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The Assimilative Capacity of the Athabasca River for Organic Compounds

> Project WS 2.3.2 August 1980



15th Floor, Oxbridge Place 9820 - 106 Street Edmonton, Alberta, Canada T5K 2J6

### ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM RESEARCH REPORTS

These research reports describe the results of investigations funded under the Alberta Oil Sands Environmental Research Program. This program was designed to direct and co-ordinate research projects concerned with the environmental effects of development of the Athabasca Oil Sands in Alberta.

A list of research reports published to date is included at the end of this report.

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The Assimilative Capacity

of the Athabasca River for Organic Compounds

Project WS 2.3.2

This report may be cited as:

Wallis, P., E. Peake, M. Strosher, B. Baker, and S. Telang. 1980. The assimilative capacity of the Athabasca River for organic compounds. Prep. for the Alberta Oil Sands Environmental Research Program by Kananaskis Centre for Environmental Research, The University of Calgary. AOSERP Project WS 2.3.2. 106 pp. The Hon. J.W. (Jack) Cookson Minister of the Environment 222 Legislative Building Edmonton, Alberta

Sir:

Enclosed is the report "The Assimilative Capacity of the Athabasca River for Organic Compounds".

This report was prepared for the Alberta Oil Sands Environmental Research Program, through its Water System, under the Canada-Alberta Agreement of February 1975 (amended September 1977).

Respectfully,

acherone, W. Solodzuk, P.Eng.

Chairman, Steering Committee, AOSERP Deputy Minister, Alberta Environment

## THE ASSIMILATIVE CAPACITY OF THE ATHABASCA RIVER FOR ORGANIC COMPOUNDS

### DESCRIPTIVE SUMMARY

Understanding the functioning of the aquatic ecosystem within the mainstem Athabasca River is of paramount importance if protection against the input of contaminants from oil sands developments is to be afforded to the Athabasca River itself, the Peace-Athabasca Delta, and Lake Athabasca. The term assimilative capacity has been applied to denote the dynamic ability of aquatic ecosystems to remain viable and productive in the face of external factors (natural or anthropogenic). An implicit assumption within this definition is the fact that aquatic ecosystems possess the ability to change in response to external factors while maintaining their productivity and diversity. The rate and extent of this adaptive capability is the underlying process of assimilative capacity which must be understood and therefore examined.

AOSERP originally addressed the concept of assimilative capacity in 1977-78 with project AF 2.6.1 (WS 2.3) which initially was intended to examine the assimilative capacity of the Athabasca River due to degradation of organic compounds. However, through a redirection of emphasis, this project examined the chemical and microbial metabolism of carbon compounds in the Athabasca River. This line of investigation was continued in 1979-80 with project WS 2.3.1 examining the microbial metabolism of carbon compounds in the Athabasca River in close proximity to oil sands mining operations.

In 1978-79, project WS 2.3.1 presented a discussion paper which: (1) compiled a list of input parameters contributing to the river system; (2) provided a summary of the processes and effects relating to the inputs to the river; (3) priorized these inputs, processes, and effect; and (4) provided a concise discussion which justified the priorization. This report (project WS 2.3.2) addresses the assimilative capacity concept (in terms of organic compounds) as it applies to the Athabasca River system by addressing the following objectives:

- To analyze available hydrometric, sediment, and water quality data pertinent to the organic regime of the river;
- To synthesize the data into a framework of understanding (working conceptual model) that would eventually be suitable for obtaining the organic assimilative capacity of the Athabasca River;
- 3. To identify data gaps that require filling in order to operate the model as a simulation tool; and
- 4. To arrange and conduct a workshop for information users in both Government and Industry.

While a succinct understanding of the assimilative capacity of the Athabasca River remains an illusive quarry, the authors are thanked for their contribution which has led one step closer to achieving that ultimate goal.

This report has received external review and the Research Management Division recommends that it be published. However, because this report constitutes a program planning document for the AOSERP study area rather than a source of significant and original scientific data, it will receive limited distribution.

W.R. MacDonald, Ph.D Director Alberta Oil Sands Environmental Research Program

# THE ASSIMILATIVE CAPACITY OF THE ATHABASCA RIVER FOR ORGANIC COMPOUNDS

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ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM

Project WS 2.3.2

August 1980

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#### EXECUTIVE SUMMARY

The assimilative capacity of the Athabasca River has been defined as the ability of the river to respond to effluent loading and still maintain its productivity and diversity. In order to estimate the assimilative capacity, it is necessary to understand the processes of degradation, the amounts and types of effluent which reach the river, and seasonal effects. In order to do this, a working conceptual model of the river must be established and built up to the point where predictions of the effects of effluent loading can be made.

The Athabasca River cuts through several Devonian and Cretaceous formations in the AOSERP study area, including the heavy oil-bearing McMurray Formation and the highly saline Methy Formation. Only 5 to 15% of the Athabasca River discharge originates in the study area. Below Fort McMurray the river is laterally stable and less incised downstream. No valley walls exist by the time the river reaches Embarras. The bed material or substrate is variable and ranges from bedrock through cobble, bitumen, sand and mud. The river is turbid at all times although the suspended sediment load is strongly dependent upon the discharge. Mixing characteristics have been examined under winter conditions and calculations show that complete mixing will not occur in less than 94 km if the effluent is injected at the edge of the river.

