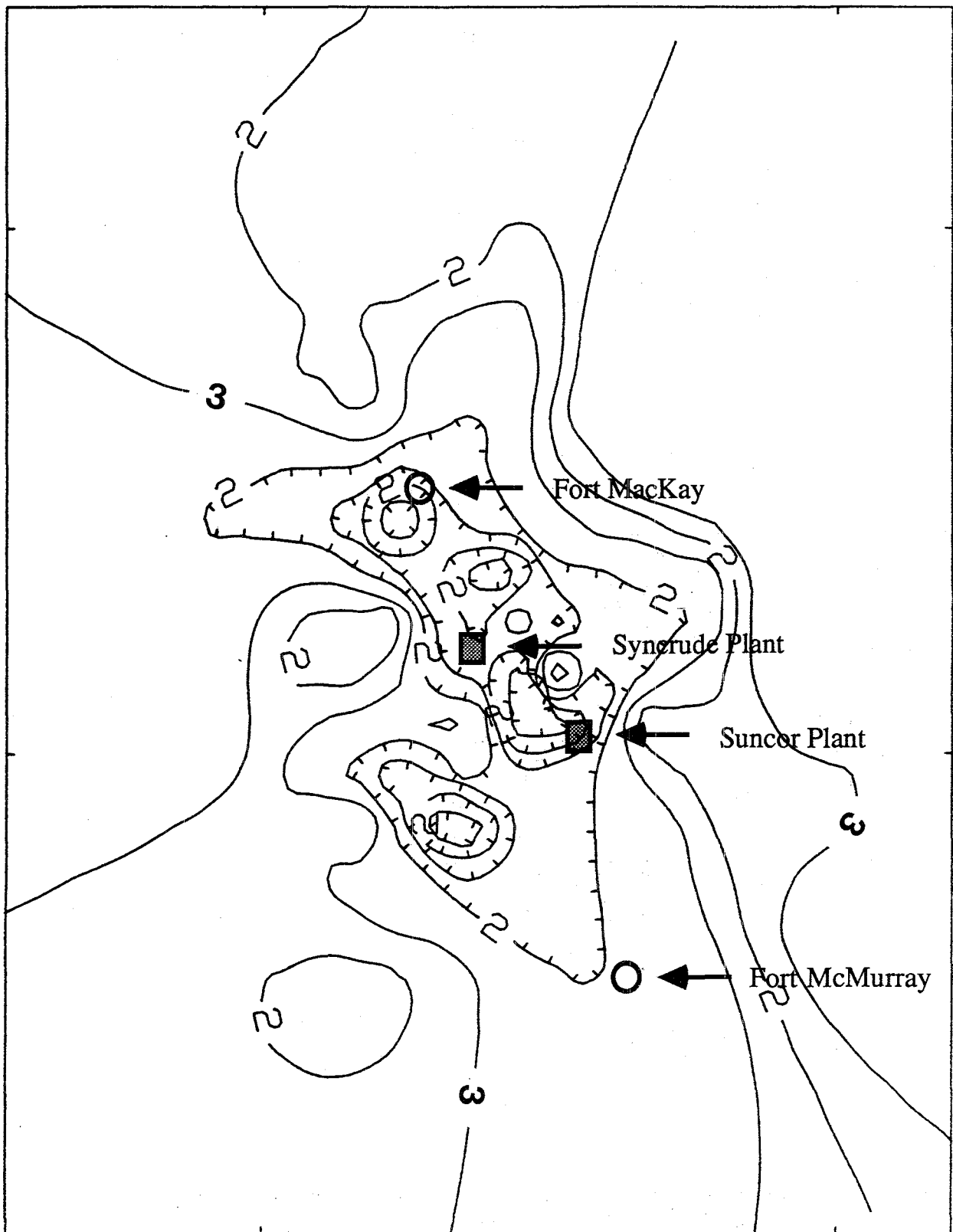


Figure 17

Relative lichen vitality in the oil sands region of Alberta in 1983 at the following sites: 4, 5, 7, 8, 9, 11, 12, 13, 14, 18, 21, 24, 25, 26, 27, 29, 30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 43, 44, 45, 48, 49, 51, 52, 53, 54, 55, 56 [see Figure 18]. Vitality rating scale (3=no damage, 2=damage, 1=morbid, 0=absent).

general vitality of the lichens within a 15 km radius of the plants had decreased from 1976 to 1983. A trend of "overt toxin involvement" (typified by lichens which were deformed and necrotic) affecting diversity was also reported for that region by Loman (1978).

## 2.4 BIOACCUMULATION

In addition to establishing the permanent lichen quadrats at each of the 56 network sites in 1976, bulk samples of two lichens (*Parmelia sulcata*, *Peltigera aphthosa*) and two mosses (*Hylocomium splendens*, *Pleurozium schreberi*) were collected, air dried and packaged into 8 oz. plastic jars with tight fitting lids for future analysis.

The objectives of this portion of the vegetation biomonitoring study were:

- to determine if there had been any significant change in the elemental content of lichens and/or moss tissues in the study area during the period 1976 to 1984, and
- to determine if any relationship existed between the predicted elemental deposition patterns outlined in Section 2.1 and the elemental concentrations measured in lichen and moss tissue samples.

In 1983, to initially test the study design and methodologies, a subset of both the 1976 and 1983 lichen and moss tissue samples were submitted to extensive elemental analyses. It was assumed that no significant change in element contents of the samples collected in 1976 would have occurred during storage since they were dried and in plastic bottles with tight fitting screwcap lids. Several important observations were made on the basis of these preliminary analyses. First, the content of almost every element measured in the 1983 cryptogamic samples increased as the oil sand plants were approached. Second, this inverse relationship between elemental content and distance from emission source also existed in the samples collected in 1976. Third, the elemental content of some elements, such as S and Hg, in 1983 samples, did not drop to expected background levels within the limits of the 1976 network of lichen monitoring sites. Finally, the study design and methodologies were shown to be adequate for the objectives of the study.

In 1984, the same species were collected at 60 additional sites in an expanded area with a radius of approximately 100 km from the plants (Figure 18). In addition, *Populus tremuloides*, and *Salix* species, were added to the list of plants to be collected. All samples were refrigerated and then air dried and stored in 8 oz. plastic jars with tight fitting lids.

### 2.4.1 Methods

#### 2.4.1.1 Collection of Samples for Elemental Analysis

Samples of *Cladina mitis*, *Evernia mesomorpha*, *Pylaisiella polyantha*, *Hylocomium splendens*, and *Pleurozium schreberi*, *Salix* sp., *Usnea* sp. and *Populus tremuloides* were collected, if present, at each sampling site and placed into white bleached paper sample bags. These samples were refrigerated as soon as possible and kept cold, but not frozen, until they could be air dried and sealed in nalagene wide mouth bottles with tight fitting lids; the usual procedure for storage. Approximately one litre samples were collected at each site according to availability. Special precautions, including the use of rubber surgical gloves, were taken to prevent contamination of the samples during or subsequent to collection. In addition to collecting samples in the oil sands area, samples were collected in remote regions to provide a benchmark and to develop an understanding of how much above the "normal" expected levels, the elemental content were in samples

# Location of Study Sites Athabasca Oil Sand Area

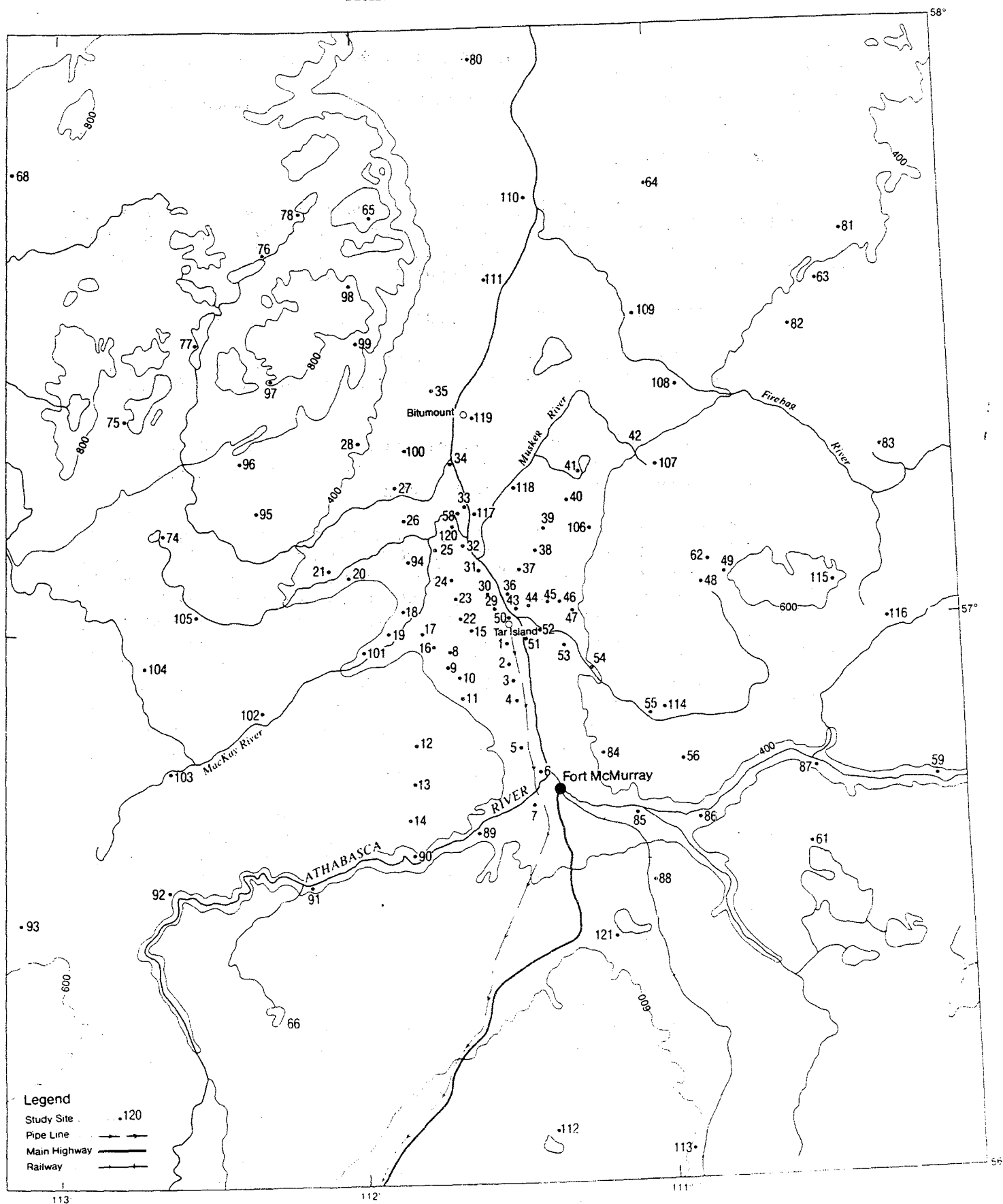


Figure 18

Location of sampling sites in the Athabasca oil sand area.

from the network. A set of samples were also collected from near Fort McMurray (FM7), Cold Lake (CLK), Whitemud Creek in Edmonton (Wm), Winterburn near Edmonton (Wtb), and Glenmore Park in Calgary (Glen) to provide a perspective on elemental concentrations in urban areas.

#### 2.4.1.2 Elemental Analysis

A total of 626 samples of *Cladina mitis*, *Hylocomium splendens*, *Pleurozium schreberi*, *Usnea* sp., *Populus tremuloides*, and *Salix* sp. were analyzed for the 48 elements (Table 15); representing over 30,000 individual concentration measurements. The concentrations of Al, As, Au, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Dy, Eu, Fe, Hf, La, Lu, Mg, Mn, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, and Zn were determined by Induced Neutron Activation Analysis. The concentrations of Ag, Be, Cd, Cu, Ni, P, and Pb were determined by Direct Current Plasma spectroscopy. The K concentration was measured by Atomic Absorption. The S and Zr content were measured by X-ray fluorescence. Hg concentration content was determined by cold vapour distillation. The analyses were performed by Nuclear Activation Services Limited, Hamilton, Ontario. All determinations were on a dry weight basis.

Table 15. Elements measured in vegetation samples from the oil sands area, along with the detection limit and units.

Element	Detection Limit	Measurement Unit	Element	Detection Limit	Measurement Unit
Ag	0.5	ppm	Mn	0.3	ppm
Al	0.01	%	Mo	0.03	ppm
As	0.02	ppm	Na	1	ppm
Au	0.1	ppb	Nd	0.1	ppm
Ba	2	ppm	Ni	1	ppm
Be	10	ppm	P	10	ppm
Br	0.005	ppm	Pb	2	ppm
Ca	0.05	%	Rb	0.6	ppm
Cd	1.0	ppm	S	50	ppm
Ce	0.1	ppm	Sb	0.005	ppm
Cl	40	ppm	Sc	0.001	ppm
Co	0.005	ppm	Se	0.01	ppm
Cr	0.1	ppm	Sm	0.001	ppm
Cs	0.01	ppm	Sr	10	ppm
Cu	0.5	ppm	Ta	0.02	ppm
Dy	0.5	ppm	Tb	0.005	ppm
Eu	0.005	ppm	Th	0.001	ppm
Fe	0.005	%	Ti	20	ppm
Hf	0.02	ppm	U	0.005	ppm
Hg	10	ppb	V	0.3	ppm
K	100	ppm	W	0.01	ppm
La	0.01	ppm	Yb	0.005	ppm
Lu	0.0001	ppm	Zn	2	ppm
Mg	500	ppm	Zr	50	ppm

#### 2.4.1.3 Computer Graphics

##### Mapping Elemental Contents

Tabular presentations of data (along with some limited descriptive statistical summaries) have been the traditional means of presenting the raw results of chemical determinations. However, large tables of numbers, presenting results for many variables and several species, are not conducive to data interpretation, understanding relationships between contaminant deposition and bioaccumulation, or to the visualization of patterns of elemental variability throughout a geographic region. A more suitable method for dealing with large sets of data is the use of computer generated contour maps and three dimensional perspective surfaces. These types of figures allow the investigator to present the results in a graphic form and thus quickly sort through large sets of data and identify patterns of element bioaccumulation in the environment which might not have been detected by more traditional statistical techniques.

SURFACE II, a commercially available mapping software package, was used to prepare elemental content contour maps from elemental concentration data sets.

Interpretation of the resulting maps must be done with the following caveat in mind: computer generated contour maps are based on extrapolation, therefore, their reliability increases as the number of data points in the area of interest increases. Generally, however, computer generated maps are more reliable than maps drawn by hand, in the sense that introduced bias is less, or at least is consistent both over the entire mapped area and between maps.

##### Comparison of Elemental Content

Several methods exist which can be employed to compare the elemental concentration data bases. A valid and intuitively satisfying approach to data base comparison is by map comparison. Thus, the first step in this study was to visually inspect the contour maps prepared from the data base.

After visual inspection, several more sophisticated techniques were employed to compare spatial distributions, and to give overall measures of similarity or differences between the two data sets (Davis 1973).

##### Overall Similarity

After similar patterns of element content in two data sets (e.g., bioaccumulators and air quality distribution data) were identified by visual inspection, the significance of these relationships were measured. Overall similarity can be measured by the computation of correlation coefficients of one data set with the other. This correlation coefficient is a measure of overall correspondence between the two variables. A major draw back of this simple approach is that a given correlation value does not necessarily reflect the degree of correspondence over the entire study area, and may be the result of a large deviation in a small region of the study area.

##### Isopach Maps

The results to date provide a set of reference values from the 1976 samples which were compared with 1983-84 results to identify areas where elemental contents had increased, decreased or not changed.

When two maps are compared, based either upon the same variable measured in the same region at different times (i.e., Ni content in a lichen in 1976 and 1983) or upon predicted versus observed values, it is useful to construct an isopach (difference) map. To prepare an isopach map, the two data matrices generated by the mapping program to produce contour maps are subtracted from each other and the resulting matrix is used to produce an isopach contour map. The isopach contour map shows where changes have occurred, their magnitude, and the degree of agreement between observed values, say, and those predicted by a dispersion model. When data sets from three or more time periods are available, it is possible to determine rates of accumulation.

One problem inherent in comparing maps based on predicted and observed variables is that the two maps may be expressed in different units. In order to compare maps in this study, it was necessary to first convert them to a standardized, unitless, form. To do this, the concentration data were converted to standard normal form:

$$Z_i = (X_i - X_{avg})/\sigma$$

where  $X_i$  is the elemental measurement at site  $i$ ,  $X_{avg}$  is the average concentration over all sites, and  $\sigma$  is the standard deviation. After the data on each map had been standardized they were contoured in the conventional manner. The contour values are in units of standard deviation from the mean.

### Product Maps

Difference maps produced by isopach techniques can be ambiguous; for example, a positive difference can result by subtracting a large negative area from a low positive area or by subtracting a low positive area from a high positive area.

If parts of two surfaces deviate from the mean in the same direction and are subparallel, a series of points common to both surfaces would be positively correlated. The more closely the two surfaces correspond, the higher the correlation between them. Conversely, if two surfaces deviate from the mean in opposite directions, they would be negatively correlated.

When the surfaces have been standardized, it is not necessary to compute a correlation coefficient to obtain a measure of similarity between them. Instead, the surfaces can be multiplied together. If both surfaces deviate from the mean in the same direction, their product will be positive. If they deviate in opposite directions, their product will be negative. Product maps were utilized in the present study to identify areas of positive and negative correlation between elemental deposition predicted by models and observed bioaccumulation.

### 2.4.2 Summary of Results

To interpret and understand the results it is important to note that the mineral content of a lichen is variable and depends on the nature of the ecosystem in which it is growing, its substratum and the background elemental composition of precipitation and airborne particulate matter, as well as the urban-industrial fallout patterns. Unlike higher plants, lichens do not have a well-developed cuticle and hence there is no physical barrier to impede elemental exchange with the environment. Consequently, lichens can accumulate mineral elements to levels far greater than their expected physiological needs. Lichens are perennial and this feature, together with the other characteristics, has led to the use of these plants as long-term integrators of deposition from the atmosphere of elements originating from both natural and man-made sources.

The trapping of particulates, and their subsequent decomposition, contributes significantly to the elemental levels found in lichens. Thus lichens reflect the elemental composition of the particulate matter deposited on the thalli. The differences between lichen samples collected at sites near, and remote from industrial installations, reflect the differential deposition of industrially discharged particulates.

In studies utilizing lichens as integrators, it is typical to clean samples of debris, dry and then mill them (or crush them in liquid nitrogen and subsequently dry them).

All samples collected were carefully cleaned of debris, as is the practice in large scale regional lichen and moss heavy metal bioaccumulation surveys (e.g., Steinnes 1977; Folkesson 1981; Rinne and Barclay-Estrup 1980; Pilegaard *et al.* 1979; etc.). The unwashed samples were then oven dried and ground before analysis.

There was concern that a vigorous washing technique capable of removing surficial particulate matter, such as is found on lichens growing near roadways, would leach out soluble metal compounds (Lawrey and Rudolph 1975), and compounds weakly bound by extracellular binding or complexing processes (Nieboer *et al.* 1978). Samples collected well away from roads, however, do not experience this type of contamination. All of the sites in this study were located well away from road ways; in fact, the majority were accessed by helicopter.

Particulate matter deposited on lichen thalli rapidly becomes inextricably bound within the matrix of the cortex as the fungal hyphae grow up and around the deposited particles. The weak acid properties of lichen thalli and the metal-complexing ability of some of the extra-cellular lichen substances found on the hyphae provide conditions favourable to the chemical decomposition of trapped particulates. The biogeochemical weathering is further facilitated by the natural periodic drying and wetting of the lichen thalli (Nieboer *et al.* 1978). The contraction and expansion accompanying the wetting and drying may also aid in the mechanical distintegration of the particles (Syers and Iskandar 1973).

Any trace element detected in the tissues of woody angiosperms may have entered by a variety of routes, some of which potentially may contribute more than others. Uptake from the soil, in most circumstances, would be expected to be the major route. Factors affecting the amount of metal taken up via the roots include the degree of soil contamination, the availability of the various metals to plant roots, the distribution of the metals in the soil profile relative to the rooting depth of the tree species under consideration (Martin and Coughtrey 1983), the degree of mycorrhizal infection of the roots (Jones *et al.* 1985), and whether or not any acidic compounds have been added to the soil which can affect the solubility of metals in the soil.

Atmospheric deposition and uptake via the leaves and bark generally account for a much smaller proportion of the trace elements entering trees. Although foliar uptake and translocation of lead nitrate and cadmium chloride have been demonstrated (Hemphill and Rule 1975), there is little evidence to suggest that foliar uptake of particulate heavy metals is anything more than of minor importance in contributing to the metal concentrations in wood or leaves. The majority of heavy metals deposited on leaves are, as particulates, of extremely low solubility in that environment (Martin and Coughtrey 1983). Thus, while heavy metal burdens of leaves provide a reliable index of particulate matter deposition, they may over estimate the bound, heavy metal tissue levels. Once the elements have entered the tree, however, there will be a certain amount of redistribution via translocation, radial transfer and diffusion (Lepp 1975).

As a consequence of the fact that heavy metals in particulates are likely to be more soluble in the acid environment of soil, and because the heavy metals are not readily translocated to upper parts of the tree, root development and health could be affected before, and to a greater extent, than physiological processes in the upper parts of the tree. As a result, an imbalance could develop between the above and below ground parts of the plant. At this time, little information is available about heavy metal deposition on soil or metal content of the roots of woody angiosperms in the Athabasca oil sands region.

#### 2.4.2.1 Sulphur

##### Lichens and mosses

The regional pattern of S concentration in *Pleurozium schreberi* as of 1976 is illustrated in Figure 19A. At that time, the maximum S concentration was approximately 2100 ppm. The region of maximum S content was associated with the Suncor plant. The flat base represents the expected background concentration (based on literature survey and analysis of samples from remote sites) and the observed S content of *Pleurozium schreberi* does not drop to that level within the area of the 1976 network of sites. The sharp drop-off near the edge of the figure represents the extrapolation limits of the computer map.

Figure 19B presents the S concentration measurements of *Pleurozium schreberi* sampled from a larger area in 1983 and 1984. In this figure, the central peak was in the same location, but the base was much broader and the maximum value approached 2500 ppm. In addition, greater detail was added to the deposition surface pattern as a result of the increased number of sampling sites in the study area. For example, a second minor accumulation of S can be detected in association with the Birch Mountains in the extreme northern regions of the study area. This accumulation peak may have existed in 1976 but no samples were collected for such remote sites in 1976, thus these peaks would have gone undetected. It is important to recognize that elevated S concentrations were detected at less remote sites, 50 km away from the oil sand plants, in both 1983 and 1976.

Figures 20A and 20B present transects from N-S and NW-SE over the oil sand plants. It is apparent that, within the limits of the original lichen monitoring network, the S content was generally about double the expected background level by 1976. By 1983, the S content of *Pleurozium schreberi* in the region had increased by about the same increment as from 1966 to 1976 (based on expected background values extrapolated from an extensive review of the published scientific literature as well as analysis of samples collected from remote sites) (Figures 21A and 21B). Therefore, there is little evidence of an increase in the rate of accumulation except at the sites nearest to the oil sands plant (Sites 29 and 30).