Although all rivers ultimately obtain their energy from the sun, food chains in the Athabasca River (like almost all rivers) are predominantly based on plant and animal detritus from terrestrial sources (Hynes 1963, 1970). Algae are the most noticeable primary producers in the Athabasca River but the extent of their energy contribution is unknown. The main source of energy, however, is allochthonous organic matter of terrestrial origin. Bacteria cling to stationary submerged surfaces in a slime matrix and also colonize organic particles drifting in the current. These particles

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are eaten by a variety of filter feeders in the benthic community such as *Simulium* and various Trichoptera. Where light levels are high enough to support the growth of phytoplankton, these are incorporated in the slime matrix and form a rich food substrate for scrapers such as *Baetis* and *Heptagenia*. Insects and fish in turn feed upon these herbivores. Predatory fish such as northern pike may in turn eat smaller fish.

The most productive time of year in the Athabasca River seems to be the winter when flow is at a minimum, turbidity is reduced, and numbers of phytoplankton and animals are high. At this time the substrate is relatively stable, permitting increased colonization by benthic invertebrates in areas where discharge would be too violent at other times of the year. Fish are generally absent from the river at this time except for pike, trout-perch, chub, shiners and some arctic grayling. With the advent of spring, discharge increases and much of the river bed becomes unstable and therefore unsuitable for many of the species which had lived there during the winter. Increased discharge increases the turbidity which further limits primary production. This trend in combination with the return of many fish persists into the summer and fall. As the autumn progresses, conditions become more stable and the cycle repeats itself.

A considerable variety of data were provided by AOSERP including several organic water quality parameters. Unfortunately many of these data are compromised by missing analyses, a random sampling program which often extended over several days, and some analytical inconsistencies. These problems are discussed at more length in the text and the results are summarized below.

Total organic carbon data are very nearly equal to dissolved organic carbon data, an unusual occurrence which may have been caused by incorrect analytical procedures for total organic carbon. Both of these chemical parameters may be observed to increase below Fort McMurray and in the vicinity of Suncor and Syncrude. Concentrations are often higher in the summer and autumn than in the winter. It is not known whether this is the result of changes in effluent loading or in the assimilative capacity of the river. The analysis of nitrogen compounds in natural waters is a complex process. The total kjeldahl nitrogen test is too general to use for any measurement of the assimilative capacity as it cannot tell the difference between a simple amino acid and a toxic nitrogen compound. Although total kjeldahl nitrogen was observed to increase near the existing oil sands plants, it is impossible to interpret the data further because of the general nature of the test.

The chemical oxygen demand test suffers from the same lack of specificity. Although COD is higher near the oil sands plants and below Fort McMurray, it is not significantly related to total organic carbon as it should be (r = 0.19). No conclusions may be made from these data. Tannins and lignins are produced by pulp and paper operations as well as from the natural decomposition of plant material. The concentration of tannins and lignins is higher in the tributaries than in the Athabasca River, possibly reflecting the closer contact with decaying vegetation characteristic of headwater regions. No significantly high concentrations of tannins and lignins were found. Humic acids are more refractory compounds which result from the degradation of plant material. Some increases in concentration were observed near Fort McMurray but the reason for this is unclear. It is possible that they represent the end products of the degradation of municipal wastes but this has not been proven. Fulvic acid data are unreliable because of the analytical technique used.

Phenols are known to be present in oil sands effluents and have been detected in the Athabasca River near the Suncor and Syncrude plants in high concentrations. Unfortunately the analytical method used only detects the simple phenols which are readily degradable by abiotic mechanisms. No data are available on more dangerous phenolic compounds in the Athabasca River. Many

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phenol analyses were found to be over the legal limit, especially in the winter under ice conditions. Oil and grease concentrations were also higher in the vicinity of the oil sands plants but the data are variable. This may have been the result of sampling difficulties. This test is not sufficiently specific to detect the presence of dangerous oil sands by-products as it is unable to distinguish between these and naturally occurring erosion (of the McMurray Formation) products. These data may therefore not be used to determine the influence of the existing extraction plants upon the river. Hydrocarbon data are not significantly related to oil and grease data although they should be. This observation supports the contention that the standard chemical tests are inadequate for the analysis of the complex organic effluents which are known to enter the Athabasca River.

The monitoring of organic water quality parameters serves to check for compliance to water quality standards and also to measure the disappearance or accretion of organic compounds in the river. The problems described above with existing analytical methods show that they are neither accurate or adequate to deal with the complicated assemblage of organic compounds in the river. The need for improved analytical techniques is clear. Although some research is required to work out the details of a new analytical scheme, a starting point is suggested in the text. Once a standard analytical procedure has been established, uptake measurements may be made in the field by combining a comprehensive sampling plan with discharge measurements calculated by a computer program. These data permit the calculation of a chemical budget over a selected test reach of the river so that net losses of different compounds may be detected. These data are essential for modelling purposes as both rates and amounts lost may be calculated if the method works.

Organic compounds enter the Athabasca River from several sources. Plant and animal degradation products are natural organic compounds which come from upstream sources, groundwater, tributaries,

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and some of the more refractory compounds (such as humic acids) may be generated in the river. Oil sands related compounds include mine depressurization waters, groundwater containing dike seepage and the by-products of *in situ* work, upgrading plant effluents, erosion products (of the McMurray Formation), and spills of crude, sludge, or refined oils. It is of great importance to know the volume of effluent discharges as well as their chemistry for modelling purposes. Unfortunately many data of this sort are not available at this time. Municipal effluents from the town of Fort McMurray and the oil sands plants have an appreciable biological oxygen demand. More data are required regarding both the volume and chemistry of municipal effluent discharges for modelling purposes. The addition of methoxychlor and the possible presence of pesticides in municipal effluent may adversely affect any future biomonitoring studies which are carried out.

Insufficient oxygen data are available at present for winter conditions under ice. Future oxygen modelling for upstream regions should include the AOSERP study area as well. The data which are available indicate that oxygen conditions under ice are not critically low.

Losses of organic compounds to sediments may occur by biological uptake or chemical adsorption and precipitation. The rate of water transfer and of uptake should be investigated. The toxicity of organic compounds should be investigated within the larger context of toxicity in all four systems. This work will be aided by the results of biomonitoring and the calculation of chemical budgets.

Biomonitoring should be undertaken according to the plan put forward by McCart (1980). This consists of a preliminary consolidation of background information, the selection of suitable test organisms, and the establishment of a routine biomonitoring program. The results from biomonitoring will serve to integrate the cumulative effects of many effluent discharges on the aquatic flora and fauna and demonstrate any changes in community structure which may result.

### ACKNOWL EDGEMENTS

This research project WS 2.3.2 was funded by the Alberta Oil Sands Environmental Research Program, established to fund, direct, and co-ordinate environmental research in the Athabasca Oil Sands area of northeastern Alberta.

### INTRODUCTION

The development of the Athabasca Oil Sands will necessarily result in the addition of industrial, municipal, and other effluents to the Athabasca River and its tributaries. All of these effluents will contain various amounts and types of organic compounds which will influence the Athabasca River and the Peace-Athabasca Delta. In order to preserve the integrity of the river and its delta, it is important to understand how these organic inputs will influence the plants and animals which live in them. In order to do this it is necessary to consider their sources, concentration in the river, mixing characteristics, processes of degradation, and toxicity. Although a great deal of work has been done, gaps in the data remain. Of even greater importance is the lack of a framework of understanding which might be developed into a working predictive model. This report will synthesize the data which do exist into such a framework of understanding and will attempt to specify the work which needs to be done in order to create a model with the ability to predict the effects of various organic inputs to the river.

1

### 1.1 PROJECT OBJECTIVES

This project is intended to provide a problem analysis of the goal to determine the assimilative capacity of the Athabasca River with special regard to organics. Objectives for the project are:

- To analyze available hydrometric, sediment and water quality data pertinent to the organic regime of the river;
- To synthesize the data into a framework of understanding (model) that would eventually be suitable for obtaining the organic assimilative capacity of the river; and
- To identify data gaps that require filling in order to operate the model as a simulation tool.

1.

The data used in this report were all either provided by Alberta Oil Sands Environmental Research Program (AOSERP) or taken from other reports. None of the data used in this report were produced by the Kananaskis Centre except those quoted from Strosher and Peake (1976, 1978, 1979) under the terms of reference for previous projects.

1.2 DEFINITION OF ASSIMILATIVE CAPACITY

The term "assimilative capacity" implies that there is a level of input (in this case organic) which the river can absorb without being harmed or changed. Rivers are very dynamic ecosystems which (when healthy) have the ability to change in response to many external factors and still support life. Changes have already occurred because of oil sands development and they will continue to occur as long as the amount and type of organic inputs changes. Whether or not the adaptations which occur in the river are harmful and should be stopped is another question altogether. At the moment it is necessary to understand the processes of adaptation which are taking place in the river so that predictions may be made as to long term effects and the consequences of changes in the loading rate. When this is understood and an effective predictive model has been created, it will be easier to decide what effects can be tolerated and what must be regulated.

The term "assimilative capacity" is therefore defined as the ability of the river to respond to changes imposed upon it by man's activities and still maintain its productivity and diversity. It does not assume that a certain amount of stress may be absorbed without harmful effects. Only by understanding the processes which are occurring in the river can this possibility be evaluated.

1.3 BACKGROUND INFORMATION IMPORTANT TO THE PROBLEM

1.3.1 Hydrogeology

The stratigraphic sequence in the AOSERP study area (Figure 1) begins with an impermeable bed of crystalline

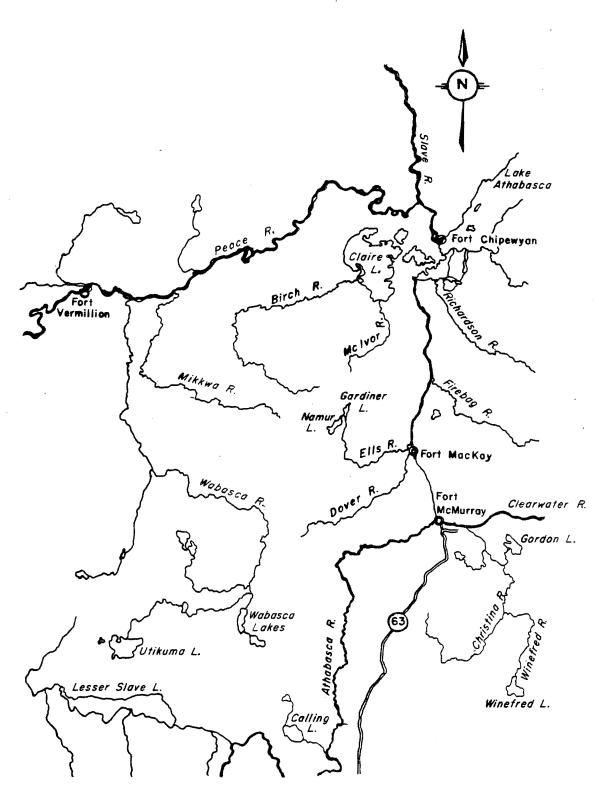


Figure 1: The AOSERP study area.