##### Vascular plants

Elevated sulphur levels which accompany SO<sub>2</sub> exposure in nonvascular plant samples presented the possibility that vascular plants might also have elevated S levels as a result of the same SO<sub>2</sub> exposure. Regional patterns of S content of *Populus tremuloides* as of 1984, are shown in Figure 22. In general, S concentration was greater in the immediate vicinity of the oil sands plants, especially along the Athabasca River Valley. Higher S contents were also found in the Birch Mountains, Muskeg Mountains, Thickwood Hills, and Stony Mountains.

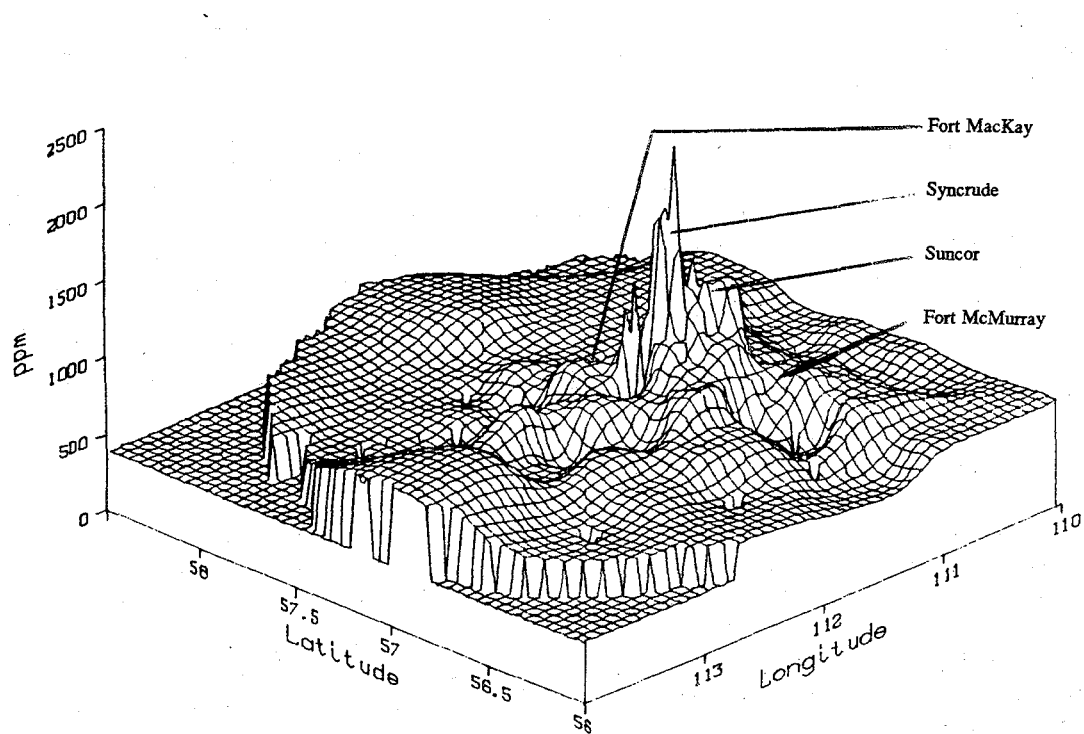
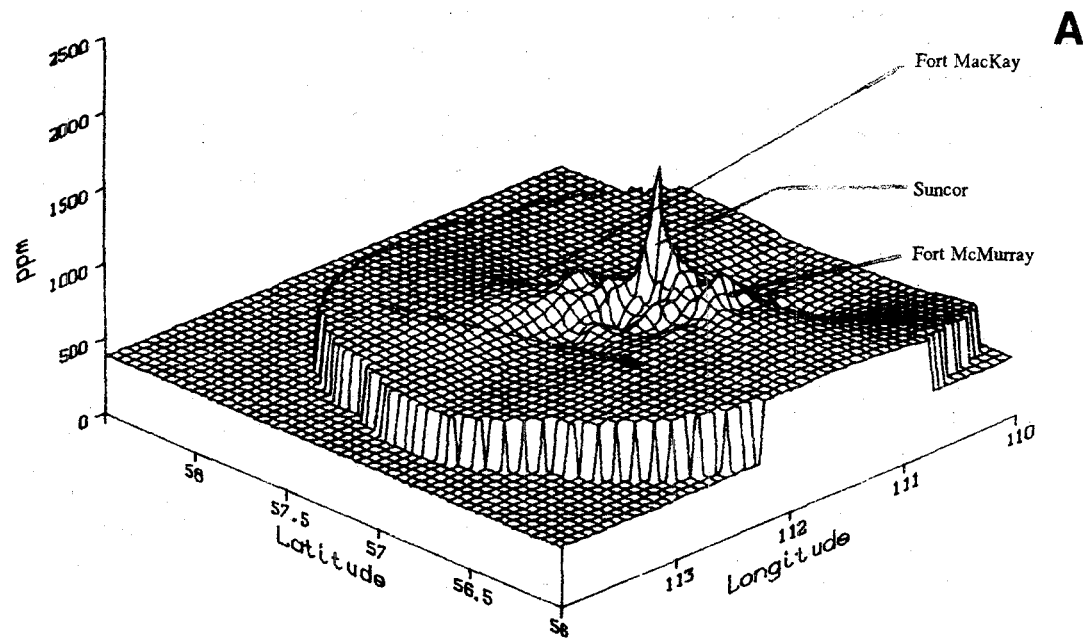


Figure 19

Regional pattern of S content in *Pleurozium schreberi*, as of 1976 (A) and 1983-84 (B).

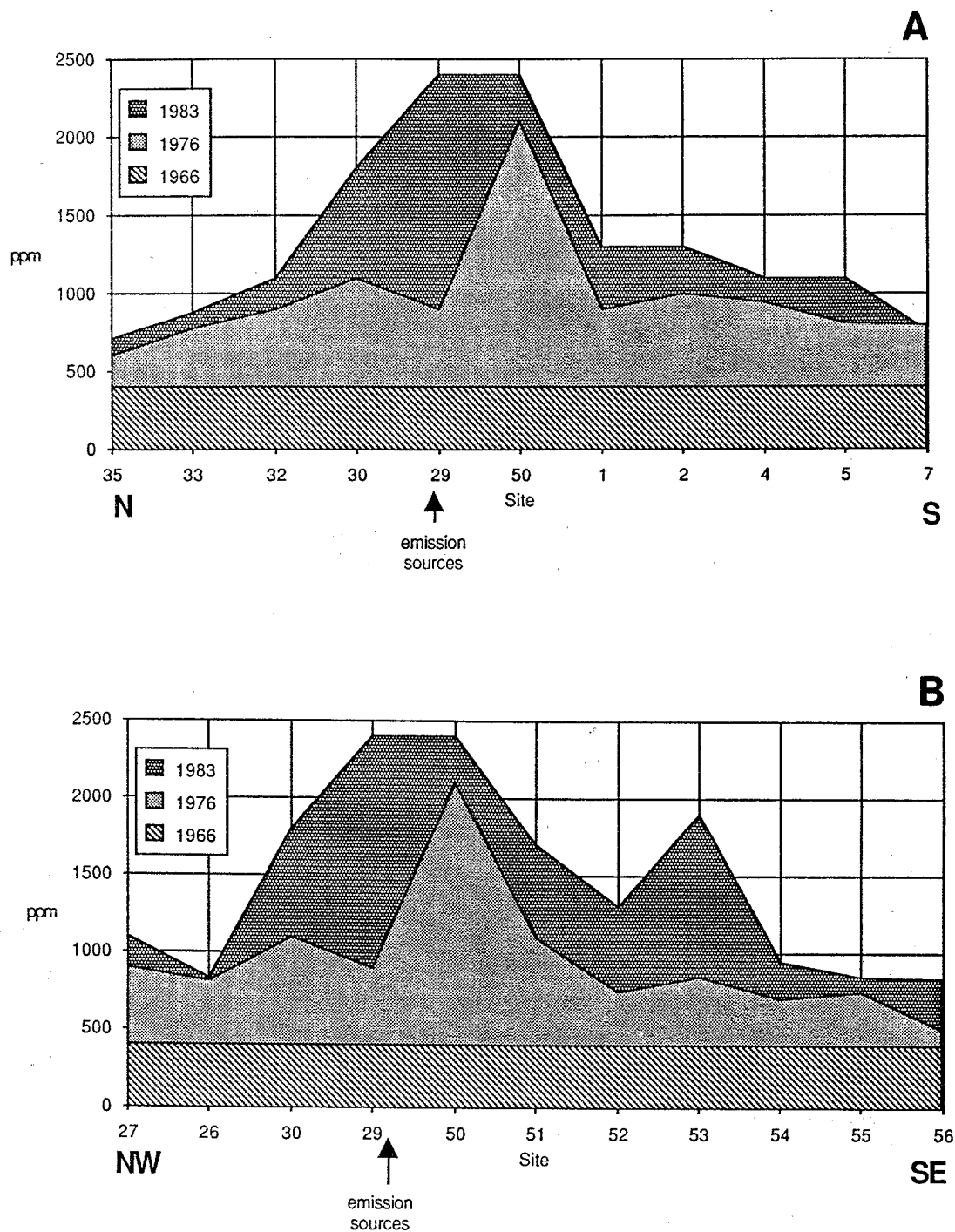


Figure 20 Changes in S content of *Pleurozium schreberi*, at the sampling sites along N-S (A) and NW-SE (B) transects crossing over the oil sands plants.

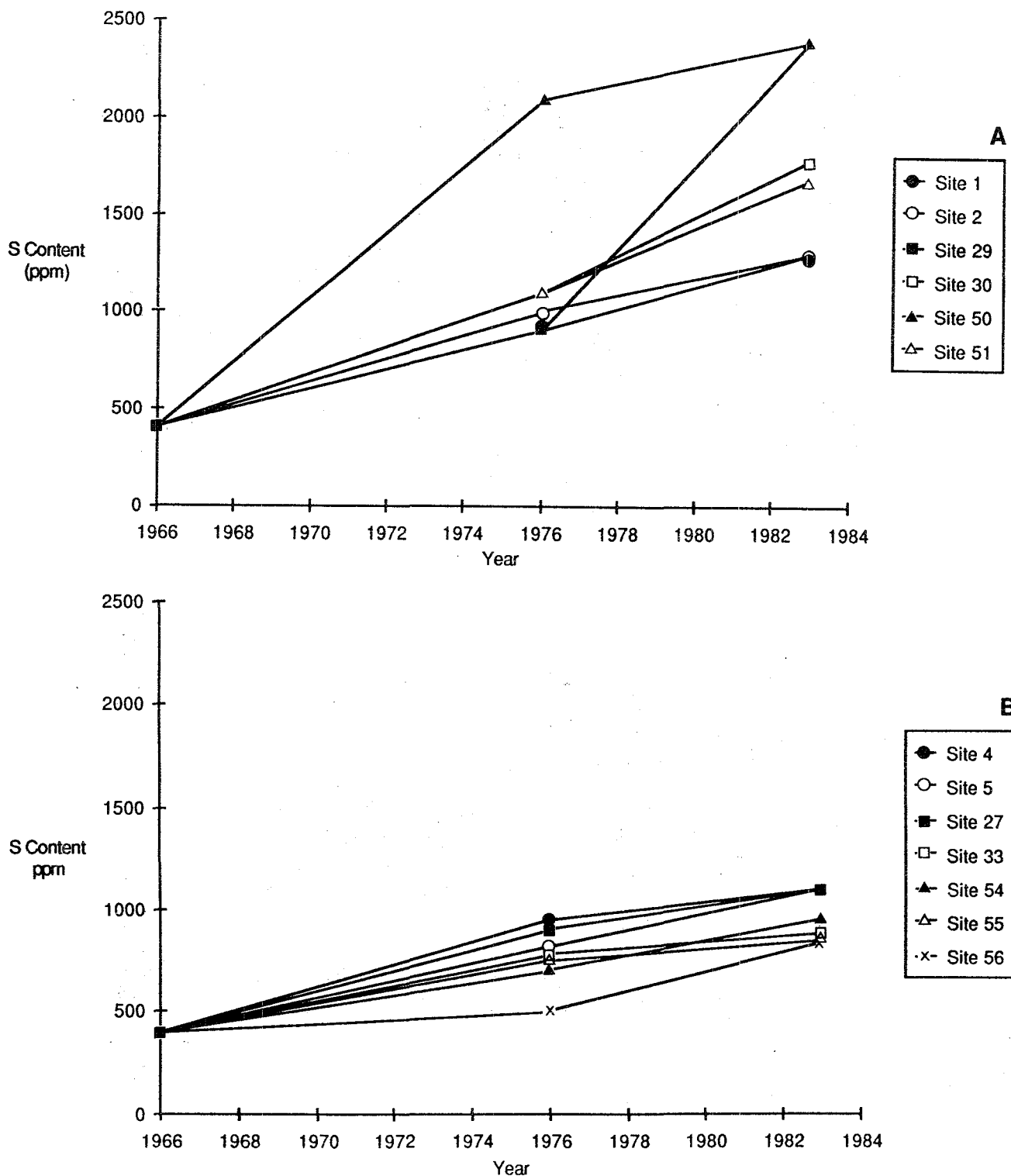


Figure 21

Changes in S concentration in of *Pleurozium schreberi*, at sites near (A) and remote from (B) the oil sands plants, from 1966 (pre-Suncor [formerly GCOS] start up) (value based on measurements for remote sites and a literature survey) to 1983 (see Figure 18).

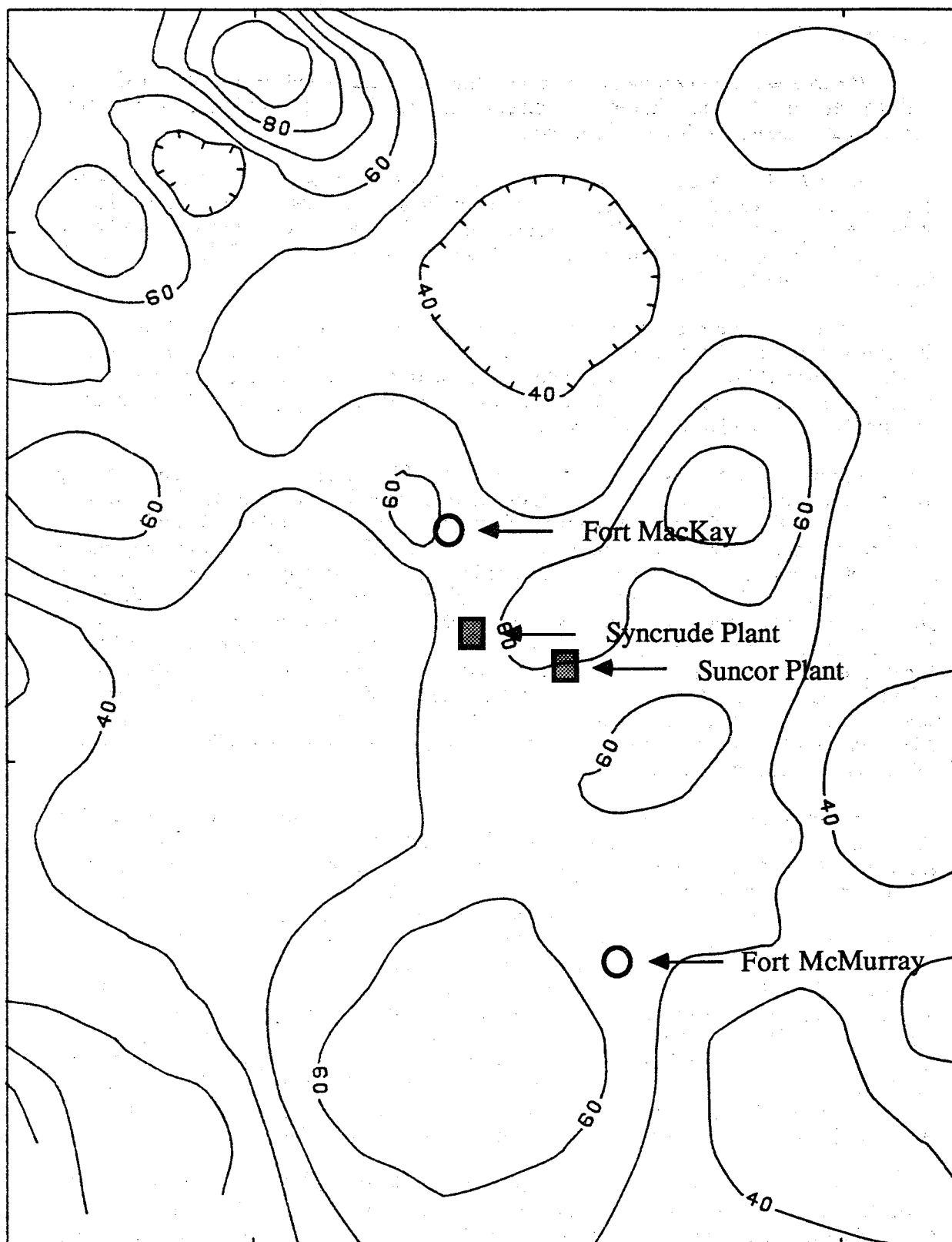


Figure 22

Regional pattern of S concentration (ppm) in trembling aspen (*Populus tremuloides*) in the oil sands region of Alberta, 1984. Contour interval is 10 ppm.

#### 2.4.2.2 Heavy Metals

##### Lichens and Mosses

*Pleurozium schreberi* elemental concentration measurements revealed the existence of three patterns of accumulation: (i) elements associated with particulates; (ii) elements dispersed as vapour; and (iii) traffic related.

In 1976, the concentration of those metals associated with particulate emissions (e.g., Al, As, Fe, Mg, Ni, Ti, V, etc.) increased in lichen and moss tissues as the oil sand plants were approached (Figure 23A). Other studies also showed elevated levels of heavy metals in lichens growing in the vicinity of oil sands plants in the late 1970's (Loman 1978; Addison and Puckett 1980).

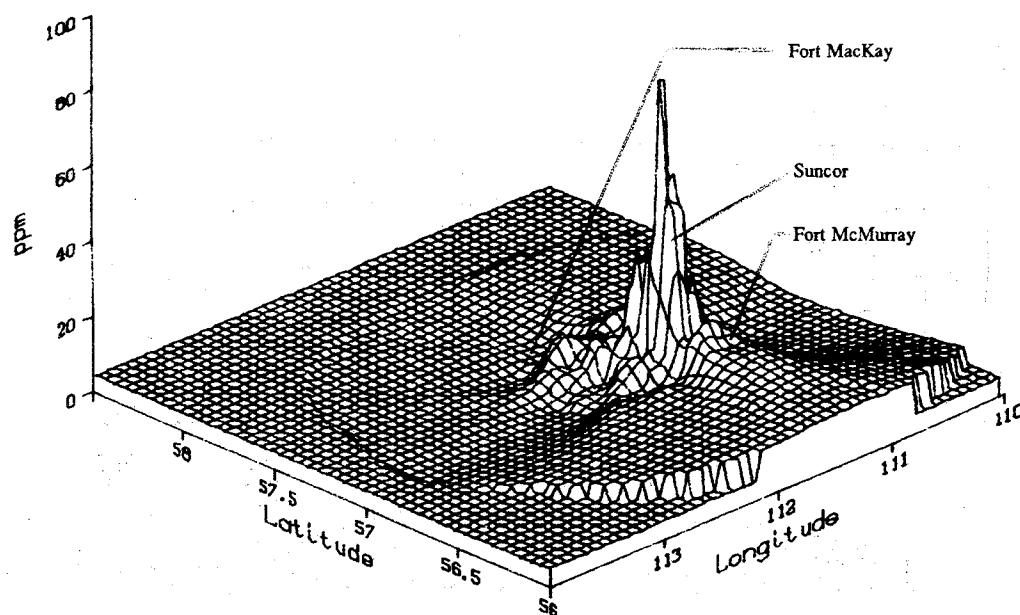
Analysis of the *Pleurozium schreberi* tissue samples collected in 1983 shows that the concentrations of these metals associated with particulate emissions had further increased since 1976. In addition, metals associated with particulates, such as Ni, were almost totally deposited within a 50 km radius of the oil sands plants as little evidence of enrichment was found beyond this distance.

Figures 24A and 24B present N-S and NW-SE transects, respectively, crossing over the oil sand plant sites. Ni contents of *Pleurozium schreberi* collected in 1976 were elevated above the background level throughout the study area, but the region of principal increase was near the Suncor plant (sites 1, 2, 4, 29, 30, 50, 51, 52). By 1983-84, the Ni content of *Pleurozium schreberi* had increased incrementally throughout most of the study area. There was little or no increase in the immediate vicinity of the Suncor plant site (sites 50 and 51) between those samples collected in 1976 and those collected in 1983; 6 years after Syncrude commenced plant operations. Thus the rate of accumulation of Ni in *Pleurozium schreberi* has been constant or has actually decreased within the confines of the original lichen network (Figures 25A and 25B). The rate of Ni accumulation in *Pleurozium schreberi* has apparently increased slightly only at site 4. The cause for this is unknown. Ni content of *Pleurozium schreberi* samples collected in 1983 were generally greater than in samples from the same sites in 1976.

Elevated levels of Hg, emitted by oil sands plants as vapour, were measured in *Pleurozium schreberi* samples collected in 1976, with the maximum concentrations in tissue samples collected near the existing oil sand processing plant then in operation (Figure 26A). Samples of *Pleurozium schreberi*, collected in 1983-84 from the same sites, and at additional sites as well, revealed that the maximum Hg concentrations were greater than in 1976 within a 10-20 km radius of the plant sites, but that the pattern was not regularly shaped as might be expected as a result of deposition due to emissions from a point source (Figure 26B). Elevated levels also were associated with heights of land, such as Birch Mountain, Muskeg Mountain and the Thickwood Hills. This could be the result of impingement of the vaporous material on these heights of land. It could also be related to the presence of Hg containing sedimentary rocks such as the organic rich shales and sandstones near the ground surface (Kabata-Pendias and Pendias 1984). The lack of a single source would explain the lack of a systematic concentration drop off to a background level within the limits of the original network, in either 1976 or 1983.