Precambrian rock (Gorell 1974) that dips southwest at the rate of about 5.3 m/km (Hackbarth 1977). This bed is overlain by a sequence of Devonian rocks ranging in thickness from over 762 m in the western part of the area to less than 152 m in the east and consists of carbonates and evaporites (Figure 2). The principal carbonate aquifer is the Methy Formation whose hydrostatic head often extends above the oil layer and sometimes to the surface (Gorell 1974). The Methy is overlain by the Prairie Evaporite or Upper Elk Point Formation which consists largely of salt. Extensive cavities have been created in this formation by solution (Figure 3) and it communicates over wide areas with the Methy aquifer. These two Devonian members are the source of the troublesome saline groundwaters in the area.

The Devonian section is overlain by a sequence of Cretaceous members including the oil bearing McMurray Formation. Dissolution of salt from the Prairie Evaporite Formation can cause communication between the major Devonian aquifer (Methy) and the major Cretaceous aquifer (McMurray)(Gorell 1974). Extended pumping of the McMurray aquifer may therefore cause an increase in the salinity of the mine depressurization water in conjunction with the organic compounds contributed by the oil sands in the McMurray Formation. The resulting mixture is either discharged into the Athabasca River via channels and tributaries or reinjected into the ground. The Cretaceous members are overlain by glacial deposits of Pleistocene age ranging in thickness from up to 183 m in the east to less than 30 m in the west (Hackbarth 1977).

The Athabasca River cuts through several formations during its passage through the AOSERP study area, including the oil bearing McMurray Formation. Although a detailed list of all the formations which the river does intersect is not available, an examination of cross-sections provided by Schwartz (1979) reveals that it does cut through several Devonian and Cretaceous members at or below the water surface (Figure 4). According to Neill and Evans (1979) it is reasonable to assume that there is substantial

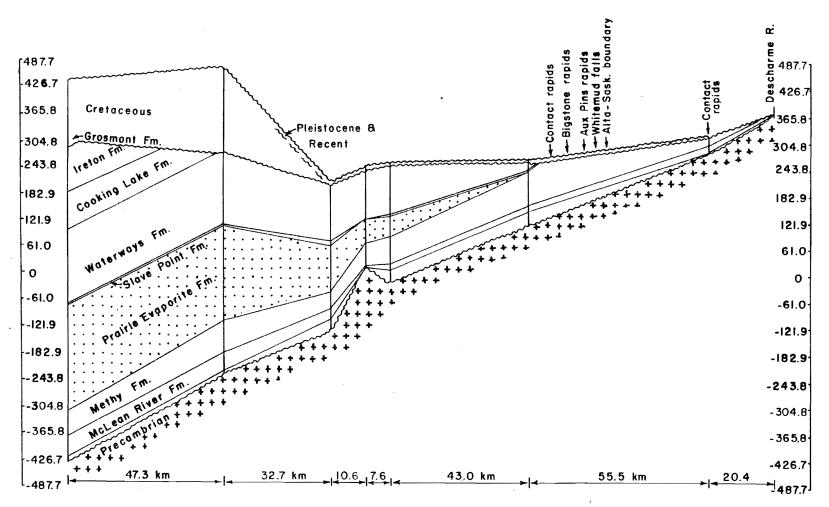


Figure 2. Cross-section showing Paleozoic sequence (from Norris 1973 in Gorell 1974).

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EAST

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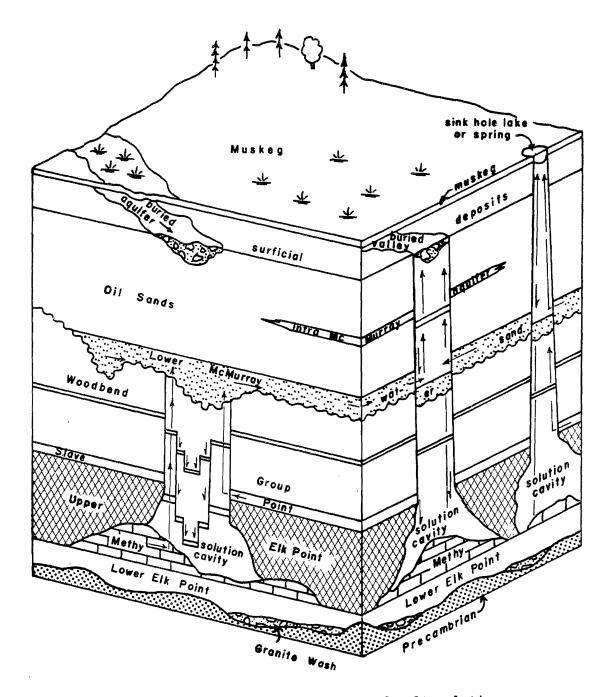
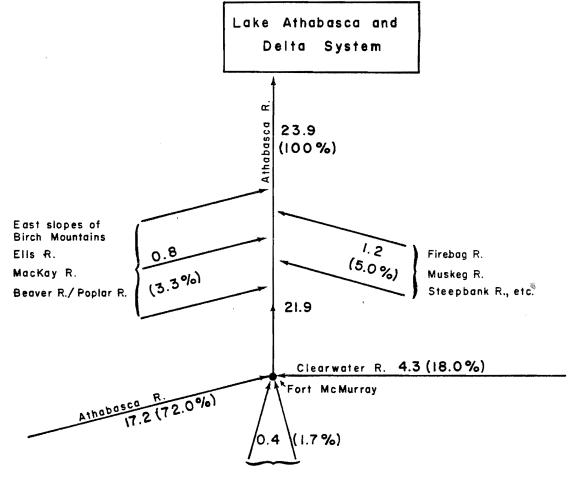


Figure 3. Sketch showing possible effects of salt solution on groundwater systems (not a scale) (from Gorell 1974).

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Horse & Hangingstone Rivers

Athabasca River inflow to lake system: 17.2 + 0.4 + 4.3 + 0.8 + 1.2 = 23.9Lake outflow to Slave River: 23.9 + 1.2 + 2.6 + 9.4 + 8.2 = 45.3Units of  $km^3 (= 10^9 m^3)$ 

Figure 4. Mean annual streamflow balance (Neill and Evans 1979).

subsurface flow into the Athabasca River, although few data are available. In the Muskeg River basin, Schwartz (1979) found that between 12 and 40% of streamflow during the late spring, summer, and autumn months is supplied by groundwater. Groundwater discharge from various aquifers to the Athabasca River most probably occurs at intervals throughout its length although its magnitude is unknown. No attempt seems to have been made to measure groundwater flow into the river probably because of inherent inaccuracies in river gauging. It would appear, however, that organic compounds from the McMurray Formation and salts from the Methy Formation are probably entering the river from groundwater sources.

### 1.3.2 Surface Water Hydrology

Neill and Evans (1979) have synthesized the available data pertaining to surface water hydrology. They state that between 5 and 15% of the Athabasca River discharge originates from within the AOSERP study area (see Figure 5) and that the great majority of the discharge in the river originates from above Fort McMurray. Roughly 80% of the rainfall in the study area is evapotranspired and this amount is normally limited by moisture supply rather than by atmospheric capacity. This information suggests that although groundwater recharge may be occurring through the Athabasca River bed, the amount is low in comparison to total river discharge. In 1976, snowmelt runoff consisted of only 33% of the water content of the late winter snowpack. The remainder of the water was either recharged into the ground or evaporated. About 20% of the precipitation in 1976 appeared as runoff but the variability between sub-basins was large. On the whole, Neill and Evans (1979) concluded that the data were not extensive enough for accurate analysis but that this situation will change as monitoring continues over the next five years.

Doyle (1977) has provided a description of the characteristics of the Athabasca River itself. In general, the river below Fort McMurray is laterally stable and deeply extended in its valley. The river itself becomes less incised downstream and

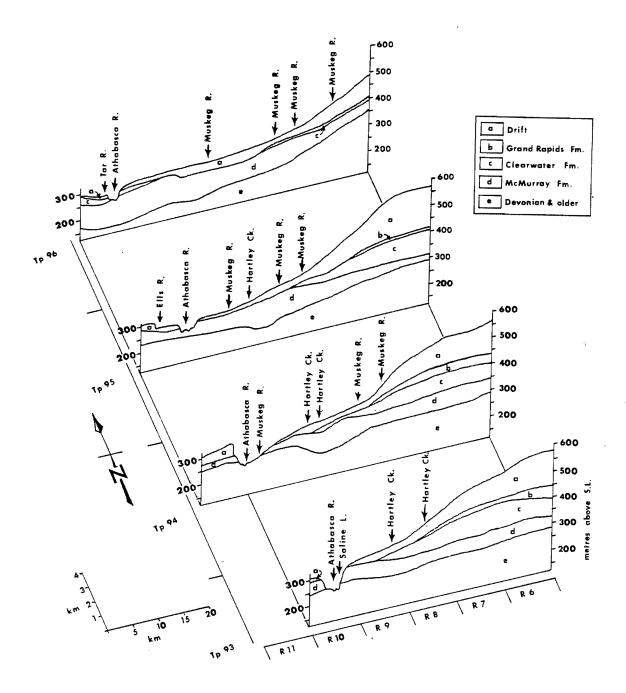


Figure 5. Geology of the Muskeg River Basin showing formations intersected by the Athabasca River (from Schwartz 1979).

no valley walls exist at all downstream of Embarras. At this point, the river begins to meander over a wide floodplain culminating in the Peace-Athabasca Delta. The average channel depth increases dowmstream and the average velocity decreases. The channel appears to be stable although the river bed is very active over much of its reach and bed material size increases downstream from Fort MacKay (which is unusual). Spring ice jams may back up water to levels which exceed summer floods. The overbank flow and the relative volume of tributary flow can cause considerable difference in flood peaks and travel time. If flood peaks exceed  $3200 \text{ m}^3$ /sec at the gauge below Fort McMurray, the peak volume of water which reaches the Embarras gauge is generally reduced because of these two machanisms. In the tributaries, about half of the annual peak discharge is attributable to snowmelt and these waters may comprise a large part of the total flow at Embarras.