Pb content of *Pleurozium schreberi* tissue collected in 1976 was about twice the expected background level throughout the study area (Figure 27). The greatest accumulations were in the areas with the greatest vehicular traffic. By 1983, the Pb loading of *Pleurozium schreberi* tissue had further increased over the 1976 values in the vicinity of the oil sand plants. The greatest accumulations were associated with Highway 63 north of Fort McMurray (Figure 28). There were smaller peaks associated with the road to the

**A**



**B**

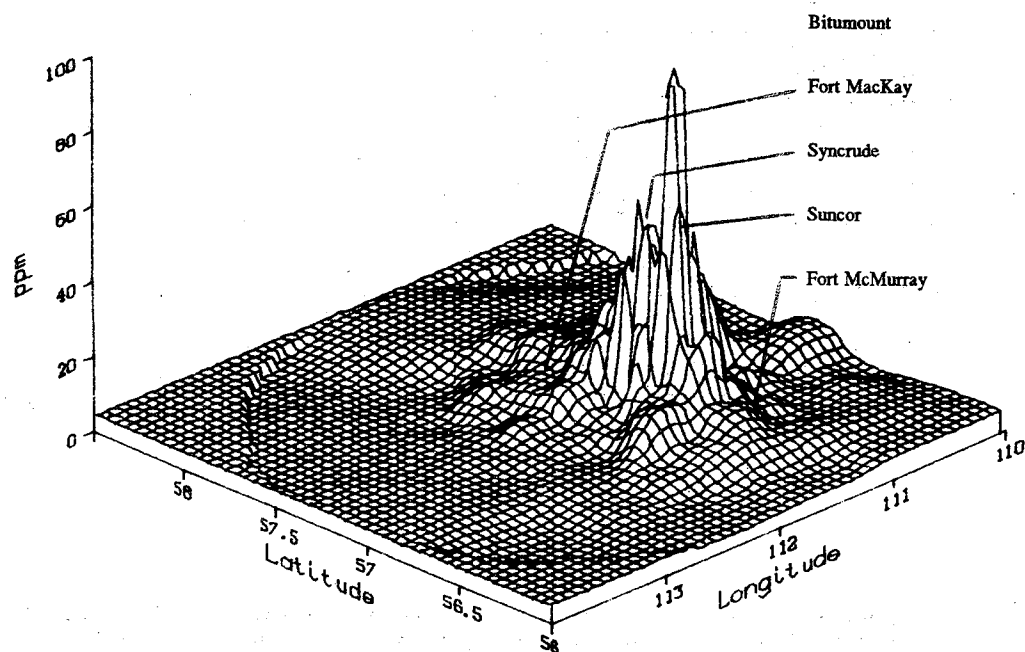


Figure 23

Regional pattern of Ni concentration (ppm) in *Pleurozium schreberi* in the oil sands region of Alberta, 1976 (A) and 1983-84 (B). This pattern was typical of most elements measured which are associated with particulates.

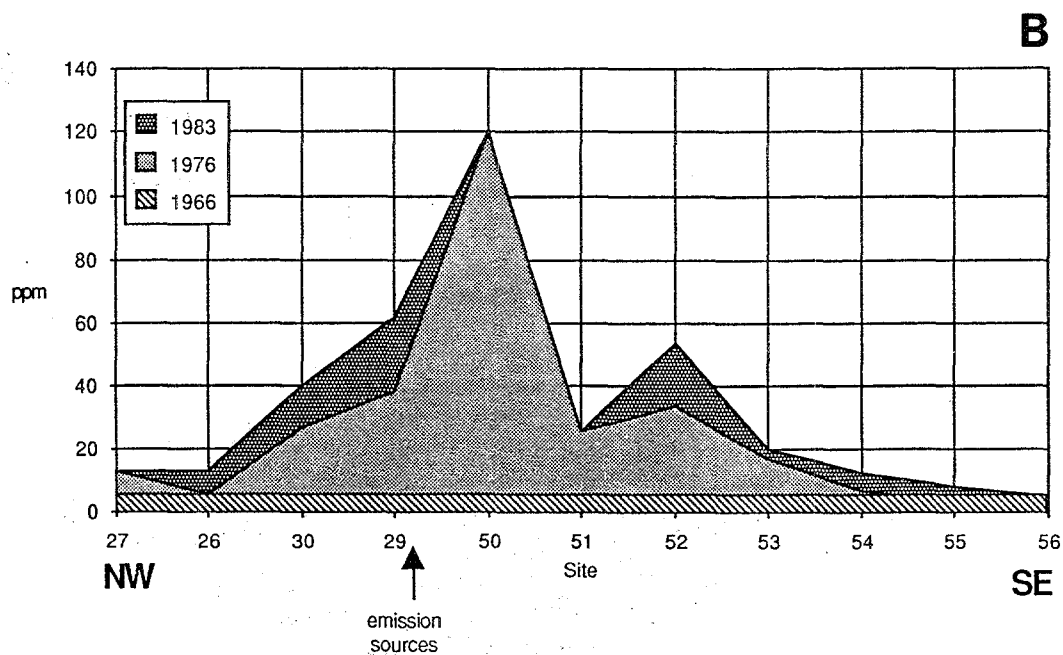
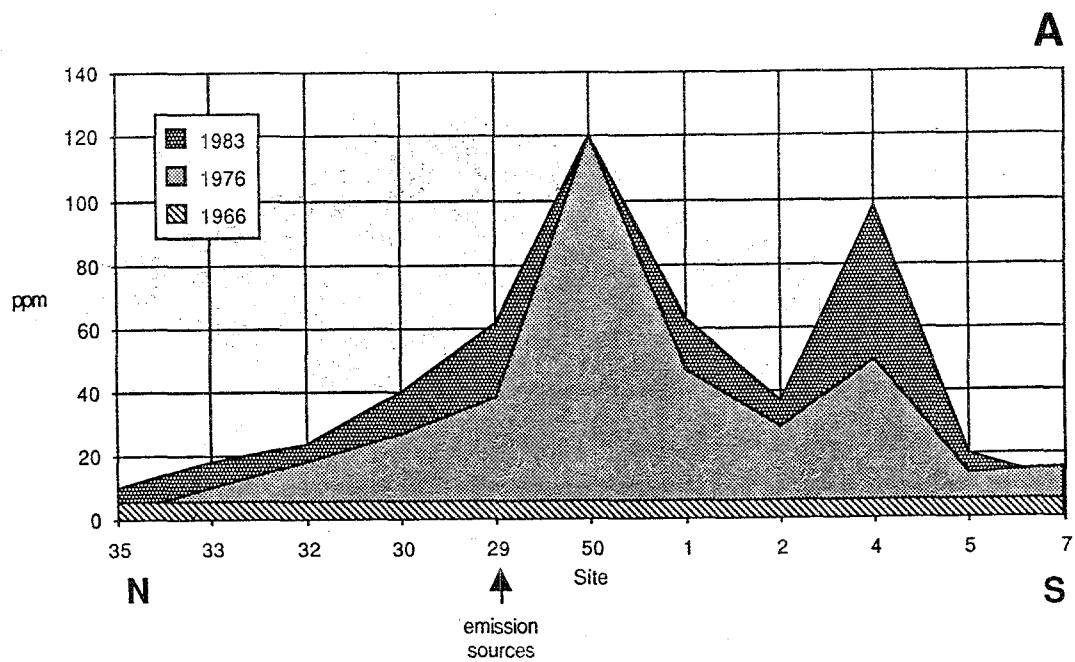


Figure 24

Changes in Ni concentration (ppm) of *Pleurozium schreberi*, at sites along N-S (A) and NW-SE (B) transects crossing over the oil sands plants. This pattern was typical of most elements measured which are associated with particulate emissions.

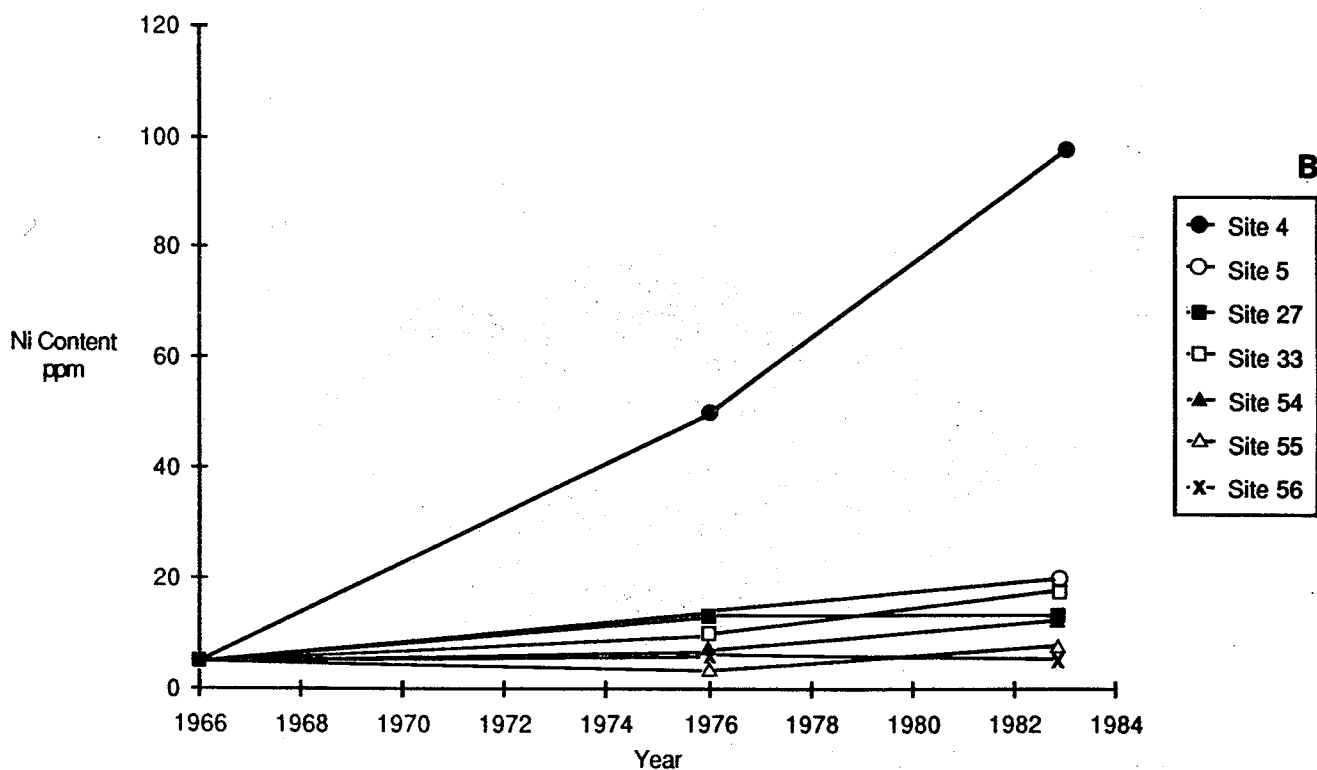
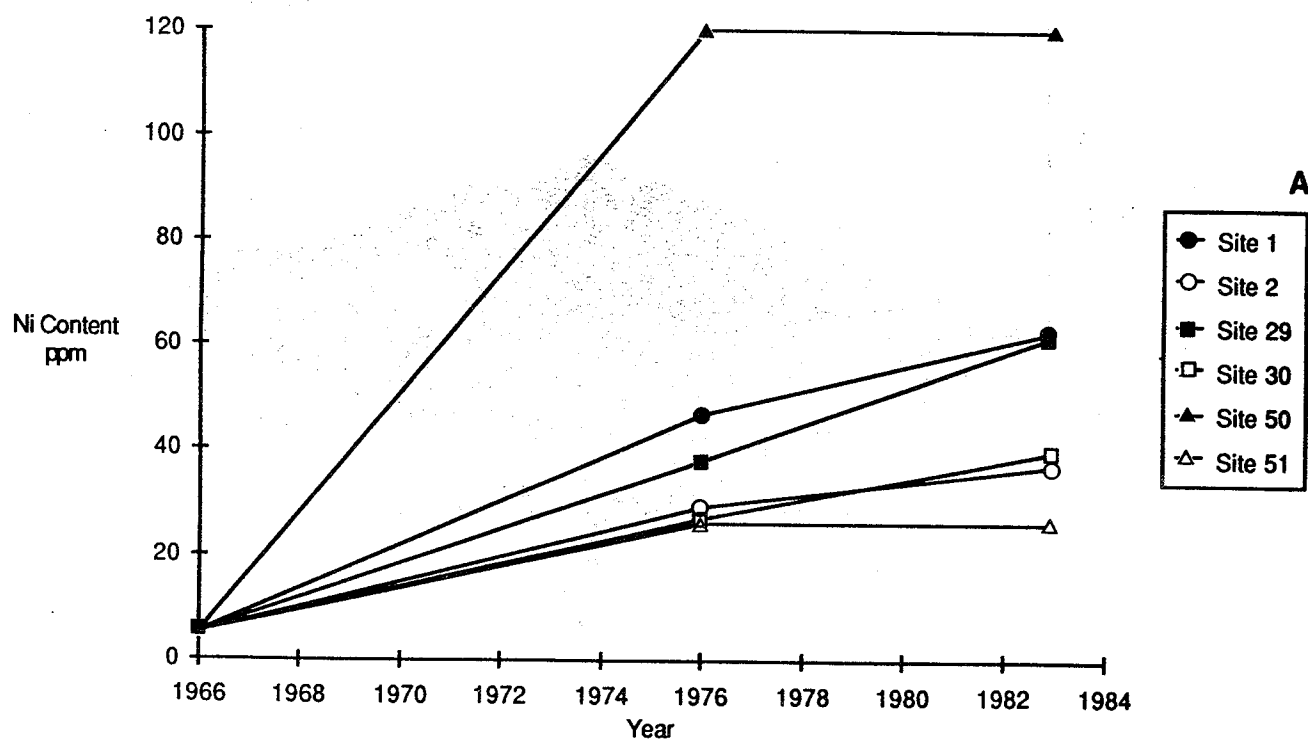


Figure 25

Changes in Ni concentration (ppm) of *Pleurozium schreberi*, at sites near (A) and remote from (B) the oil sands plants from 1966 (value based on measurements for remote sites and a literature survey) to 1983 (see Figure 18).

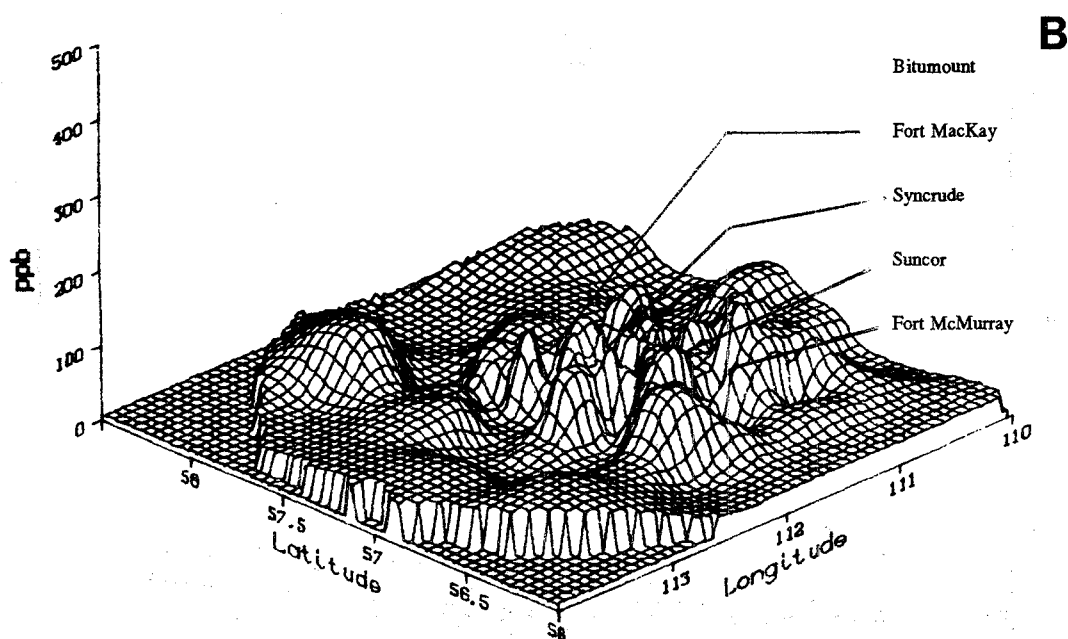
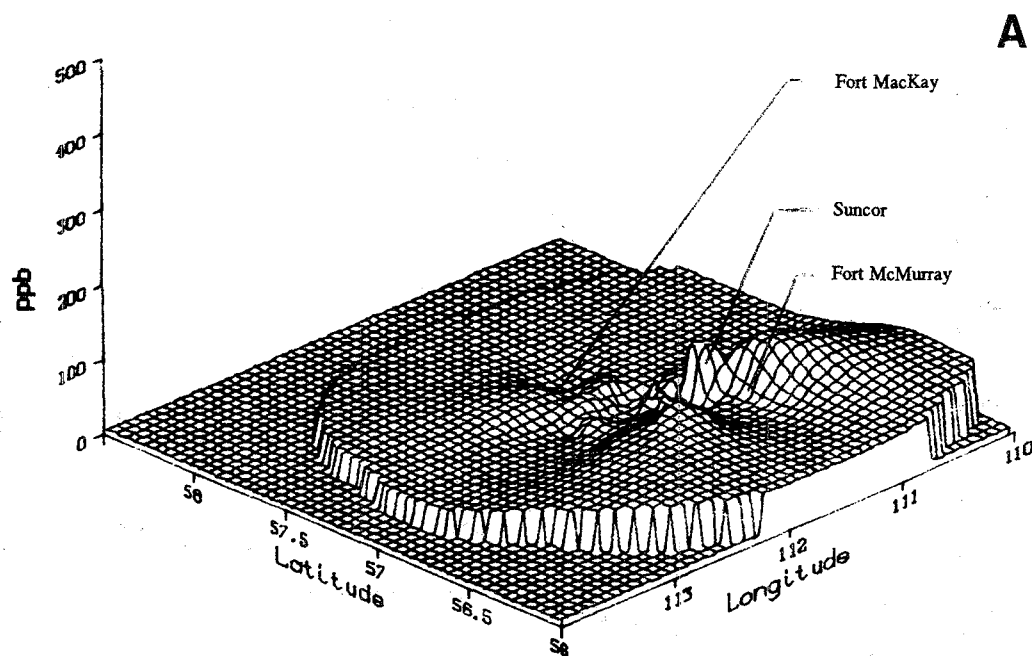


Figure 26 Regional patterns of Hg concentrations (ppb) in *Pleurozium schreberi* in the oil sands region of Alberta, 1976 (A) and 1983-84 (B).

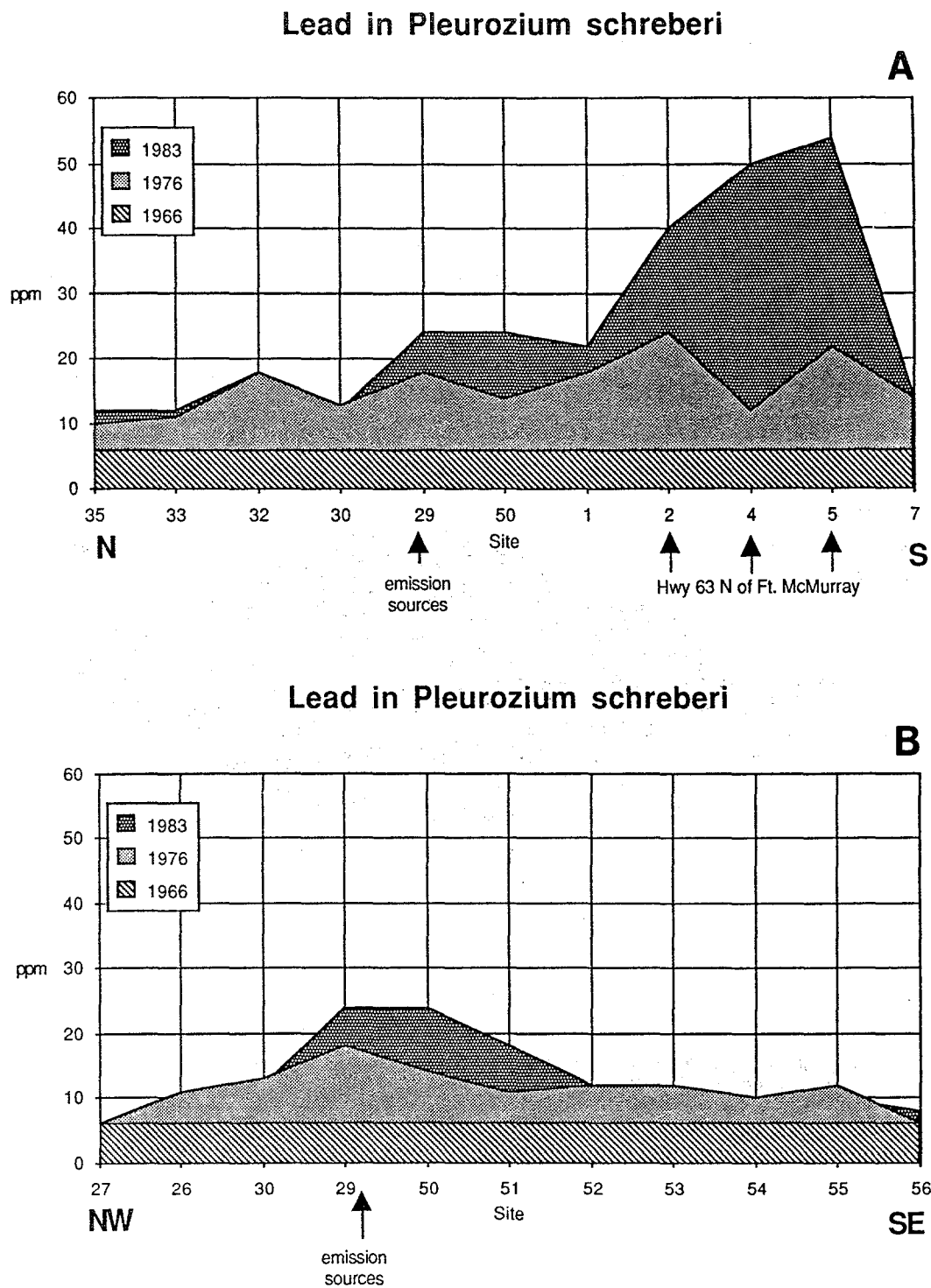


Figure 27

Changes in Pb concentrations (ppm) in of *Pleurozium schreberi*, at sites along N-S (A) and NW-SE (B) transects crossing over the oil sands plants.

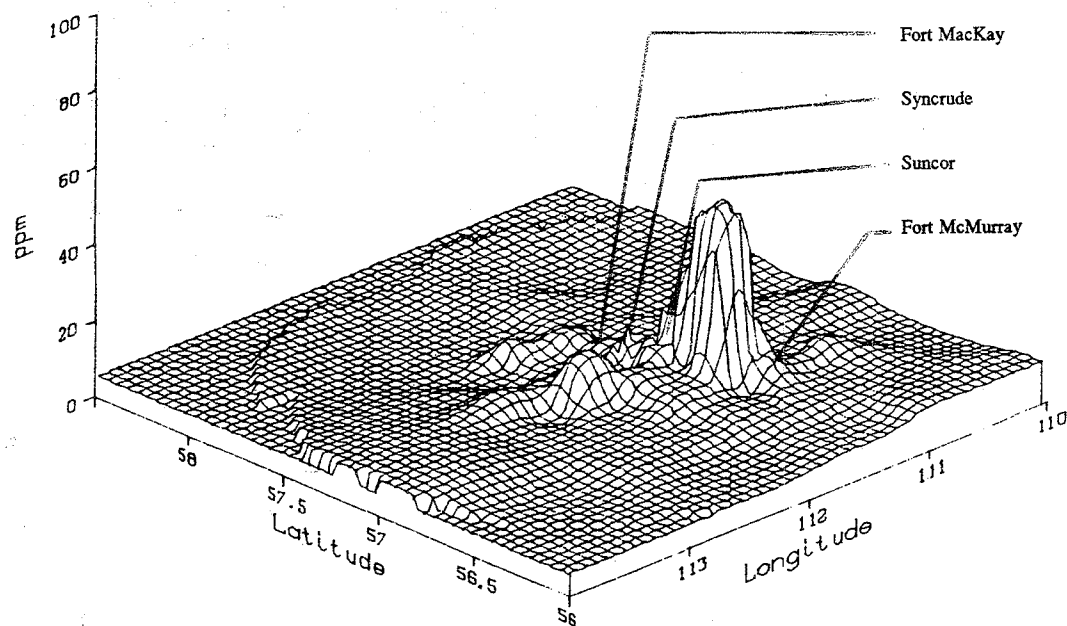


Figure 28

Regional patterns of Pb concentrations (ppm) in *Pleurozium schreberi* in the oil sands region of Alberta, 1983-84. This pattern appears related to vehicular traffic in the region.

Thickwood Hills forestry lookout tower (a popular recreational route) and in the vicinity of the plants. It appears that the main source of Pb in the study area is exhaust fumes from vehicles burning leaded gas.

Pb content of *Pleurozium schreberi* tissues have increased slightly (at a relatively steady rate) or not at all, at most sites (Figure 29). The rate of accumulation at sites 4 and 5, however, has increased, presumably because of increased traffic along the highway.

### Urban Perspective

S content of *Pleurozium schreberi* tissue samples in the immediate vicinity of the oil sands plants (sites 1, 2, 30 and 51) was higher than in background samples and generally higher than levels measured in samples from urban settings (Figure 30). Samples collected at sites in the oil sands area, but at some distance from the processing plants (sites 55, 58, 118, 120) had S levels comparable to samples from an urban environment.

Ni content of *Pleurozium schreberi* tissue samples from the oil sands area (sites 1, 2, 30, 51, 55, 58, 118, 120) were much greater than the levels found in samples from either background or urban sites (Figure 31). The Ni level measured in samples from site 55 and from Fort McMurray were quite similar, as these sites are equidistant from the oil sands plants in the downwind direction.

Pb levels in *Pleurozium schreberi* samples from the oil sands area were generally similar to those measured in samples from background areas, except in the vicinity of high traffic flow (Figure 32). Pb levels in urban samples of *Pleurozium schreberi* were much higher than those from either the oil sands or background areas.

### Vascular Plants

Lichens and mosses are much more sensitive to sulphur dioxide injury than vascular plants. However, heavy metals are generally more toxic to vascular plants than to lichens and mosses (James 1973). If the lichens and mosses of an area do not show visible injury or a build up of S and/or heavy metals above the expected background levels, then the more resistant vascular vegetation of that area should not be in danger of suffering sulphur dioxide and/or heavy metal injury. However, the fact that accumulations of these elements were detected in the nonvascular vegetation, and that these accumulations were coincident with visible injury and decreased growth, suggested that similar accumulations might be occurring in the higher plants of the region.

Elemental analysis of aspen (*Populus tremuloides*) foliage revealed no clearly significant correlation between S content of aspen and moss collected at the same sites. However, the content of some heavy metals in aspen, such as V, which is not naturally abundant in the environment, but is emitted by the oil sands plants, was significantly correlated with that of *Pleurozium schreberi* at the same sites (Figure 33). A study of the trace element concentrations in white spruce sapwood at five locations ranging from 5 to 67 km from the Syncrude and Suncor plants was not able to demonstrate any relationship with emissions from the oil sand plants (Pauls *et al.* 1985). However, in spite of the small sample size and the natural variability in trace element availability, differences in Al, B, Ba, K, Mg, Mn and Zn concentrations were noted between some sites, and in Cu, Fe, K and P concentrations in wood formed during the intervals 1958-67, 1969-77 and 1978-84, at other sites (Pauls *et al.* 1985).

There are many sources and routes of metal uptake to xylem of trees, and this is complicated by cycling of metals in the environment (Martin and Coughtrey 1982). In the study area, metal contamination is primarily in the form of airborne particulates and the soil

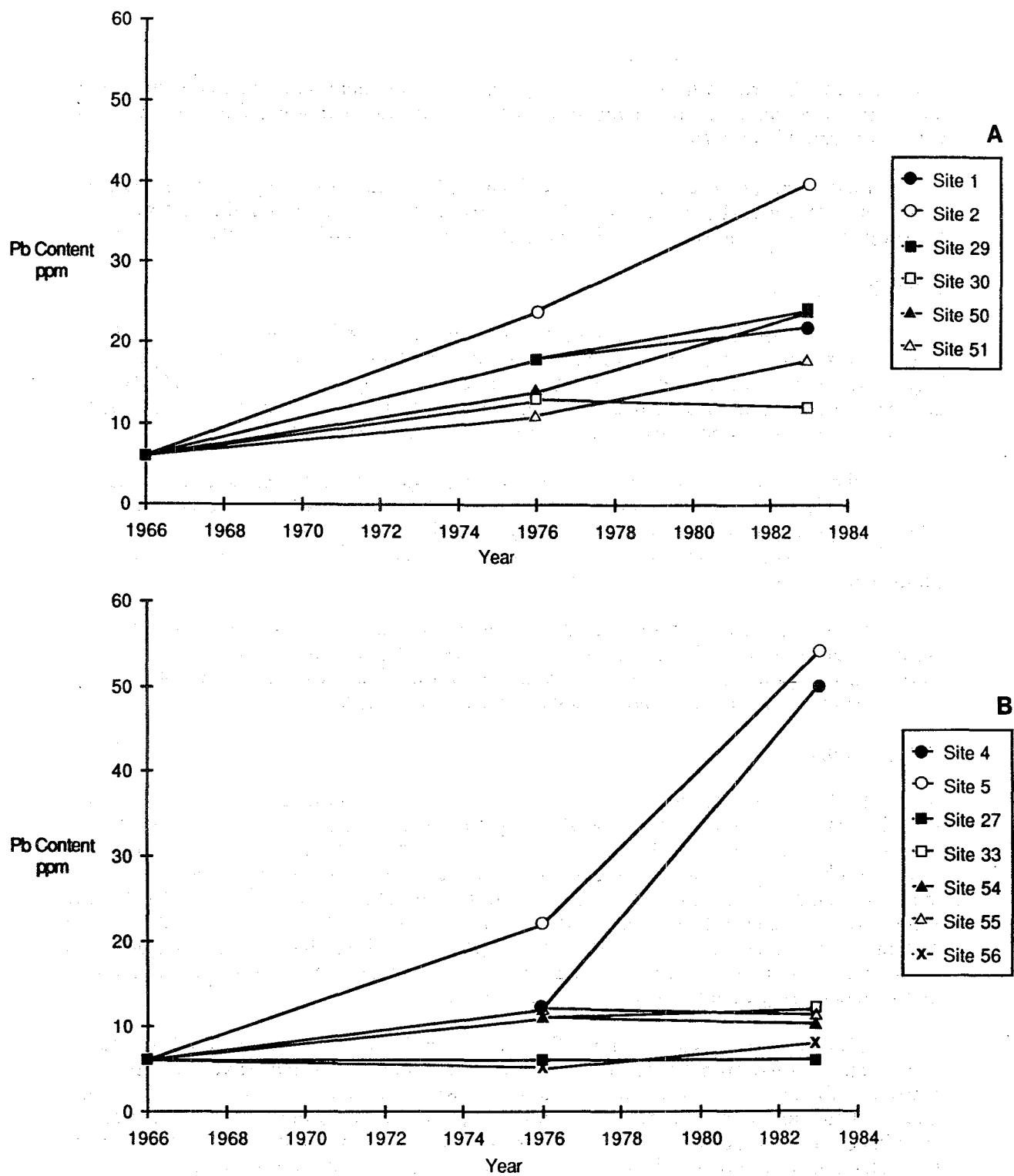


Figure 29

Changes in Pb concentration (ppm) in of *Pleurozium schreberi*, at sites near (A) and remote from (B) the oil sands plants from 1966 (value based on measurements for remote sites and a literature survey) to 1983 (see Figure 18).

## Sulphur in Pleurozium

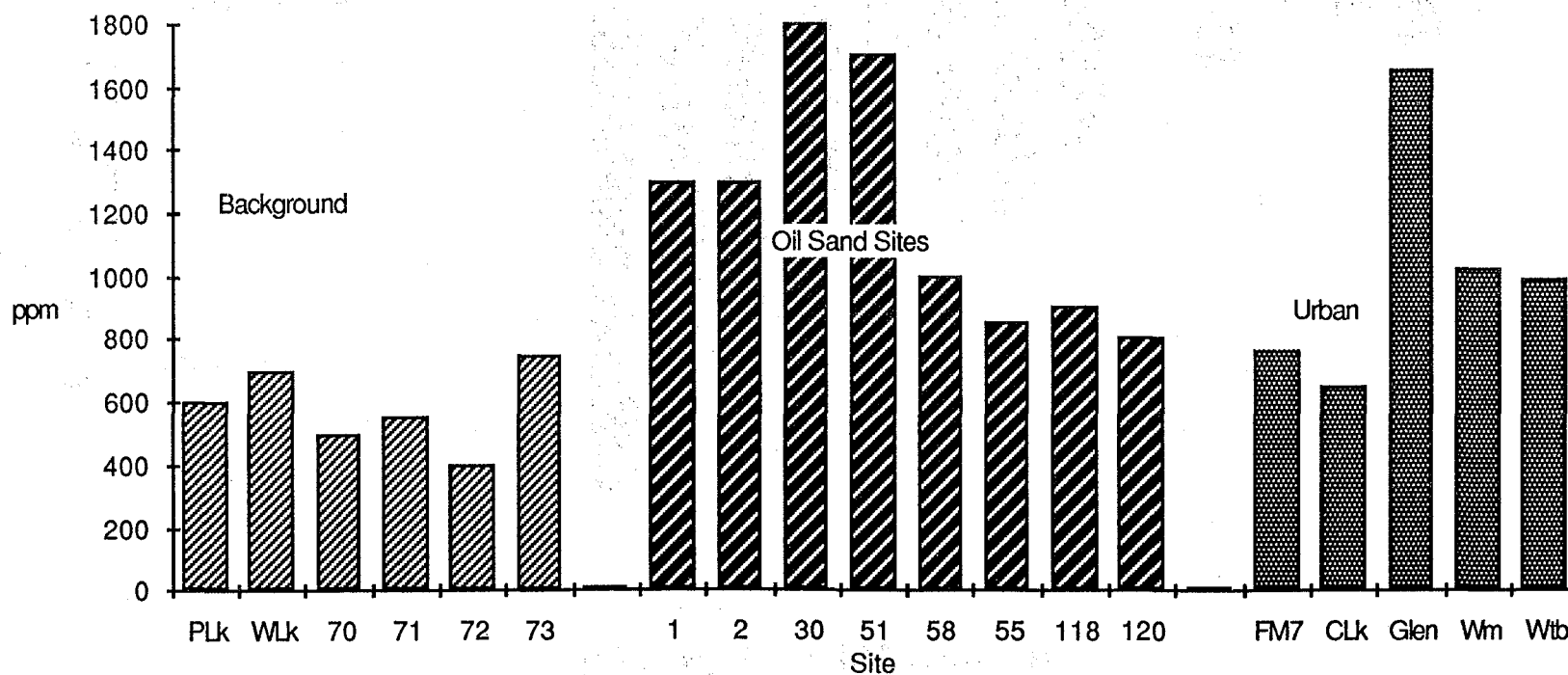


Figure 30

Comparison of S contents in selected 1983-84 samples from urban, background and oil sand areas. (PLk = Primrose Lake; WLk = Wolf Lake; FM7 = Fort McMurray; CLk = Cold Lake; Glen = Glenmore Reservoir, Calgary; Wm Whitemud Freeway, Edmonton; Wtb = Winterburn)

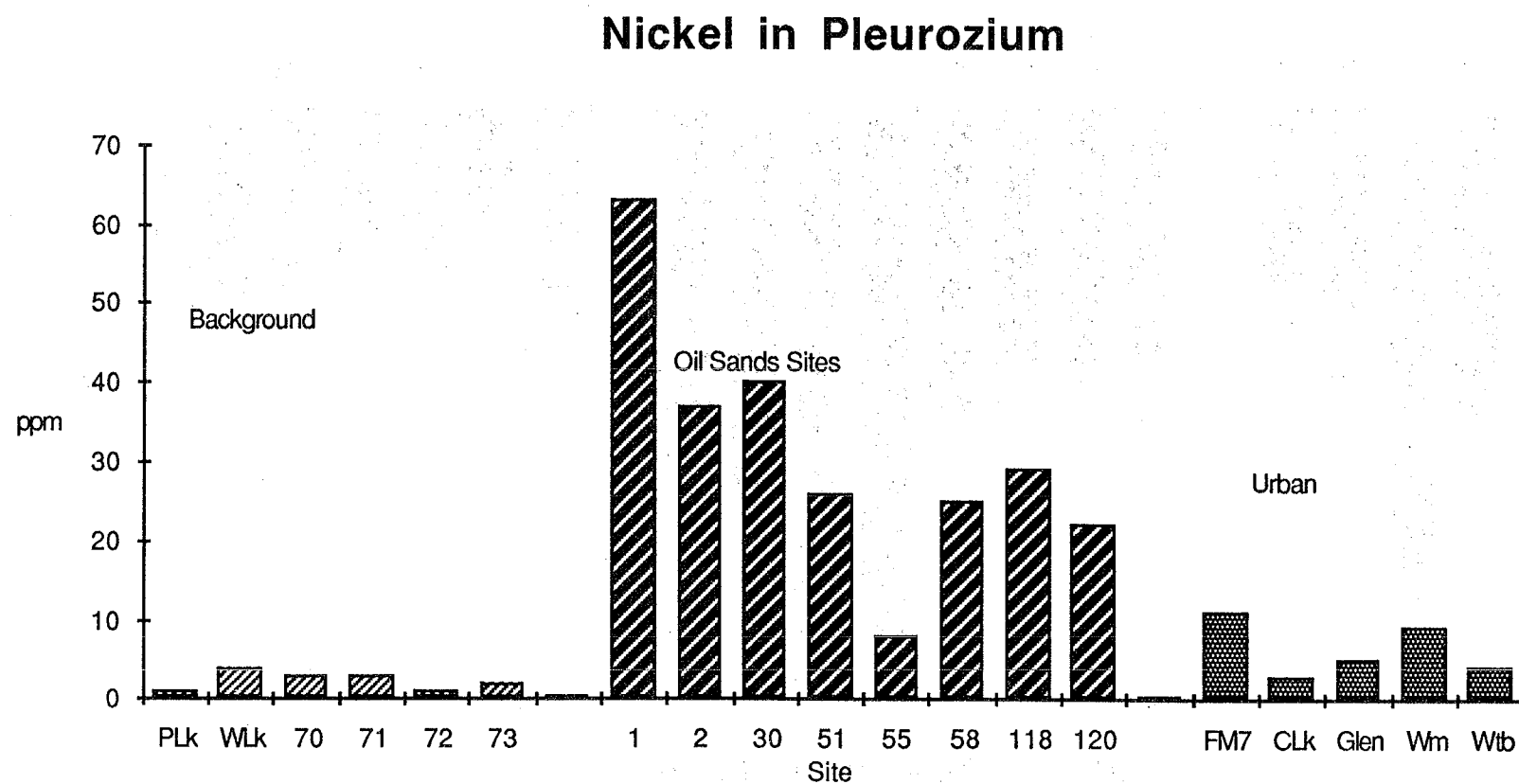


Figure 31

Comparison of Ni contents in selected 1983-84 samples from urban, background and oil sand areas. (PLk = Primrose Lake; WLk = Wolf Lake; FM7 = Fort McMurray; CLk = Cold Lake; Glen = Glenmore Reservoir, Calgary; Wm = Whitemud Freeway, Edmonton; Wtb = Winterburn)

## Lead in Pleurozium

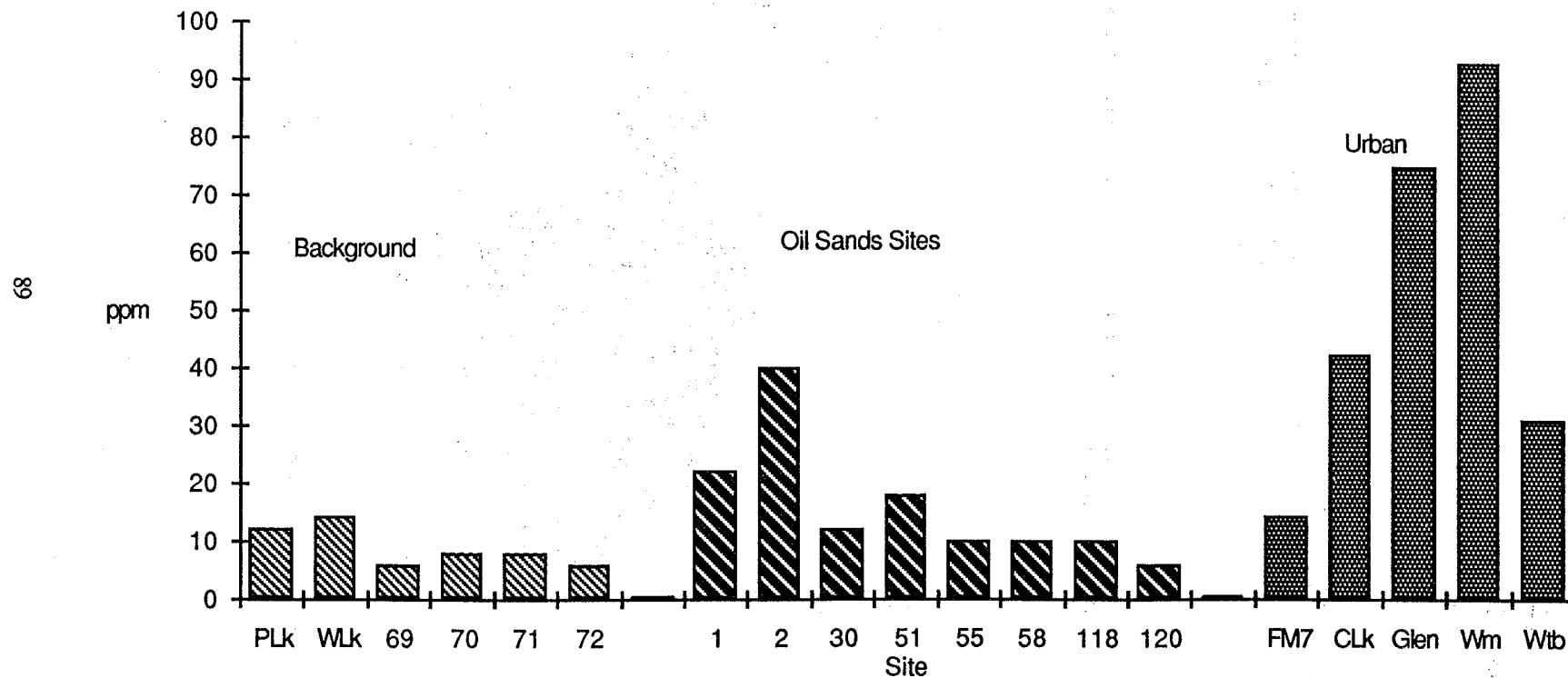


Figure 32

Comparison of Pb contents in selected 1983-84 samples from urban, background and oil sand areas. (PLk = Primrose Lake; WLk = Wolf Lake; FM7 = Fort McMurray; CLk = Cold Lake; Glen = Glenmore Reservoir, Calgary; Wm = Whitemud Freeway, Edmonton; Wtb = Winterburn)

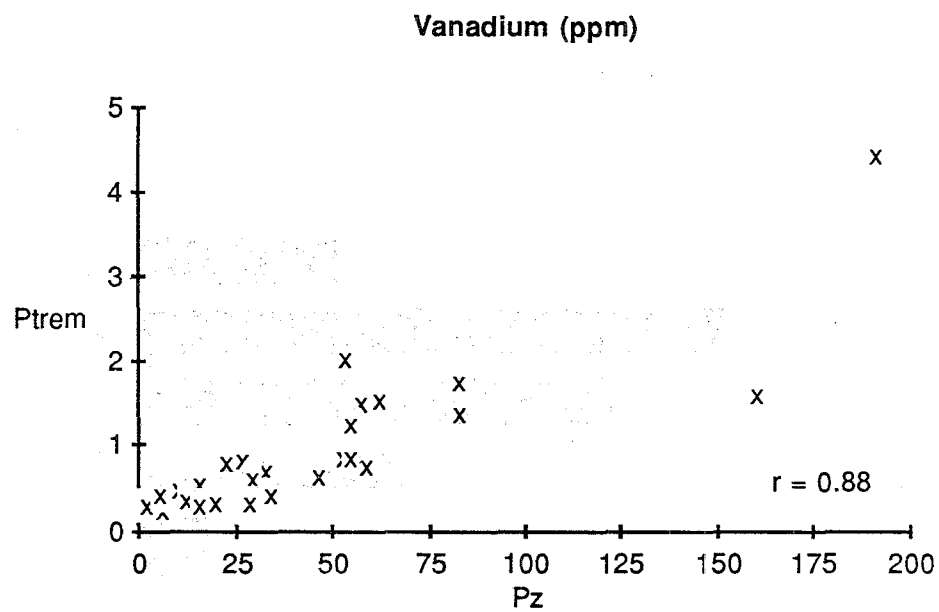


Figure 33

The V content of *Pleurozium schreberi* (Pz) and *Populus tremuloides* (Ptrem) were significantly correlated.