Bed materials, which are so important to benthic organisms in the river, vary along the course of the river. At Fort McMurray the bottom consists of sand with local gravel over limestone. The banks at this point are 80% erodable rock and 20% clay and gravel. By the time the river reaches Embarras, the channel has become moderately unstable with meanders progressing downstream. The bed material is sand which is probably quite deep and the banks are composed of alluvial sand, silt, and clay. The river channel throughout the oil sands region is dotted with small islands, sand bars, and spits; all of which may change from year to year. As discharge increases, the suspended sediment load also increases. The mean particle size of suspended sediment at Fort McMurray appears to be consistently between 0.01 and 0.02 mm (Warner and Spitzer 1979) although these data have not received comprehensive analysis. The data which appear in Warner and Spitzer, and any others which may be available, should be analyzed more fully in order to determine sedimentation rates and the stability of the stream bed. Although the turbidity of the Athabasca River may be expected to influence its biology (by reducing the light penetration for example), very little seems to be known about it.

The evaluation of the effects of the introduction of effluents to the river must also take into account the mixing patterns of the river channel. If complete mixing took place immediately downstream of the injection point, as often happens in small channels, prediction of the concentration of effluent at downstream sites would be simple. Mixing in the Athabasca River, however, is considerably more complicated because of variations in discharge, varying bed morphology, the presence of islands, and the large size of the river itself.

Beltaos (1979) has reported the results of mixing experiments carried out under the ice during low flow conditions. He presents numerical solutions to the problem of predicting the concentration of a neutral tracer downstream of an injection site under winter ice conditions. It should be noted that these results apply only to low flow conditions below Fort McMurray and that further testing would be required for predictions to be made during higher discharges. If a point source at the edge of the river is considered (which would be the case for an effluent discharge or a spill), complete mixing would occur within 94 km and 85% mixing would occur within 66 km. If an injection point closer to the centroid of the flow is used, these figures are reduced to 25 and 17 km respectively. If effluents from the existing Suncor and Syncrude plants are considered they would be thoroughly mixed by the time they reached the Firebag River. Above this point the plume would not completely fill the river under winter low flow conditions and a concentration gradient would be found across a transverse section of the channel. The implications of incomplete mixing of a toxic contaminant to plants and animals living in the river will be discussed below. One very important conclusion of this work is that effluents will be well-mixed before they reach the Peace-Athabasca Delta.

### 1.3.3 Biology of the Athabasca River

Although a rigorous discussion of all the aquatic biological work done in the Athabasca River is beyond the scope of this report, a brief description of important trends and the yearly cycle of events is essential. Data have been collected in the river for algae, bacteria, benthic invertebrates, and fish. Each will be treated in turn and the important points summarized at the end.

1.3.3.1 <u>Algae</u> Very little work appears to have been done on algae in the Athabasca River. The only published report appears to be that of McCart et al. (1977) with some chlorophyll  $\alpha$  data presented by Barton and Lock (1979). The following discussion is taken almost entirely from the former source.

The two most obvious factors limiting the growth of algae in the river are turbidity and discharge (both velocity and water level are important). An analysis of the former relationship is difficult as there are neither turbidity nor suspended sediment data available for 1975 (the year of the study of McCart et al.). There are data for 1976 and it would appear, by extrapolation, that standing stocks of algae increase when turbidity is lowest in the late autumn and winter. This winter period is characterized by relatively high light penetration (despite the ice cover) and stable flow patterns, both of which are conductive to growth. Water temperature appears to be less influential. An examination of the 1975 discharge hydrograph reveals that high standing stocks of algae exist at periods of both high and low flow. During this time interval, however, the discharge in the river varied from 198 to 2 548 m<sup>3</sup>/s so that much larger portions of the river channel were flooded during periods of high discharge. This would allow increased growth in the river as a whole, a fact which is not shown by standing stocks measured on a square metre basis.

Attached algal communities found throughout the year in the Athabasca Riber were dominated by diatoms (Bacillariophyceae, 61.3%) followed by green algae (Chlorophyta, 17.8%), blue-green algae (Cyanophyta, 11%), non-diatom Crysophyta (8.9%), and unicellular flagellates (Cryptophyta, 1%). During the period of ice cover (January to April in this study) the periphyton community was dominated by the Cyanophyta with some Crysophyta present. Crysophyta became dominant from June to August when discharge, river velocity, and turbidity were high. The Cyanophyta return in large numbers in the autumn and persist through the winter. Diversity, as calculated by the Shannon-Weaver Diversity Index and the Equitability Factor, remained reasonably high throughout the year with increases in the spring and autumn. 1.3.3.2 Bacteria Bacteria may be divided into planktonic and sessile groups. Planktonic bacteria have been studied in the Athabasca River by Costerton and Geesey (1979) who made direct counts on raw water samples and attempted to relate bacterial numbers to water chemistry. They found that populations ranged from 1 X  $10^5$  to 2 X  $10^6$  cells/mL. Planktonic bacteria are generally free-floating with some colonization of organic detrital materials. Despite the high turbidity in the river, silt particles were found to be generally free of bacteria. No correlation was observed between total kjeldahl nitrogen, total organic carbon, or flow and bacterial enumeration. A slight negative correlation of bacterial numbers with turbidity and total unfilterable residue was found. From this work, they concluded that no effect on the river was detectable from the mining activities of either Suncor or Syncrude.