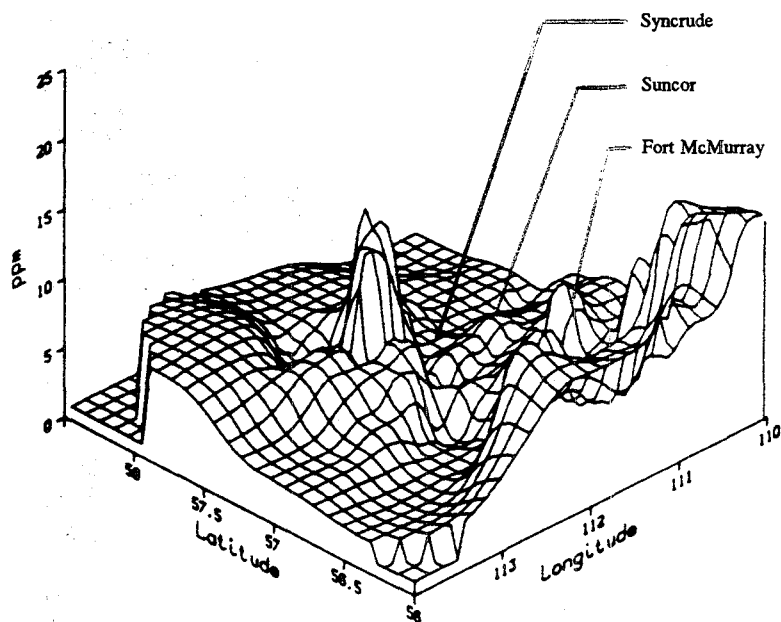


Figure 34

Regional patterns of Ni content in *Populus tremuloides* in the oil sands region of Alberta, 1984.

becomes the ultimate sink for the major proportion of the metals. Unfortunately, little information is available on the elemental content of soils in the area or the actual measured deposition of metals. The reliability of dendroanalysis will be increased greatly after quantification of deposition, uptake (by leaves, bark, roots), translocation, and radial transfer.

Examination of the accumulation patterns of elements in aspen leaves revealed that these trees obtained their trace elements not only from the emissions of the oil sands plant, but from other sources such as the soil. For example, Figure 34 suggests that factors other than the oil sands plant emissions strongly influence aspen Ni content. Research in this area is limited, Hardy Associates (1983) reported a decline in metal uptake on fly ash treated plots. Notwithstanding, soil chemistry undoubtedly plays a predominant role in determining the elemental makeup of the vascular plants. However, an analysis of soil chemistry was not part of this study.

## CHAPTER 3 : RELATIONSHIPS BETWEEN OIL SANDS PLANT EMISSIONS AND VEGETATION

### 3.1 COMPARISON OF DEPOSITION PATTERNS WITH IMPACT ON VEGETATION

Several authors have observed that the yield of timber and various crops can be depressed due to environmental contamination resulting from the release of excess amounts of elements which may otherwise be necessary as nutrients (Linzon 1971; Bell and Clough 1973; Heck 1973; Guderian 1977; Kabata-Pendias 1984). The generalized effects on vegetation of exposure to heavy metals, as summarized diagrammatically in Figure 35, can be separated into three stages. In the first stage, there may be an initial increase in yield as exposure to low levels of pollutants supply nutrients which had been in limited supply in the environment. A classic example of this "fertilizer effect" is the increased productivity of some species growing in S deficient soil when they are exposed to low levels of  $\text{SO}_2$  (Salonius 1985).

In the second stage, other environmental factors (such as water, sunlight, and temperature) become limiting as pollution levels increase and yields level off. In this stage, inputs of contaminants can largely be compensated for by metabolic repair and maintenance and excretory mechanisms; albeit at the expense of metabolic reserves. Transient visible injury symptoms of the types reported in Section 2.2.4 of this report, and by Loman (1981), also begin to appear and resistance to disease and infestation decreases.

At still higher levels of contamination, or after long periods of exposure, a third stage develops. As the ability of the organisms to avoid or deal with the contaminants is overcome, significant pollutant accumulation is accompanied by decreasing yield. The accumulation results in toxicity; either acute toxicity if the organisms compensatory mechanisms are overwhelmed in a short period of time or chronic toxicity if the condition develops over a relatively long period. There is a breakdown of cellular processes in all, but the most resistant individuals or species, which in turn results in changes in plant community composition and decreases in yield (Heck 1973). This can be complicated by the deposition of acid forming pollutants, which in turn increase the solubility of potentially toxic metals in soil and/or emitted particulates (Jones *et al.* 1985).

The metals incorporated into plant tissues may also be transferred into the food web (McIntyre and Mills 1974; Luckey and Venugopal 1977; Underwood 1977; Venugopal and Luckey 1977; Friberg *et al.* 1979; Nriagu 1979; Brown and Sunderman 1980; Rennert and Chan 1985a, 1985b).

#### 3.1.1 Nonvascular Plant Stress

In 1977, lichen diversity, productivity and vitality were uniformly depressed within a 5 km radius of the Suncor (GCOS) plant and possibly further (Loman 1978). The 1983 resurvey of the lichen biomonitoring network revealed that within 15 km of the oil sands plants and along the Athabasca River valley and its tributaries, the epiphytic lichens exhibited both signs of air pollution injury and elevated metal content in their tissues. This area was also characterized by depressed lichen growth and vigor, relative to more remote areas (Figures 16 and 17). At many sites the epiphytic lichens were not reproducing; only relic communities of mature thalli remained. This condition would be associated with stage 3 of the air pollution impact curve (Figure 35).

Beyond 15 km from the plant sites, to a distance of about 30 km from the plants, the lichens and mosses sampled in 1983, continued to show elevated amounts of all the

contaminants emitted by the processing plants. Lichens in this area exhibited varying degrees of visible damage symptomatic of air pollution injury, yet growth does not appear to have been depressed appreciably. The levels of contaminants, to which lichens in this region were exposed, were apparently not sufficiently high to impact their growth. However, by 1976, the elemental concentrations had already increased significantly above the expected background level and had further increased by 1983. The lichens of this region would, therefore, be associated with stage 2 of the impact curve (Figure 35) since the lichens were, for the most part, able to maintain their integrity.

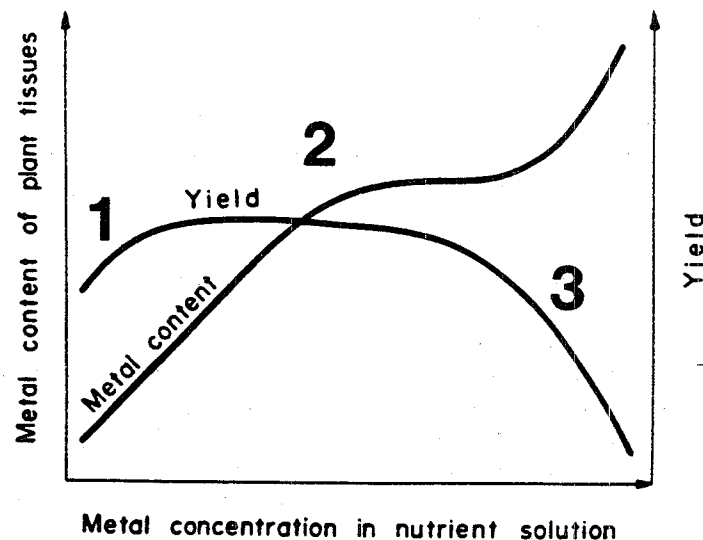


Figure 35 Generalized effects of heavy metals on yield and metal content of vegetation (after Kabata-Pendias and Pendias 1984).

Beyond 30 km from the plants, the lichens exhibited little visible injury and patterns of depressed growth were not evident. Accumulations of some contaminants significantly greater than the expected background levels were, however, detected at distances of more than 50 km from the oil sands plants. Lichens associated with this zone would, therefore, be associated with stage 1 of the air pollution impact curve (Figure 35) since the elemental concentrations, although elevated, were not associated with increased incidence of injury symptoms or reduced growth.

### 3.1.2 Vascular Plant Stress

The majority of the vascular vegetation stress caused by dwarf mistletoe, tent caterpillars, air emissions and birch dieback was found in the vicinity of the two oil sands plants and along the Athabasca River and its tributaries, including the Muskeg, Beaver and Steepbank river valleys and Poplar Creek (Figure 14). It is not possible to consider

pollution impact in isolation from disease and infestation, since insect and disease induced stress weakens the plants leaving it vulnerable to injury by air emissions and visa versa (Malhotra and Blauel 1980). The symptoms of vegetation injury are primarily due to the direct effects of gaseous  $\text{SO}_2$ , and are not related to soil acidification and subsequent nutrient imbalances.

In order to compare S emissions to vegetation stress, the data on actual sulphate deposition patterns were used (Figures 3 to 5) because they provided a better indication of the source of S than the model predictions. High ground-level concentrations of  $\text{SO}_2$ , which are likely to cause vegetation injury, are expected to occur in the same areas which had high sulphate deposition. Thus, the sulphate deposition pattern was used as an indirect indicator of where vegetation damage might be expected to occur. High ground level concentrations of  $\text{SO}_2$  are most likely to be damaging to vegetation during the active growing season, June, July and August.

In the summer of 1978, elevated ground level concentrations of  $\text{SO}_2$ , as indicated by sulphate deposition patterns, were present in the vicinity of the Suncor plant and along the Athabasca River valley (Figure 3). Most of the vegetation stress in 1978 followed a similar pattern (Figure 13). Since the vegetation stress map was interpreted from air photos taken in July prior to the startup of Syncrude, most of the low level stress observed in 1978 was attributed to emissions from Suncor.

Large areas of vegetation stress in aspen stands east of the Suncor plant, both north and south of the Steepbank River valley, were observed by Loman (1981) in 1978. The pattern of increased ground-level sulphate deposition agrees with the stressed areas in a general way only, probably due to the widely spaced sulphation stations and consequent lack of data on the east side of the Athabasca River valley.

During the summer of 1983, high ground-level sulphate deposition is believed to have stunted the growth of needles on jack pine and white spruce trees just east of the Syncrude plant site and tailings pond. The pattern of vegetation stress (Figure 14) corresponds fairly well with the estimated sulphate deposition pattern for that period.

The pattern of vegetation stress observed in 1984 (Figure 14) generally agrees with the pattern of high ground-level sulphate deposition based on an annual average over the period from 1979 to 1983 (Figure 2). Within the bounds of the 1984 vascular vegetation stress survey, the limited S concentration data for trembling aspen also agrees, in general, with the patterns of annual average sulphate deposition and medium level vascular stress (Figure 14). It is reasonable to conclude that the pattern of future vegetation stress, due to S emissions, will continue to resemble the pattern of maximum annual average sulphate deposition, since high ground-level sulphate deposition is largely a function of  $\text{SO}_2$  concentration. This relationship is a general one only, and reflects the different scale and sampling intensity of the vegetation and emission studies. There is no evidence that the long range transport of emissions from the oil sands plants has had any impact on ecosystem in the sensitive areas of the western Precambrian shield in NE Alberta or northern Saskatchewan (Shewchuk 1985b).

It has long been thought that an ambient  $\text{SO}_2$  concentration of  $60 \mu\text{g m}^{-3}$  would not induce injury in trees even after long term exposure. Recently it has been demonstrated that ambient  $\text{SO}_2$  concentrations in the range of  $25$  to  $50 \mu\text{g m}^{-3}$  could be a detrimental influence upon conifers. Further, in the presence of heavy metal pollutants, long-term exposure to levels of  $\text{SO}_2$  as low as  $15 \mu\text{g m}^{-3}$  is enough to produce damage or physiological

imbalances leading to reduced vigour (Andersson 1985). The importance of long term exposure to low levels of SO<sub>2</sub>, in the presence of heavy metals, was emphasized repeatedly by scientists from Europe, United States and Canada at the Muskoka Conference '85, an international symposium in acidic precipitation (Andersson 1985; Dickson 1985; Johnson *et al.* 1985; Matzner and Murach 1985; Shriner 1985; Krause *et al.* 1985).

### 3.2 COMPARISON OF BIOACCUMULATOR ELEMENTAL CONTENTS WITH DEPOSITON MODEL PREDICTIONS

The results of the research summarized in this report provided the opportunity to compare the predictions of deposition models with observed patterns of bioaccumulation and stress symptomology in nonvascular and vascular vegetation. From this, certain generalizations can be made about the reliability and importance of each method.

#### 3.2.1 Sulphation predictions and bioaccumulation of S

The sensitivity of lichens and mosses to SO<sub>2</sub> and their ability to accumulate S in the presence of SO<sub>2</sub> is well documented in the scientific literature. The indirect method of monitoring regional S deposition in the oil sands region has been by the use of sulphation cylinders. Analysis of the degree of agreement between observed S contents of *Pleurozium schreberi* tissues in 1983-84 and the estimated dry deposition of S was conducted using the map comparison techniques described earlier.

Figure 36 is a matrix product contour map prepared by multiplying the standard normalized predicted sulphation data matrix for estimated average annual sulphation (derived from Syncrude data only), by the standard normalized *Pleurozium schreberi* S content data matrix (Figure 19). Only Syncrude data were used so that the agreement between the predicted and observed values could be assessed.

The tight grouping of the contours over a small area indicates that the measurements of S content of *Pleurozium schreberi* is highly correlated with the estimated dry deposition of S predicted on the basis of data from the Syncrude monitoring network. A lower degree of agreement, in the vicinity of the Suncor plant, is indicated by a region outlined by hatched lines in Figure 36. This is suggestive of S levels in *Pleurozium schreberi* due to elevated S deposition in that region which is higher than would be predicted on the basis of Syncrude emissions alone. This corroborates the observation made in section 2.1.1.3, that the SO<sub>2</sub> plume dispersion model would underestimate deposition in the vicinity of the Suncor plant.

This conclusion is supported by the isopach map produced by subtracting the estimated sulphation data matrix from the *Pleurozium schreberi* S content matrix after both were standard normalized (Figure 37). In this figure, the raised areas east of Suncor correspond to regions where *Pleurozium schreberi* tissues contained higher levels of S than would be expected on the basis of the predicted sulphation data. In the immediate vicinity of Syncrude, a depression corresponds to an area where the agreement between expected and observed S values is good.

#### 3.2.2 Heavy Metal Deposition Predictions and Measured Bioaccumulation

Figure 38 shows the patterns of *Pleurozium schreberi* Ni content in the oil sands region as of 1983. When compared to the generic contour plot for the deposition rate of 10 µm particles from the Syncrude plant alone (Figure 12), it is apparent that while there is some similarity in the patterns in the immediate vicinity of the oil sands plants, there is a

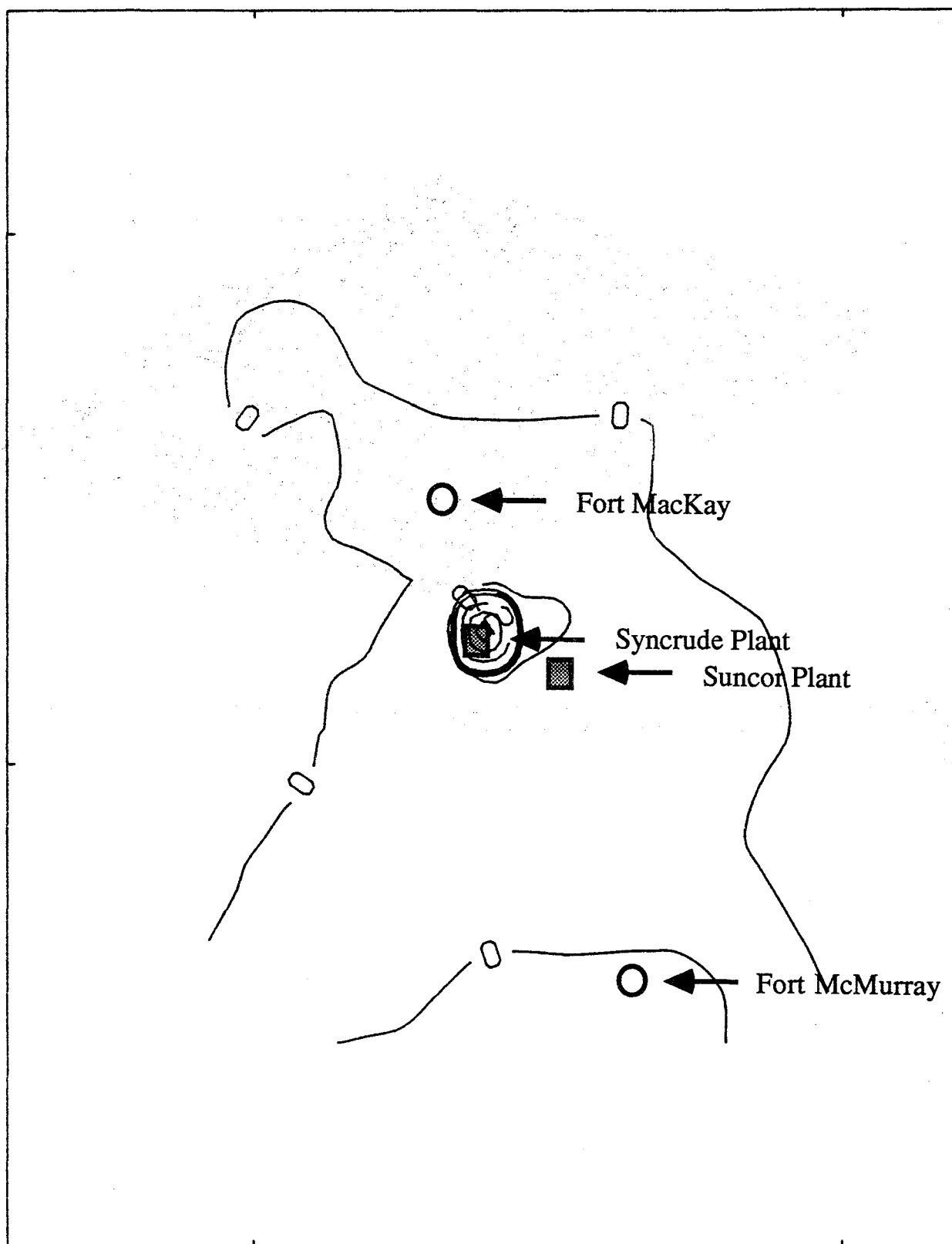


Figure 36

Matrix product map prepared by multiplying the standard normal sulphation prediction data matrix by the standard normal *Pleurozium schreberi* S content data (Syncrude only ) matrix for 1983-84. The very tight contours over the Syncrude plant indicates very strong agreement between predicted sulphation and observed S bioaccumulation in that area.

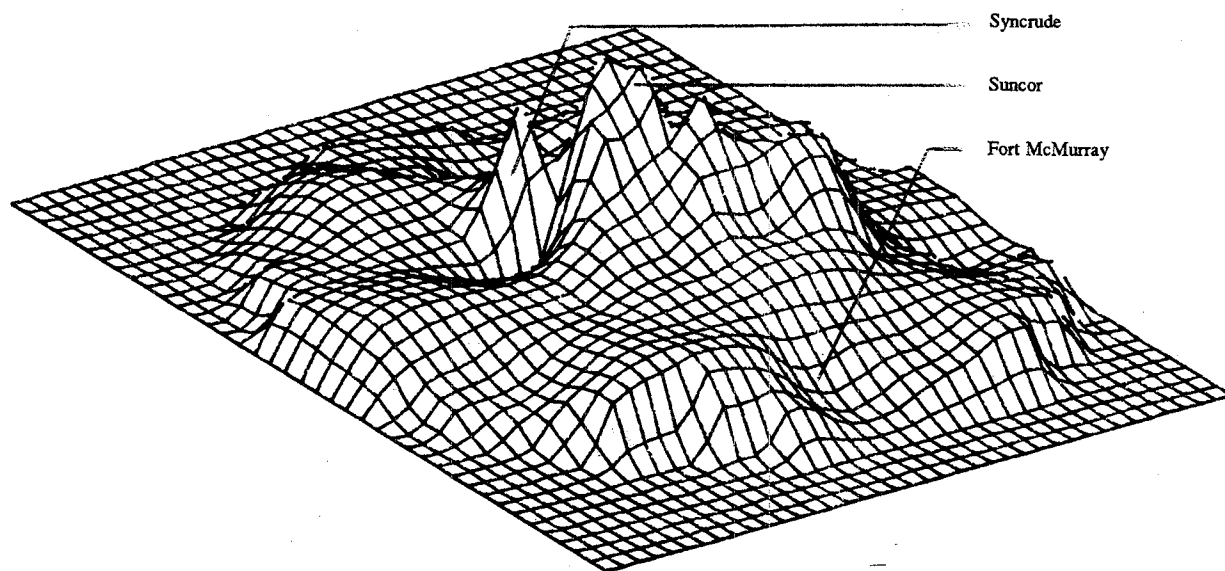


Figure 37

Isopach map of standard normal sulphate deposition prediction data (Syncrude only) subtracted from standard normal S content data for *Pleurozium schreberi*.

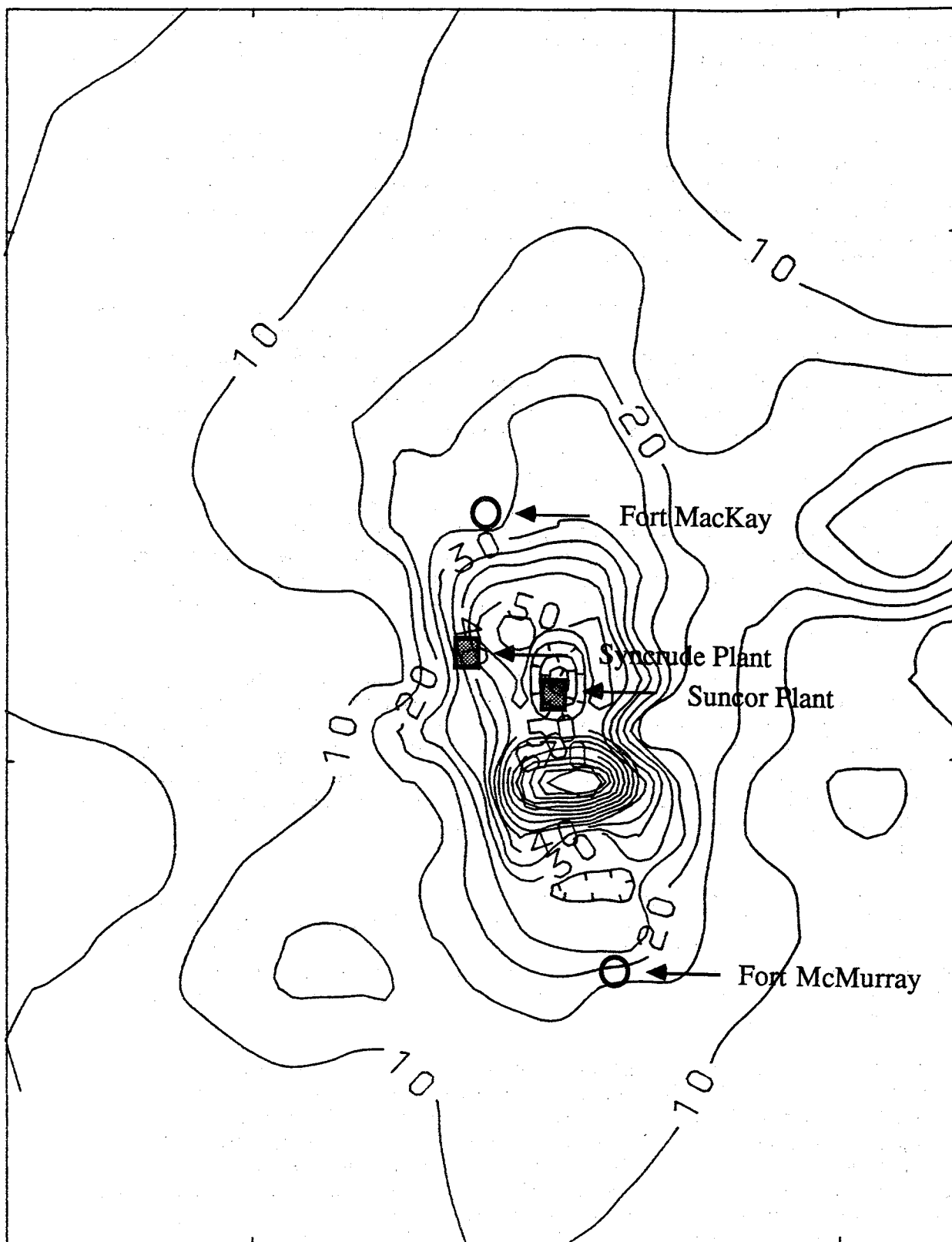


Figure 38

Ni content (ppm) of *Pleurozium schreberi* in the oil sands region of Alberta, 1983 to 1984.

southward extension of the deposition zone along the Athabasca River valley which was not predicted by the model for 10  $\mu\text{m}$  particulate emissions from Syncrude. This is not surprising since Syncrude's emissions appear to account for only 10% of the regional particulate emissions (see Section 2.1.2).