Nix et al. (1979) measured the uptake of radioactively labelled glutamic acid by planktonic bacteria in the river. Although their project was not completed, they concluded that the rate of uptake was not influenced by the effluents from the existing oil sands plants. Although the uptake rate of glutamic acid gives an indication of the general metabolism of the system, it

does not say anything about the uptake of organic effluents. A preliminary enumeration of specific physiological groups such as sulphur oxifizers, sulphide producers, hydrocarbon oxidizers, and organic acid oxidizers, on the other hand, showed that these populations may increase ten-fold or more at a site just below the area of mining activity. Of particular importance was the observation that bacteria capable of oxidizing hydrocarbons are present in the sediment of the river at all sites and in increased numbers in the upgrading pond effluent (which contains significantly more oil). Higher populations were found in the sediment which contains considerably more hydrocarbons than river water. Although Nix et al. (1979) feel that this evidence is sufficient to conclude that "any spill of refined oils would be easily assimilated by these preadapted populations of bacteria" (p. 49); actual uptake rates have not been determined, the effects of different mixing patterns have not been discussed, and field testing of this hypothesis has not taken place. The fact that spilled oil would float on the surface of the water and be in only limited contact with benthic bacteria until some time had passed is not even discussed.

Although the degradation of oil can be at least partially achieved by bacteria, breakdown is rarely complete and many fractions are not touched. Hydrocarbon oxidizing bacteria appear to be common in both soil and water although their numbers are very small. If a source of hydrocarbons becomes available, the population of hydrocarbon oxidizers will greatly increase and significant breakdown of the oil commences. Simple aliphatic hydrocarbons are broken down readily. Branched and phenolic hydrocarbons are broken down more slowly and the entire molecule is not always mineralized completely. Some of the most complex molecules are not broken down at all. Considerations such as these render the hypothesis that bacteria can easily assimilate refined oils improbable. Some breakdown will undoubtably occur, particularly in the sediments, but the length of time required depends upon the nature of the oil to be degraded, oxygen conditions, and temperature, among other factors. The role of sessile bacteria in the sediments may be very important in this regard.

Sessile bacteria growing on fixed submerged surfaces are numerically more important than planktonic bacteria and form an important component of the decomposition cycle in rivers (Geesey et al. 1978; Wallis 1979). Barton and Lock (1979) measured sessile populations in the Athabasca River on one occasion in the autumn of 1977. They found populations ranging from 8.4 X  $10^6$  to 1.9 X  $10^7$  cells/cm<sup>2</sup>, slightly lower than similar samples taken from the Muskeg and Steepbank rivers  $(1.4 \times 10^7 to)$ 1.3 X  $10^8$  cells/cm<sup>2</sup>; Lock and Wallace 1979). No other data appear to be available despite the importance of this group suggested by the results of Nix et al. (1979). 1.3.3.3 Benthic Invertebrates Flannagan (1976) has briefly described the life cycles of several common aquatic insects from the Athabasca River. Although the results of his study were complicated by the addition of methoxychlor, he was able to demonstrate life cycles up to three years in length for stoneflies such as *Pteronarcys dorsata*. Other insects such as the Ephemeropteran *Heptagenia flavescens* appear to have a simple one

year life cycle. This work was preliminary in nature and more detailed conclusions cannot be drawn from it.

The benthic invertebrate population of the Athabasca River was sampled by Barton (in press) and Barton and Lock (1979) in late 1976 and early 1977. In general, benthic populations are strongly correlated to substrate type. This complicates any study of the benthos in the Athabasca since the bottom type is very variable and may change with discharge. River discharges can fluctuate more than ten-fold in one season (Loeppky and Spitzer 1977). Pockets of organic debris exist throughout

the river and support the usual communities of shredders, filter feeders, and predators. Where rock outcrops (usually Devonian limestone) exist on banks the benthic communities are comparable to those found in tributaries to the Athabasca and to other rivers throughout the world (Barton and Lock 1979). The more unstable sand and mud substrates were dominated by the Chironomidae rather than the Oligochaeta found by other investigations on similar substrates (Barton and Lock 1979; McCart et al. 1977). Fine and medium sand were dominated by the larvae of the chironomids Polypedilum breviantennatum, Cryptochironomus, Robackia claviger, and Paracladopelma spp. All of these are predaceous, elongate forms with thick cuticles, well adapted to burrowing in unstable sands and similar to those found on comparable substrates in Russia, the southeastern U.S.A., and in large lakes (Barton and Lock 1979). Medium and fine sands in the Athabasca River are dominated by an undescribed species of chironomid designated as "Orthocladiinae B" by Barton and Lock (1979). This tiny chironomid is numerically very abundant but its biomass amounts to only 0.2  $g/m^2$ . The importance of this organism as a food resource is difficult to assess as it is too small for accurate identification in gut content analysis. Exposed limestone bedrock supported the most diverse community, probably of great importance to fish, consisting of various members of the Ephemeroptera, Plecoptera, Trichoptera, Empidae, and Chironomidae (Barton in press). The presence of bitumen in the substrates lowers both numbers and diversity of organisms (Barton and Wallace 1979). Burrowing and negatively phototropic organisms were significantly reduced on a portion of exposed bitumen in the Steepbank River studied by these authors. While less suitable than bedrock or rubble as a substrate, bitumen is more favourable than shifting sand. Communities which do live on bitumen tend to be dominated by the Chironomidae and Oligochaetae (McCart et al. 1977).