Construction of an isopach map showing the difference between the standard normal model prediction, and *Pleurozium schreberi* bioaccumulation data sets, confirmed the existence of Ni accumulations in *Pleurozium schreberi* south of the Suncor plant along the Athabasca River valley (Figure 39) that were not predicted by the model of only Syncrude emissions. However, *Pleurozium schreberi* Ni content NW of the Syncrude plant were found to be lower than expected.

The degree and area of agreement between the model predictions and observed *Pleurozium schreberi* contents are illustrated by the three dimensional surface in Figure 40. It is apparent that in the immediate vicinity (i.e., 10-20 km) of the Syncrude plant site, the agreement is high. Beyond that distance, the degree of agreement decreases rapidly. This is interpreted as being the result of the limited dispersal of Ni containing particulate matter. It appears that the principal part of these emissions are deposited within a short distance.

Most other heavy metals measured in *Pleurozium schreberi* showed patterns of bioaccumulation in the region similar to that of Ni. For example, Al, Ti and V, were found to have similar, although not identical, patterns of bioaccumulation in *Pleurozium schreberi*. (Figures 41, 42, and 43). Differences in the observed bioaccumulation patterns are likely due to different uptake rates by the *Pleurozium schreberi* and perhaps the association of these metals with particles with different aerodynamic sizes which would result in different trajectories.

Al, Ti, and V also showed similar patterns of agreement between predicted deposition due to only Syncrude emissions, and observed bioaccumulation when isopach maps were prepared by mapping the difference between standard normal predicted deposition values, and observed bioaccumulation measurements (Figures 44, 45, and 46). In all cases, the model predictions agreed very well with the observed bioaccumulations near the Syncrude plant site. However, greater than expected accumulations were detected south and east of the Suncor plant, and along the Athabasca River valley toward Fort McMurray.

Maps based on the products of standard normalized deposition predictions, and observed bioaccumulations (Figures 47, 48 and 49), confirmed that the model predictions of deposition due to only Syncrude emissions agreed well with observed bioaccumulations in *Pleurozium schreberi* in the immediate vicinity of the plant site. However, the model predictions did not agree with observed bioaccumulations in large areas to the south and east of the Suncor plant site.

Hg bioaccumulation in the area showed little positive relationship with oil sands plant locations (Figure 50). Mapping the difference between observed bioaccumulation and expected deposition due to only Syncrude emissions revealed lower than predicted Hg contents in the immediate vicinity of the Syncrude plant, as indicated by the hatched contours in Figure 51. Accumulations of Hg, which were higher than expected on the basis of predictions of the Syncrude emissions model, were detected throughout the study area. With the exception of the immediate vicinity of the Suncor plant, the area of unexpectedly high Hg content appear to be associated with heights-of-land.

A map based on the product of the standard normal model predictions and observed bioaccumulation of Hg revealed four or five regions where model predictions agreed with

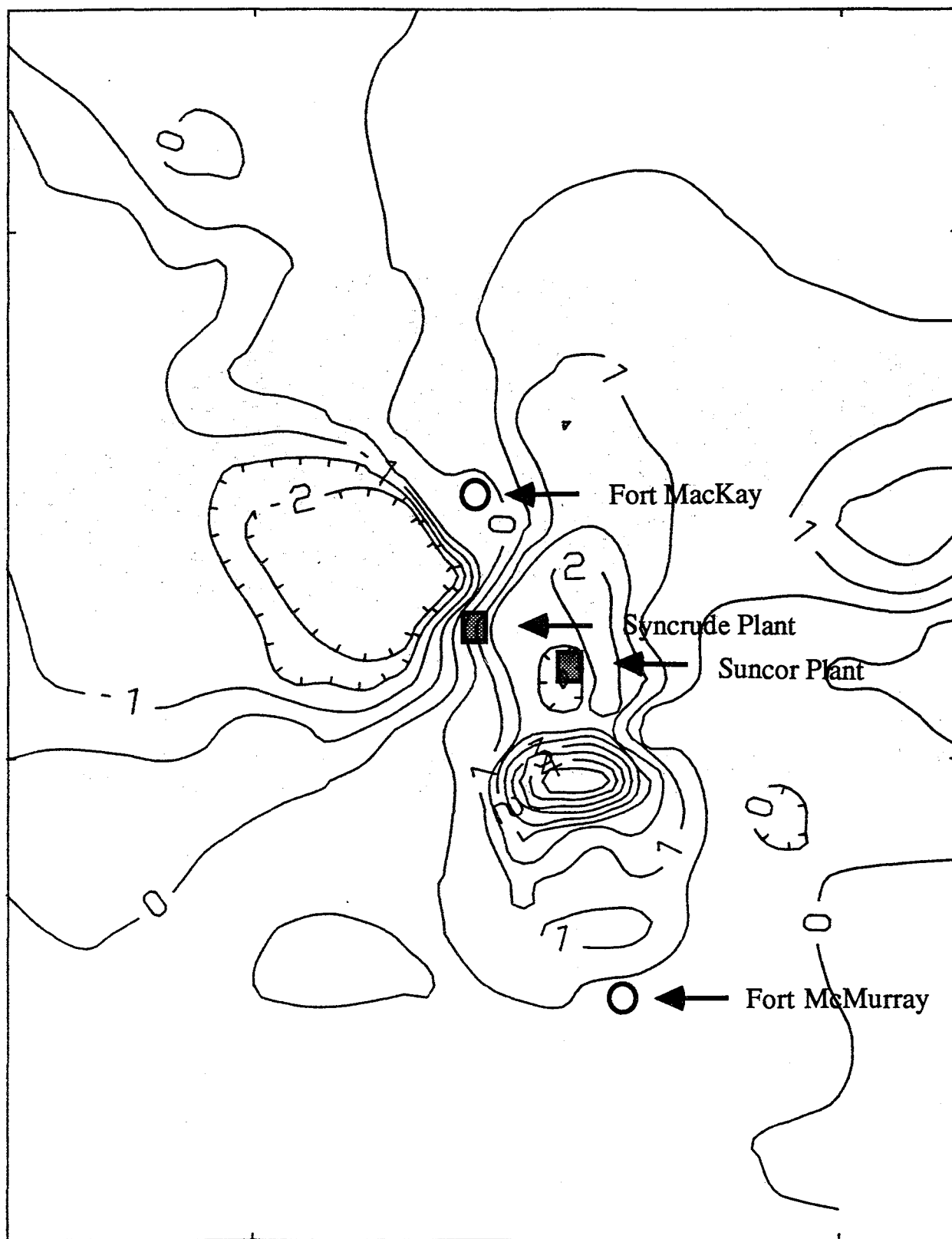


Figure 39

Isopach map of standard normal *Pleurozium schreberi* Ni content minus standard normal model predicted Ni deposition due only to Syncrude emissions. A region of higher than expected Ni bioaccumulation occurs immediately south of the Suncor plant along the Athabasca River Valley. A region of lower than predicted deposition was detected west of Syncrude.

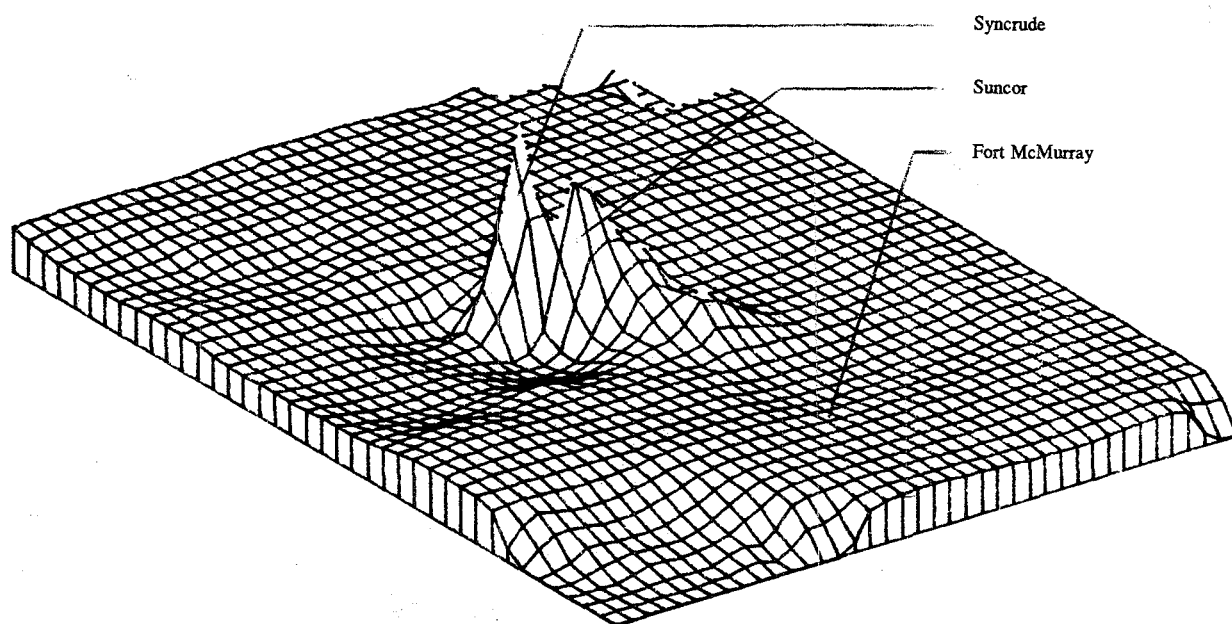


Figure 40

Map based on the products of standard normalized Ni deposition predictions for the Syncrude plant only and observed Ni bioaccumulation by *Pleurozium schreberi*. Near the oil sand plants model predictions agree with observed bioaccumulations, however, agreement decreases sharply with increasing distance.

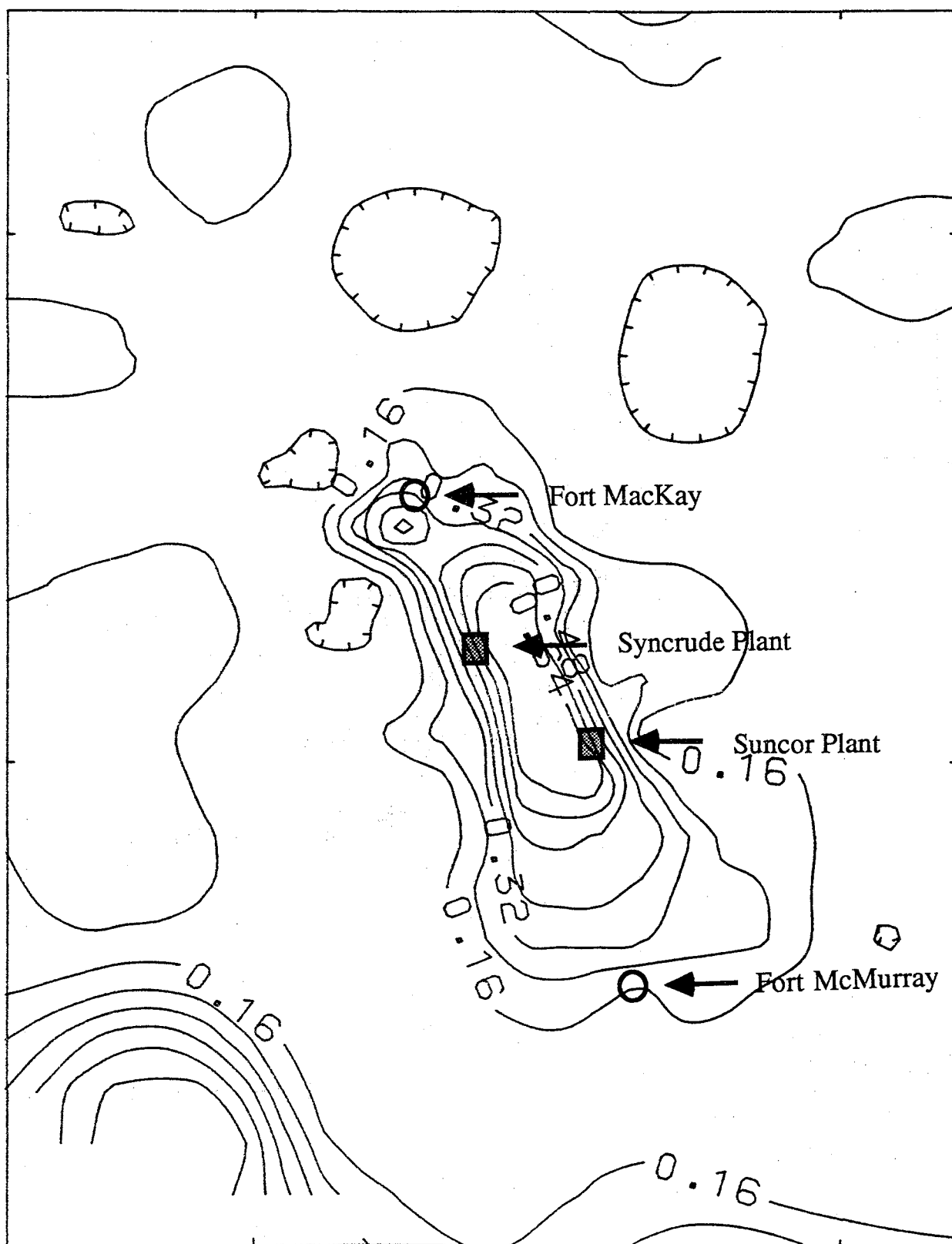


Figure 41

Al content (ppm) of *Pleurozium schreberi* in the oil sands region of Alberta, 1983-84.

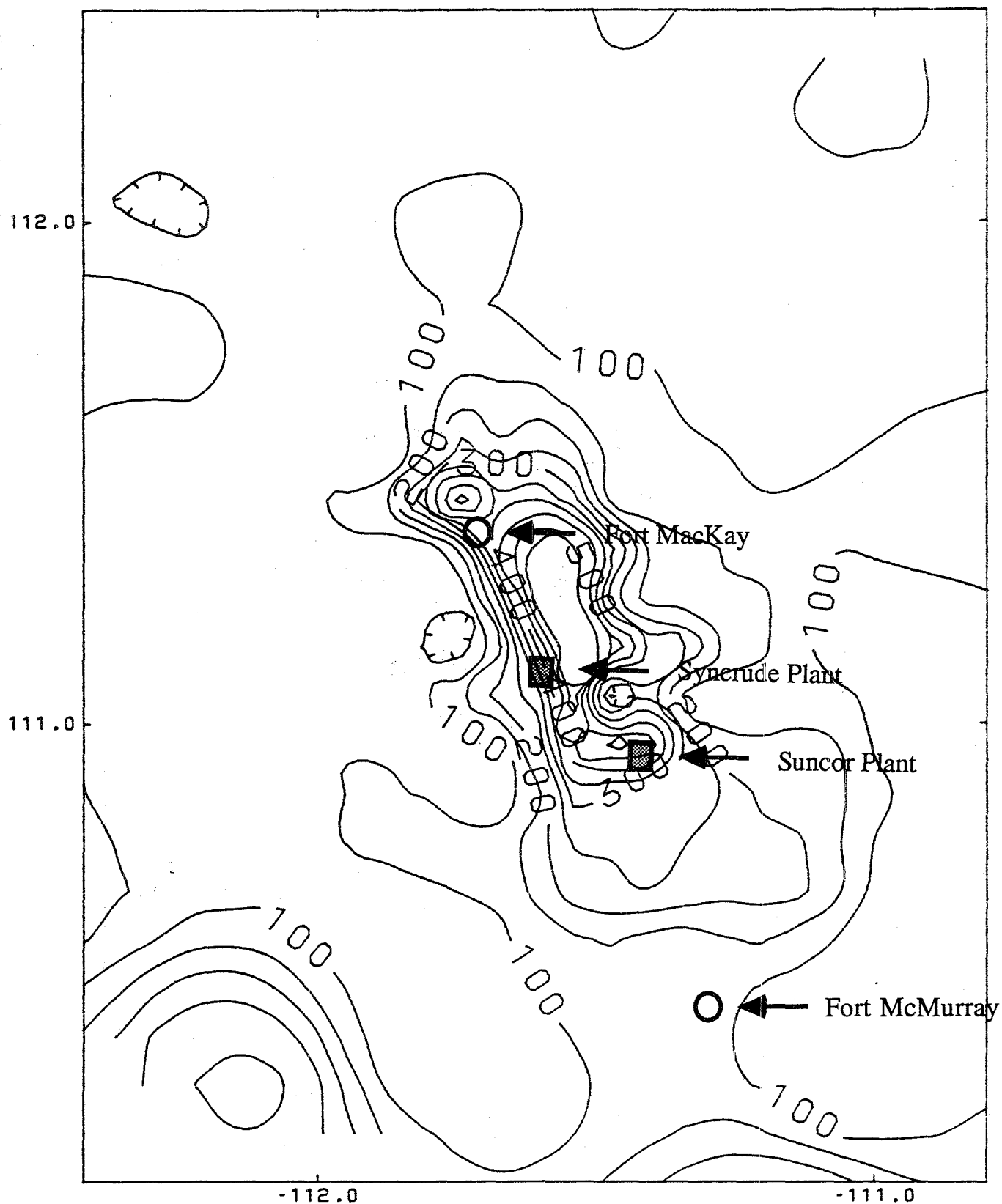


Figure 42

Ti content (ppm) of *Pleurozium schreberi* in the oil sands region of Alberta, 1983-84.

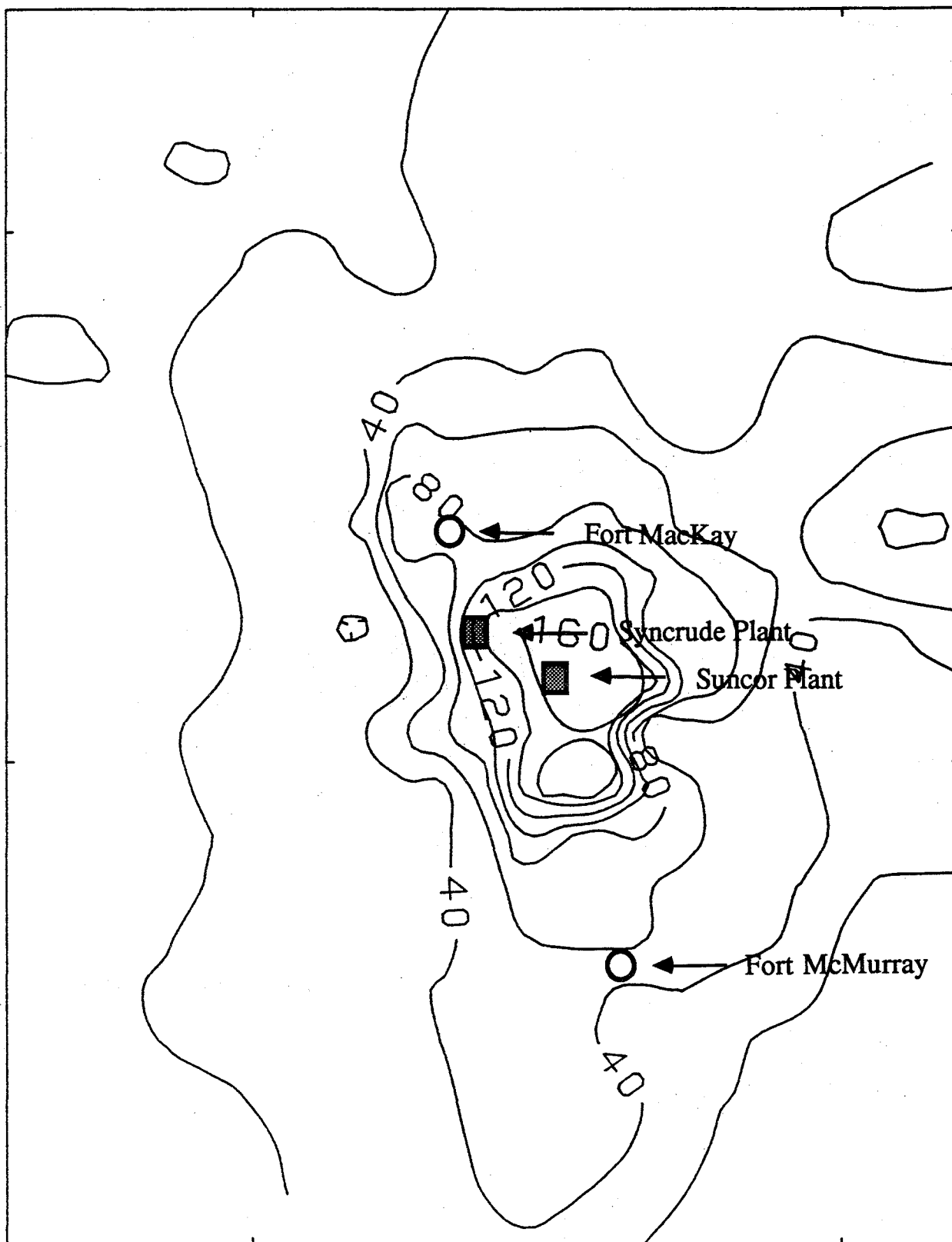


Figure 43

V content (ppm) of *Pleurozium schreberi* in the oil sands region of Alberta, 1983-84.

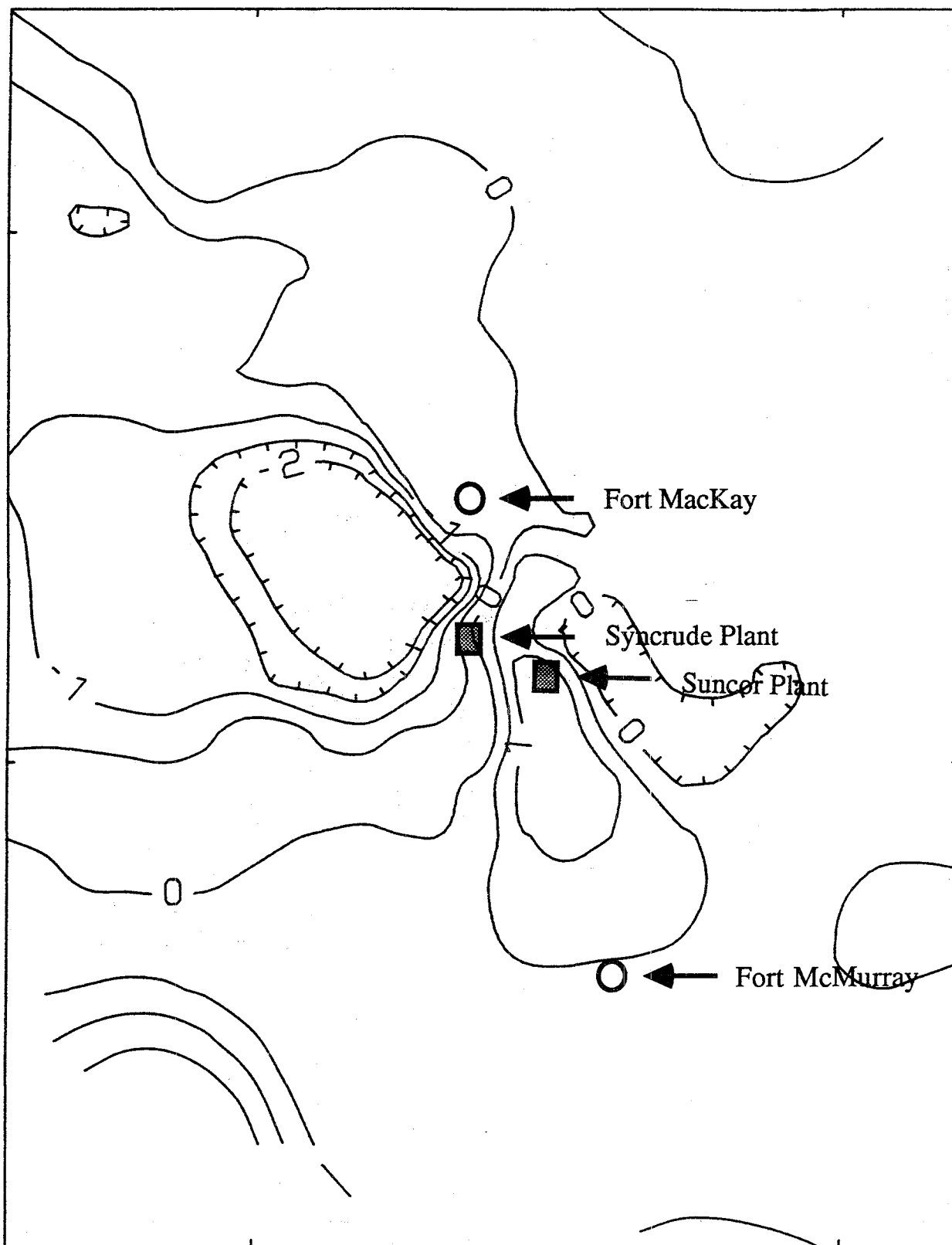


Figure 44

Isopach map of standard normal *Pleurozium schreberi* Al content minus standard normal model predicted Al deposition due to only Syncrude emissions. A zone of higher than expected Al bioaccumulation in *P. schreberi* is observed south of the Suncor plant along the Athabasca River Valley.

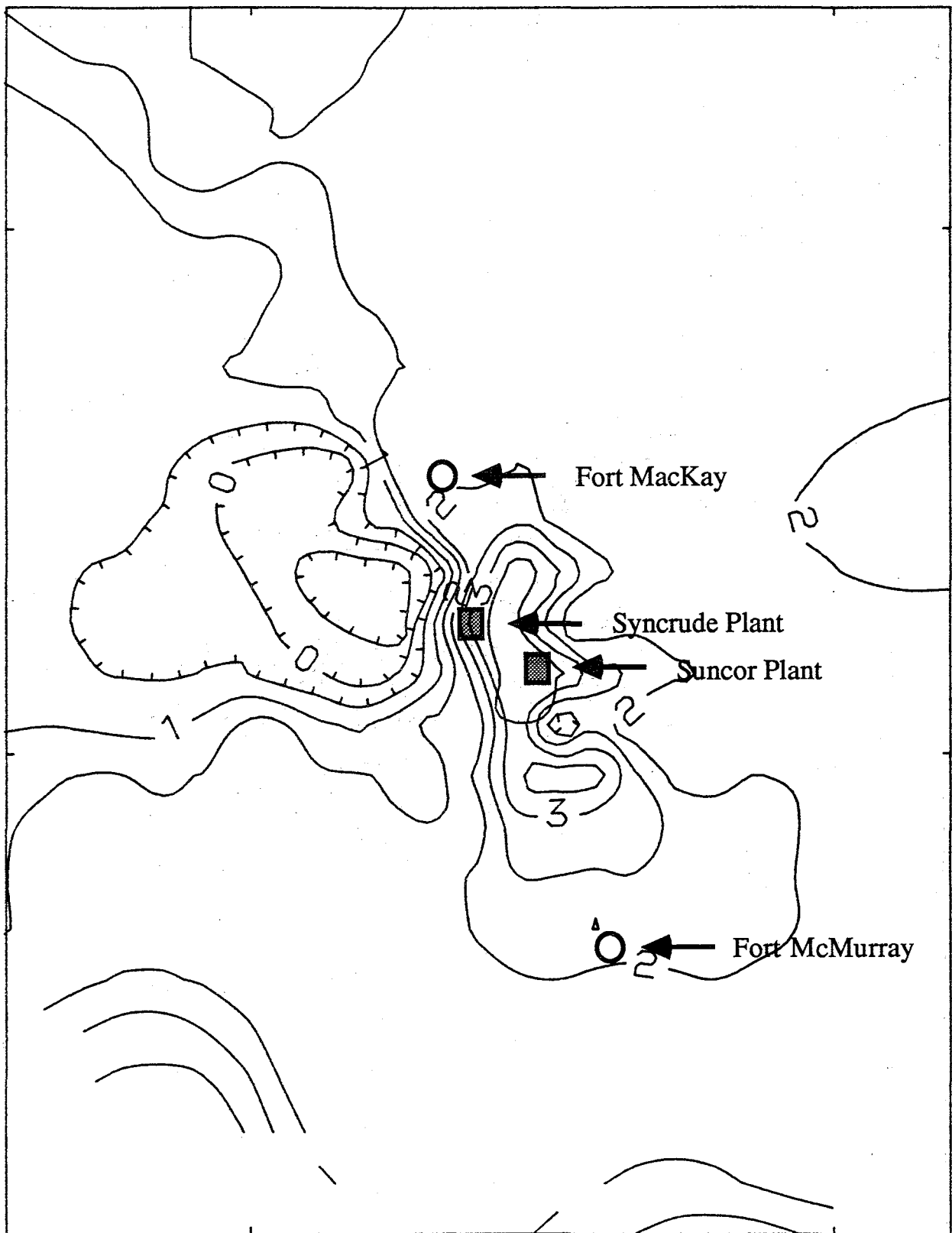


Figure 45

Isopach map of standard normal *Pleurozium schreberi* Ti content minus standard normal model predicted Ti deposition due only to Syncrude emissions. A region of higher than expected Ti bioaccumulation occurs north and south of the Suncor plant along the Athabasca River Valley. A region of lower than predicted deposition was detected west of Syncrude.

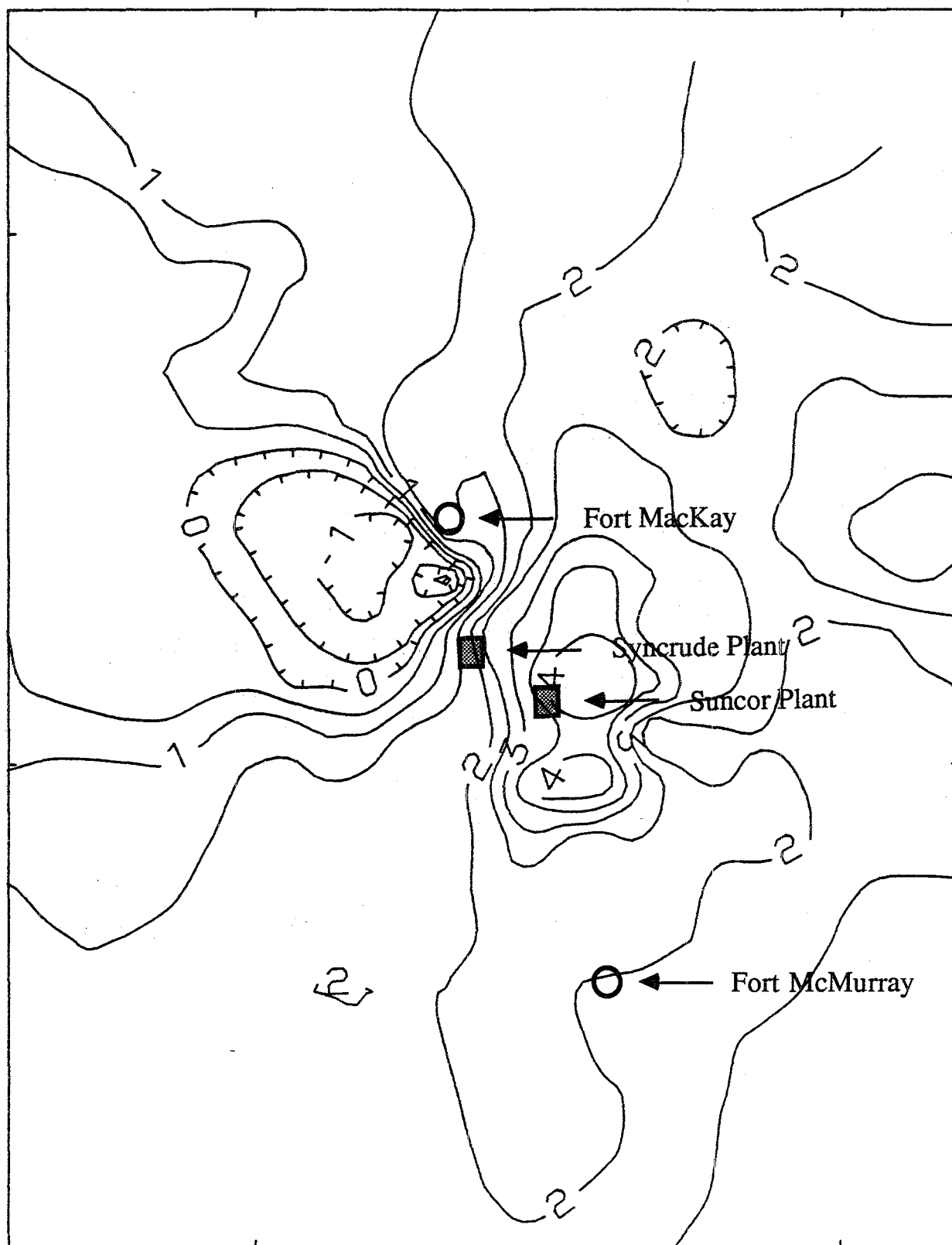


Figure 46

Isopach map of standard normal *Pleurozium schreberi* V content minus standard normal model predicted V deposition due only to Syncrude emissions. A region of higher than expected V bioaccumulation occurs north and south of the Suncor plant along the Athabasca River Valley.

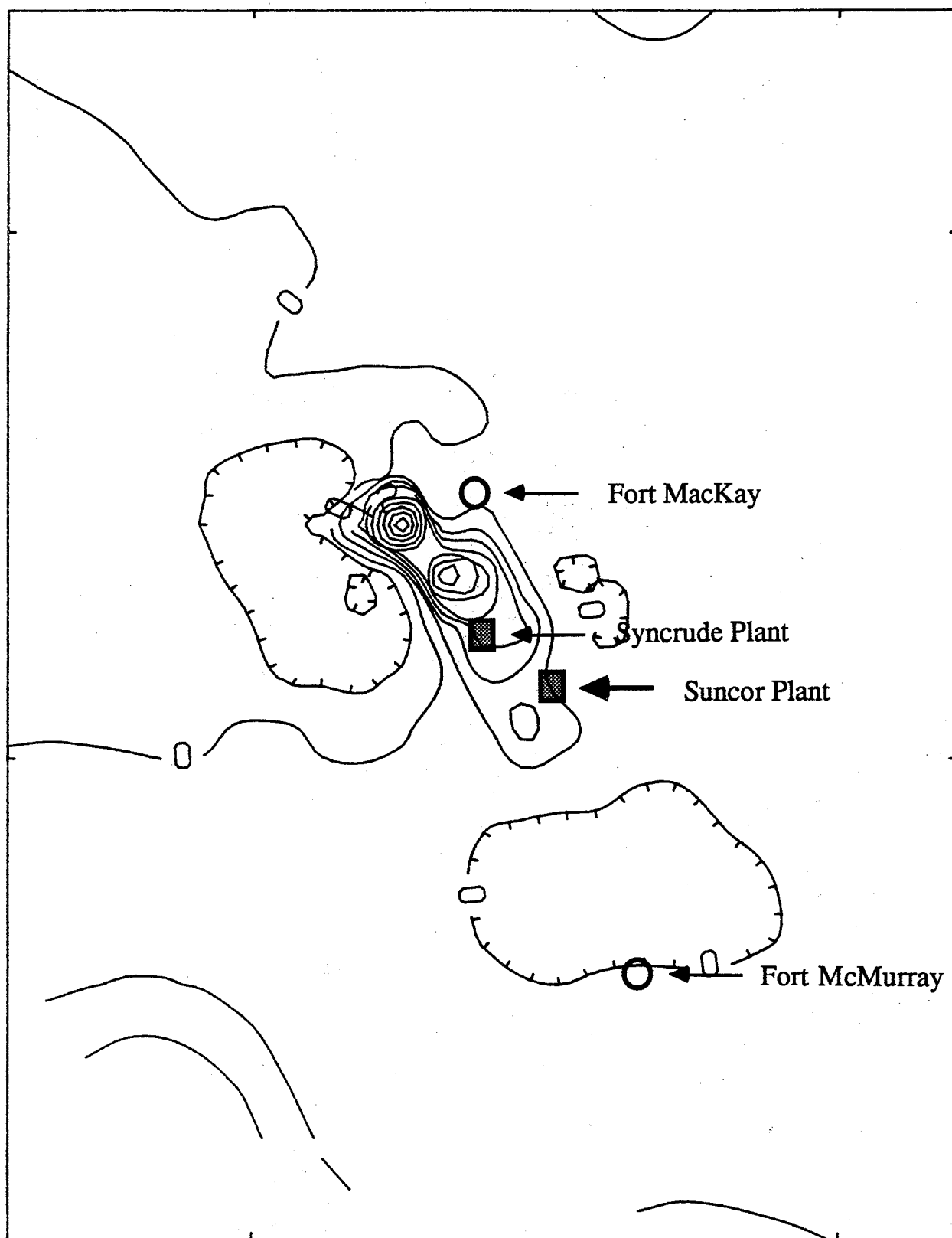


Figure 47

Map based on the products of standard normalized Al deposition predictions for the Syncrude plant only and observed Al bioaccumulation by *Pleurozium schreberi*. Near the oil sand plants model predictions agree with observed bioaccumulations.

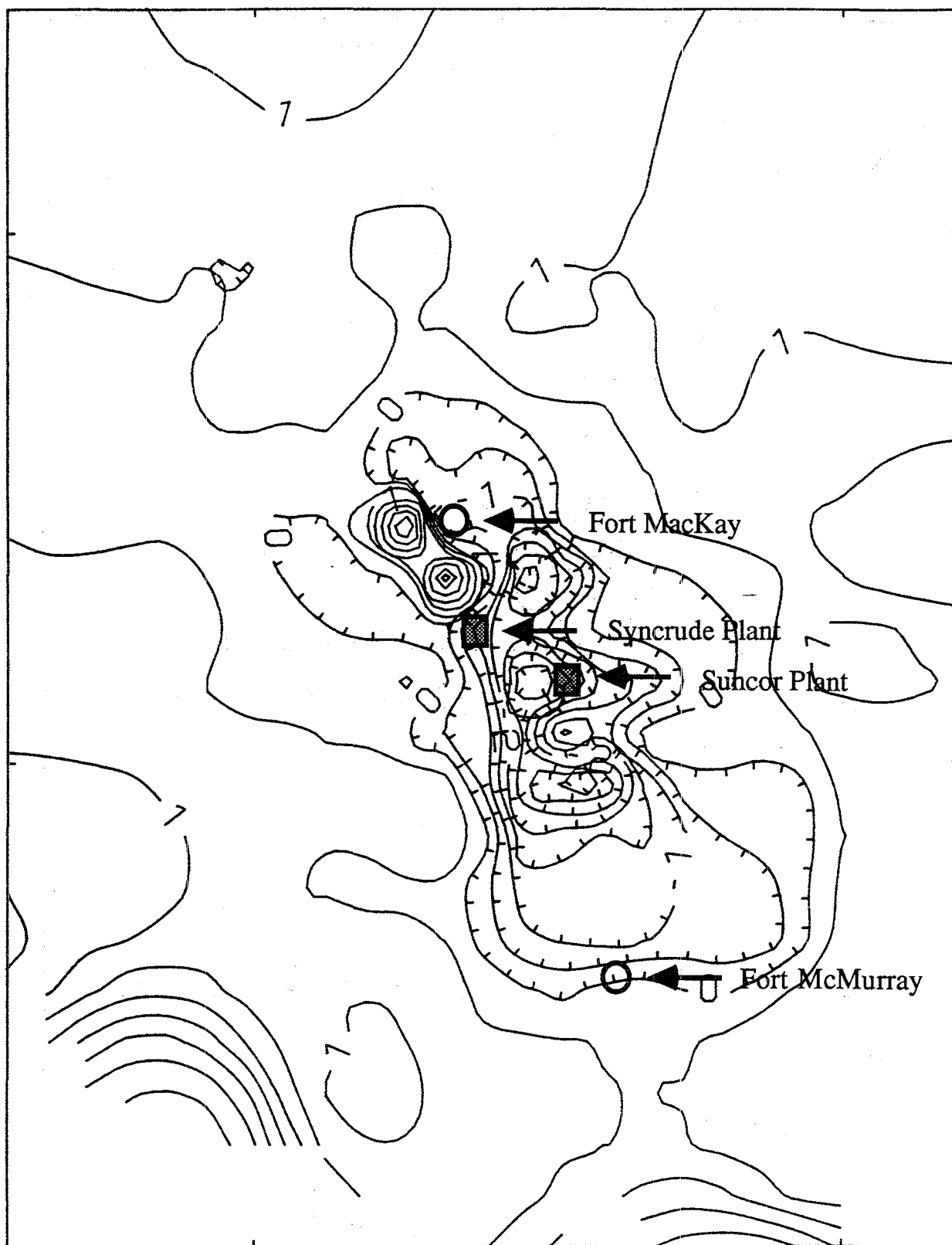


Figure 48

Map based on the products of standard normalized Ti deposition predictions for the Syncrude plant only and observed Ti bioaccumulation by *Pleurozium schreberi*. Near the oil sand plants model predictions agree with observed bioaccumulations. Moving away from the plant sites the agreement decreases as indicated by the hachured contours.

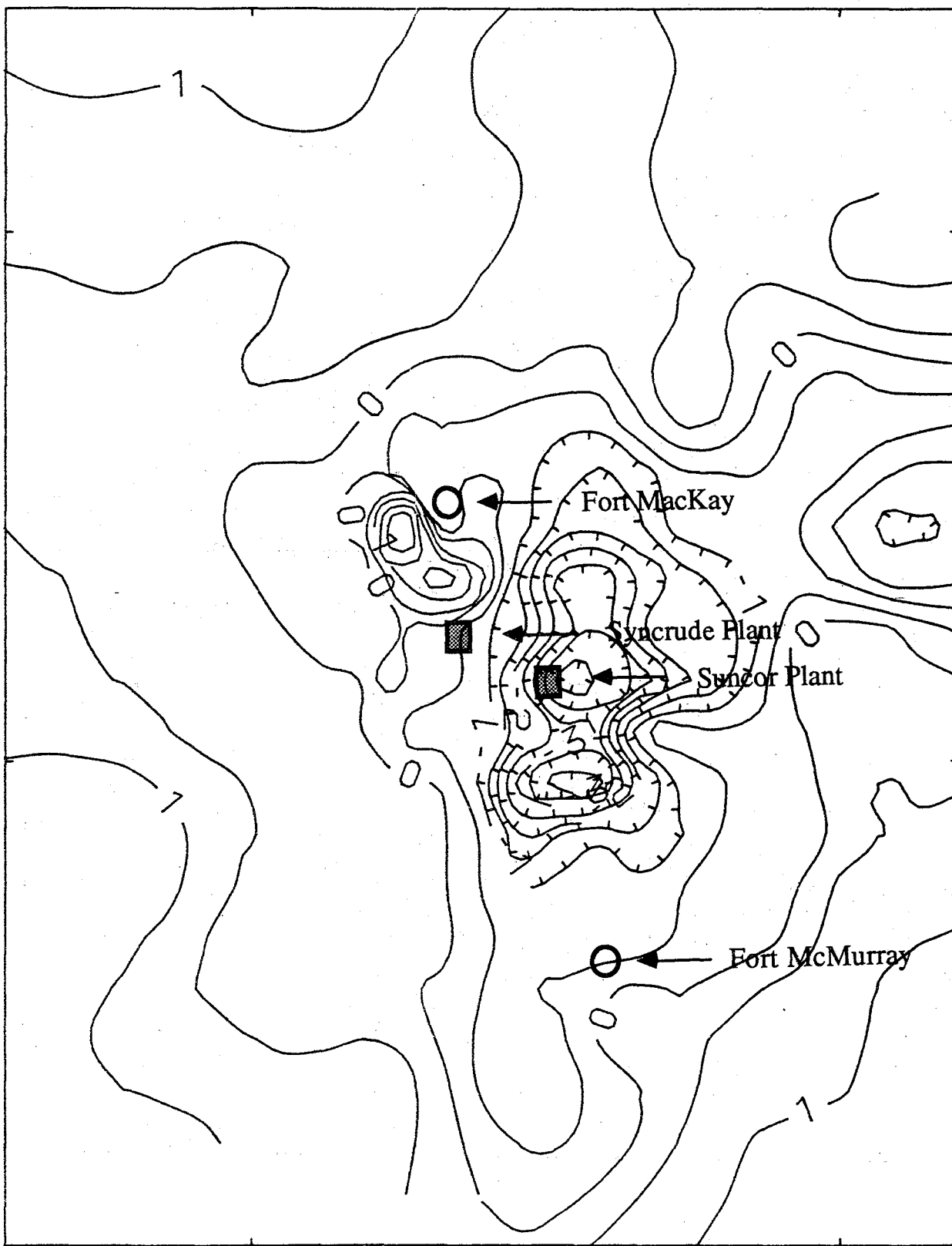


Figure 49

Map based on the products of standard normalized V deposition predictions for the Syncrude plant only and observed V bioaccumulation by *Pleurozium schreberi*. Near the Syncrude processing plant model predictions agree with observed bioaccumulations. Hachured contour lines indicate regions where observed bioaccumulation does not agree with predicted deposition.

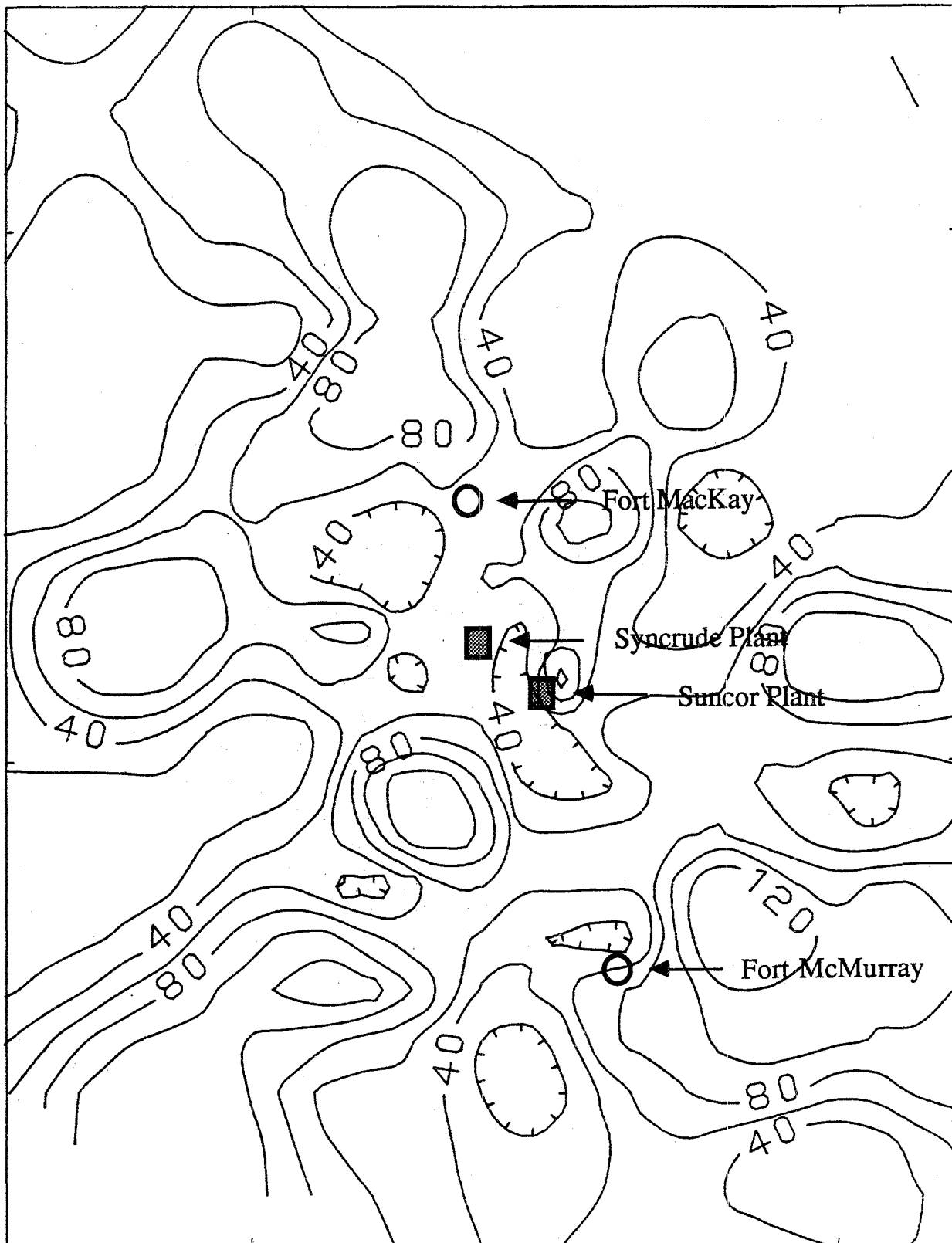


Figure 50

Hg content (ppb) of *Pleurozium schreberi* tissue in the oil sands region of Alberta, 1983-84.

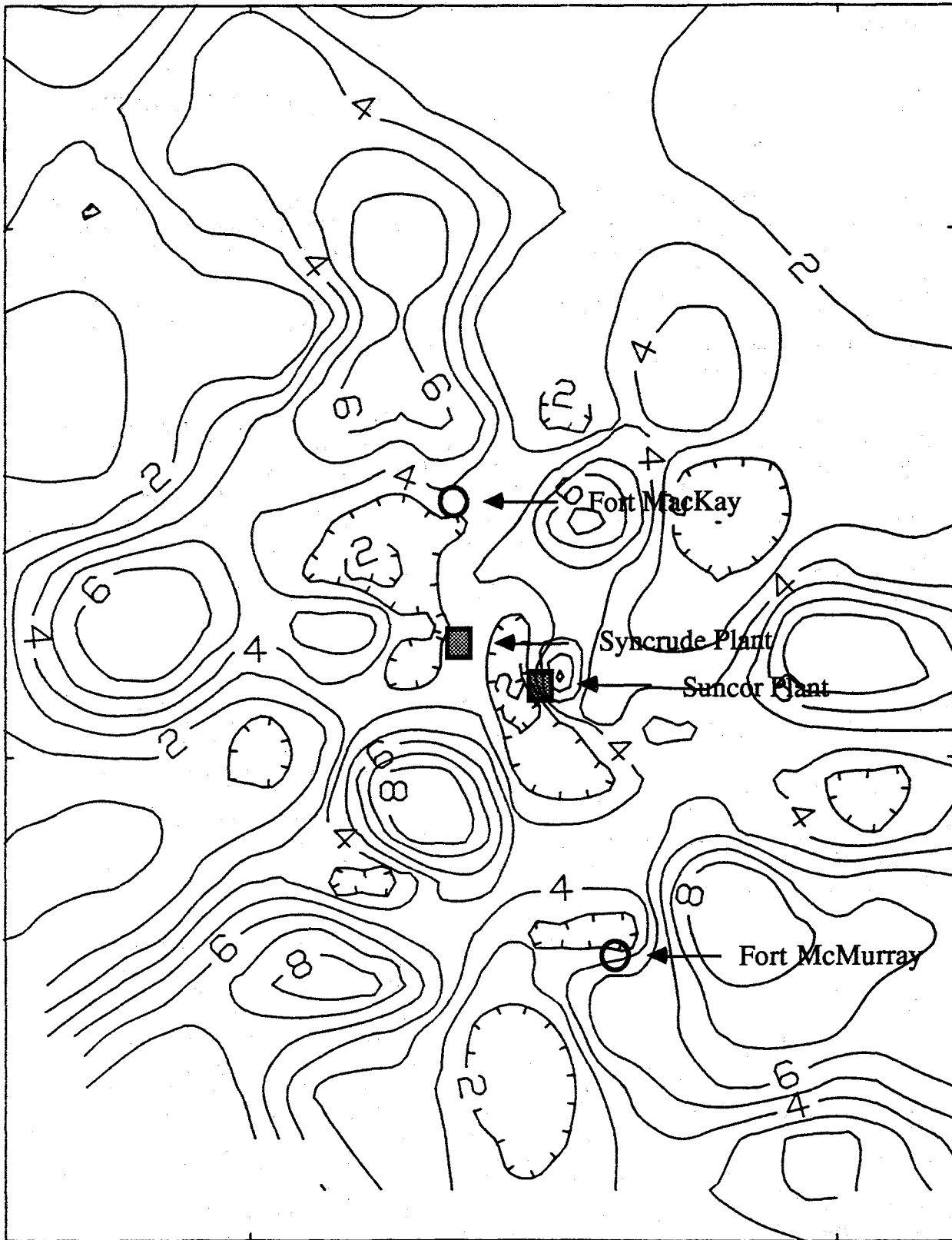


Figure 51

Isopach map of standard normal *Pleurozium schreberi* Hg content minus standard normal model predicted Hg deposition due to Syncrude emissions. A region of lower than expected Hg bioaccumulation occurs north and west of the Syncrude plant. Areas of higher than expected bioaccumulation are associated with the Suncor plant and heights of land.

observations (Figure 52). This suggests that natural sources exist in the region which contribute as much or more to the Hg content of *Pleurozium schreberi* as do industrial sources.

### 3.3 COMPARISON OF VASCULAR AND NONVASCULAR PLANT STUDIES

#### 3.3.1 Stress

Examination of vascular plant stress and elemental content revealed the presence of stress symptoms and elemental accumulations consistent with air pollution exposure in an area within 15 km of the oil sands plants and in association with the Athabasca River valley and its tributaries. This region coincides with the zone of lichen and moss species population decline reported in other independent studies (Loman 1978; Addison and Puckett 1980; Krouse and Case 1981; Case 1982). As of 1984, the vascular vegetation studied in the stress survey within the region would probably be associated with stage two or the maintenance stage of Figure 35.

In this, and other studies in the vicinity of the Suncor operations, it was found that the least luxuriant lichen condition appeared to closely follow the pattern of S content in the lichen (Loman 1978; Krouse and Case 1981; Addison and Puckett 1980). The least luxuriant lichens in 1979 were also found primarily in the vicinity of the oil sands plant along the Athabasca valley, a pattern closely resembling the areas of low level vascular vegetation stress in 1978, and areas of low and medium level vegetation stress in 1984. Thus, studies of lichen luxuriance appear to provide an early indication of areas in which SO<sub>2</sub> stress to vascular plants may be expected to occur.

#### 3.3.2 Elemental Composition

The majority of the elements accumulated by vascular vegetation enter the plants via the roots; much less gets in through the leaves. As a result, the tissue content of most elements will reflect the soil chemistry, and this is further mitigated by metabolic processes. The Fe content of trembling aspen (*Populus tremuloides*) leaves showed no increase in the vicinity of the oil sands plants (Figure 53), even though Fe is the most abundant element in particulate matter emitted by the plants (Table 6). The contribution of particulate emissions to the Fe content, for example, of trembling aspen leaves is masked by the abundance of available Fe present in the soil. No information is available about changes in elemental concentrations in vascular plant root systems.

Examination of the elemental content of vascular and nonvascular vegetation from a small number of sites revealed some similarities in their content of some heavy metals. For example, comparison of the available V concentration data for trembling aspen and *Pleurozium schreberi* revealed a statistically significant linear relationship, although the concentration in vascular plants was nearly an order of magnitude lower than in the moss (Figure 33). Accumulation patterns of some elements in vascular species showed peaks which were associated with the vicinity of the plants. In areas of increased deposition of acid forming sulphate and other sulphurous compounds, there can be an increase in the solubility of potentially toxic metals in the soil (Jones *et al.* 1985). This effect would be exacerbated in areas where particulate matter containing metals was being deposited. Long-term exposure to sulphur and heavy metals has been demonstrated to result in decreased tree growth (Johnson *et al.* 1985) and has been implicated in forest decline in Europe (Andersson 1985; Dickson 1984; Johnson *et al.* 1985; Matzner and Murach 1984; Hutchinson *et al.* 1985).

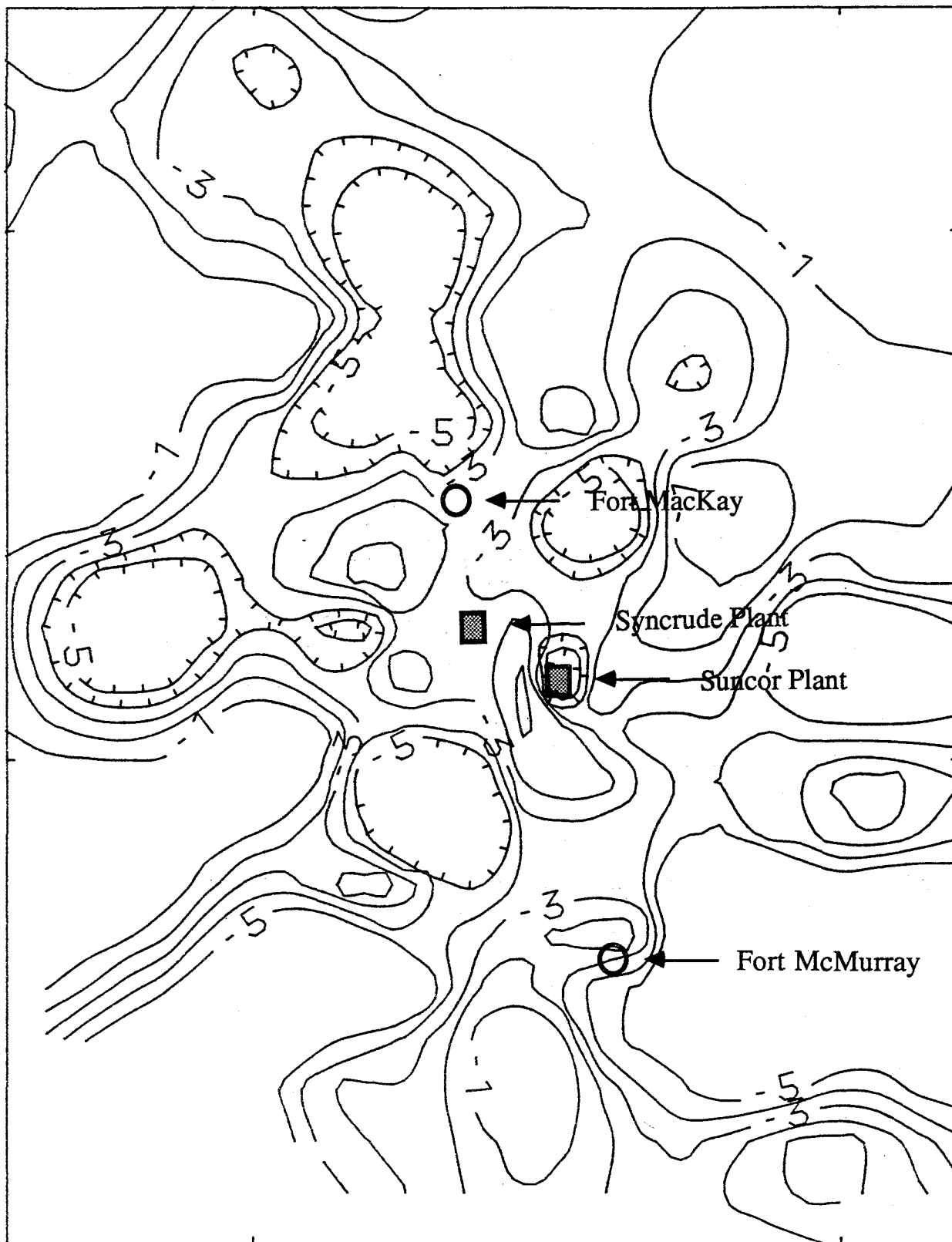


Figure 52

Map based on the products of standard normalized Hg deposition predictions for the Syncrude plant only and observed Hg bioaccumulation by *Pleurozium schreberi*. Hachured contour lines indicate regions where observed bioaccumulation does not agree with model predictions.

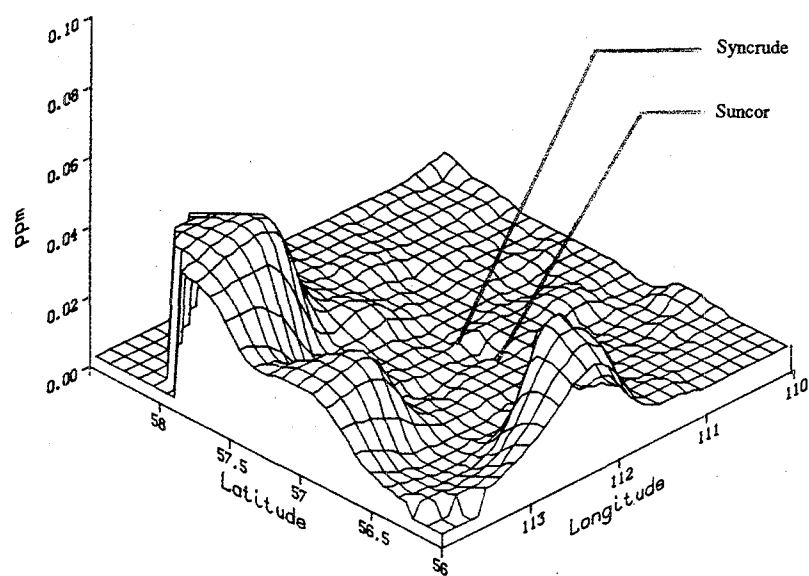


Figure 53 Fe content of trembling aspen leaves (*Populus tremuloides*) in the oil sands region of Alberta, 1983-84.

Within the confines of the vascular plant stress study area, the accumulation patterns were in general agreement with measured bioaccumulation by nonvascular vegetation and with predicted deposition patterns, but only in the immediate vicinity of the Syncrude plant site. Agreement decreased sharply in regions immediately downwind of Suncor.

Bioaccumulation of elements, within limits, agrees with the patterns of deposition predicted by deposition models. Discrepancies appear to be associated with additional sources not included in the deposition models, such as Suncor emissions, and with unidentified natural sources.

Mosses and lichens are reliable indicators of the areas and quantities of trace element deposition. Accumulations of some heavy metals has been detected in vascular vegetation in areas of highest metal content in mosses and lichens.

## CHAPTER 4: CONCLUSIONS

The conclusions presented here have been drawn from the four individual studies. Because the research programs were set-up at different times, had differing objectives and were conducted as separate programs, a range of conclusions has been developed. These results are presented in this manner to understand the work to date and to be used in the refinement of on-going, or development of any new monitoring studies.

- Sulphation cylinder analysis and dispersion modelling indicate that the total annual sulphate deposition in the region should not exceed  $25 \text{ kg ha}^{-1}$ . This compares favourably with the maximum desirable objective of  $40 \text{ kg ha}^{-1}\text{yr}^{-1}$  for total sulphate deposition. Based on  $40 \text{ kg ha}^{-1}\text{yr}^{-1}$ , there should not be any directly, harmful soil acidification effects within the region as the results of S emissions from Syncrude and Suncor.
- The measured emission rate of total particulate matter from Syncrude's main process stack is about  $35 \pm 26 \text{ g s}^{-1}$  ( $3020 \pm 2250 \text{ kg d}^{-1}$ ) at the 90% confidence level. The emission rate, therefore, would be expected to vary between 9 and  $61 \text{ g s}^{-1}$  (770 to  $5270 \text{ kg d}^{-1}$ ) at the 90% confidence level. Similarly, the equivalent emission quantity would vary between 0.014 and  $0.092 \text{ g kg}^{-1}$  of stack gas. This result is well below the Alberta standard of  $0.2 \text{ g kg}^{-1}$  of stack gas.
- The corresponding ground level concentrations of particulate matter and metals in the oil sands area, due only to Syncrude's emissions, as determined by the model calculations, were found to reach a maximum at 3 to 5 km from Syncrude. The maximum ground level concentration (annual average) at this distance was estimated at  $0.06 \mu\text{g m}^{-3}$  for total particulate matter (assumed to be  $0.1 \mu\text{m}$  in diameter). The corresponding range for metals was from  $540 \text{ pg m}^{-3}$  for Fe to  $0.01 \text{ pg m}^{-3}$  for Be. These concentrations are summarized in Figure 11, which is to be used in conjunction with Table 7. These average annual ground level concentrations of total particulate matter and its constituent metals at the point of maximum concentration (3 to 5 km) are, at most, about 10% above typical natural and man-made background levels in the region. Further away, the contribution of Syncrude's emissions is expected to be less than this amount. The estimated ambient levels of particulate matter and metals due only to Syncrude emissions, are, in all cases, more than 100 times lower than any Alberta or North American air quality standards or guidelines and about 1000 times lower than corresponding concentrations in typical populated areas of Canada and the U.S.
- The pattern of vegetation stress agrees generally with the pattern of high ground level sulphate deposition based on an annual average over the period from 1978 to 1983. It is reasonable to conclude that the pattern of future vegetation stress, due to  $\text{SO}_2$  emissions, will continue to follow the pattern of maximum annual average sulphate deposition.
- In 1978, the total area of stressed vegetation was approximately 5500 ha, of which about 4020 ha, or 73%, was due to tent caterpillar, dwarf mistletoe and low degree air pollution. The total area of stressed vegetation in 1984 was approximately 10 300 ha, of which about 8390 ha, or 81%, was caused by insects and disease in combination with low and medium degree air pollution. Large areas of stressed vegetation were located in the valleys centred near the

confluence of the Athabasca and Steepbank rivers, corresponding to the area of highest predicted sulphate concentrations.

- The Syncrude lichen network has revealed the existence of subtle long-term effects in the very sensitive components of the ecosystem as demonstrated by changes in lichen vitality, lichen growth, and elemental accumulation in lichens and mosses. Such impacts existed in 1976 and have continued since the startup of Syncrude. There is, however, little evidence that the rate of elemental accumulation has increased since the startup of Syncrude.
- The region of depressed lichen vitality had increased significantly between 1976 and 1983. Lichen growth and vitality were depressed within a 15 km radius of the oil sands plants in 1983. Reduced incremental lichen growth and vitality, and increased elemental content were correlated with distance and direction from the plants and long-term S deposition.
- The elemental content of lichen and moss samples collected in 1976 were significantly elevated above the expected background values ten years after the start-up of the first oil sands plant. By 1984, elemental contents had increased by 50% or more at most of the resurveyed sites. In addition, the area in which elemental contents were elevated above the background level had increased in size.
- Based upon elemental analysis of biological samples, it appears that metallic element containing particulate matter is deposited within a 40-50 km radius of the emission stacks, but that deposition of those elements emitted primarily in the gaseous form, continues beyond 50 km.
- The process of heavy metal accumulation in sensitive plants is taking place in other areas of the province. Lichen and moss samples from and around Fort McMurray, Edmonton and Calgary show that some metallic elements, such as Pb, have accumulated to levels higher than around the oil sands plants. Elements emitted by the upgrading facilities, however, were higher in the oil sands region.
- The vascular plant study revealed the presence of induced stress symptoms and elemental accumulations consistent with air pollution exposure in an area within 15 km of the oil sands plants and in association with the Athabasca River valley and its tributaries. This region coincides with the zone of lichen and moss population decline.

The monitoring studies were initiated to act as an "early warning" detection system. The objective was to be able to detect changes which might lead to deterioration before any serious damage takes place. The results of these research programs indicate that the early warning system is working. S and trace element accumulation is taking place with stress symptoms observed in mosses, lichens and tree species in the vicinity of the two oil sands plants. However, there is no evidence that serious deterioration of the ecosystem has taken place.

The samples from the urban areas demonstrate that similar accumulations are taking place in other regions of the province. This perspective is useful as it indicates that the oil sands region is not unique. It is essential that additional research be undertaken to address the question of the ecological significance of these monitoring results.

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