1.3.3.4 <u>Fisheries Biology</u> Griffiths (1973) carried out a detailed survey of the fisheries in the oil-sands area before any large scale disturbance had occurred in the area. Fish samples were obtained, growth patterns analyzed, and habitat evaluations were made. He identified the Clearwater River, Firebag River, Ells River, and Steepbank River basins as being particularly important to the local fishery. The information contained in this report will be of great use to environmental impact assessments made in the future.

Bond (1980) has prepared an excellent summary of the fisheries biology of the Athabasca River below Fort McMurray. Twenty-seven species of fish representing 10 families may be found in the river itself while 18 species occur in the Delta study area. Most fish populations in the Athabasca River are migratory; only pike (Esox lucius), trout-perch (Percopsis omiscomaycans), lake chub (Couesius plumteus), and flathead chub (Platygobio gracilus) appear to be year-round residents. All species, except goldeye (*Hiodon alosoides*) use the Athabasca River itself and its tributaries for spawning as the shifting sands of the Delta provide a poor substrate. Some fish spawn in the Athabasca River above Fort McMurray, particularly whitefish (Coregonus clupeaformis) (Jones et al. 1978), walleye (Stizostedion vitreum), flathead chub, emerald shiners (Notropis atherinoides) spottail shiners (Notropis hudsonius) and burbot (Lota lota) (Bond in prep.). Large runs of walleye, longnose suckers (Catostomus catostomus), white suckers (Catostomus commersoni) and goldeye occur each spring from Lake Athabasca into the river and most enter smaller tributaries before the ice leaves the Athabasca<sup>®</sup>River. The migration of goldeve is a move to summer feeding grounds which extend from Lake Athabasca to Fort McMurray. Arctic grayling (Thymallus arcticus) remain in the tributaries until just prior to freeze-up and then probably return to the Athabasca River to overwinter. Burbot are believed to spawn in the Mildred Lake area and upstream of Fort McMurray.

Northern pike spawn in marshy areas throughout the Athabasca River and its tributaries. Longnose suckers, white suckers, arctic grayling, trout-perch, and lake chub spawn in the lower reaches of tributaries, particularly the Muskeg River, the Steepbank River, and the Mackay River. Many fry of all species appear in the Athabasca River during June and July although most are believed to be carried by the current to the delta or Lake Athabasca (Bond 1980).

Benthic invertebrates are important in the diets of lake whitefish, longnose suckers, white suckers, flathead chub, emerald shiners, trout-perch, lake chub, spottail shiners and arctic grayling. Other fish, such as walleye, northern pike, and burbot, are predatory upon smaller fish. The maximum danger time for most fish species is during the spring and early summer when fish either pass through or spawn in the Athabasca River. If a large discharge of toxic effluents caught the adult fish in their annual run up the river to spawn in the early spring, a significant portion of the fishery could be wiped out. Excessive BOD loads at this time could have disasterous results as most of the run occurs while the ice is still covering the river. The same is true in June and July when large numbers of fry of all species are being swept down the delta or Lake Athabasca. The autumn is also an important time for the autumn spawning lake whitefish. Although oxygen problems are unlikely to occur at this time, toxic chemicals in the water could seriously affect the spawning of these commercially important fish.

1.4 SUMMARY OF BACKGROUND INFORMATION

The assimilative capacity of the Athabasca River has been defined as the ability of the river to respond to effluent loading and still maintain its productivity and diversity. In order to estimate the assimilative capacity, it is necessary to understand the processes of degradation, the amounts and types of effluent which reach the river, and seasonal effects. In order

to do this a working conceptual model of the river must be established and built up to the point where predictions of the effects of effluent loading can be made. The following discussion is intended to pave the way toward the establishment of a conceptual model by discussing the work already done and identifying some of the gaps in the background information. Processes which are identified in later chapters will contribute further to this model and research designed to measure rates and other pertinent information will be discussed.

The Athabasca River cuts through several Devonian and Cretaceous formations in the AOSERP study area including the oil-bearing McMurray Formation and the salt-bearing Methy Formation. Both organic compounds and salts enter the river from these formations via groundwater inputs and direct exposure through river bed erosion. Only 5 to 15% of the Athabasca River discharge originates in the study area. Below Fort McMurray, the river is laterally stable and less incised downstream. No valley walls exist by the time the river reaches Embarras. Ice jams in the spring may cause flooding greater in magnitude than summer storms and may result in bank flooding. The bed material or substrate is variable and ranges from bedrock through cobble, bitumen, sand, and mud. The river is turbid at all times although the suspended sediment load is strongly dependent upon the discharge. Islands, spits, and sand bars appear and disappear with changing discharge and shifting currents. Mixing characteristics have been examined under winter conditions and calculations show that complete mixing will not occur in less than 94 km if the effluent is injected at the edge of the river. More mixing studies need to be carried out to define the changes in this important parameter with discharge.

Although all rivers ultimately obtain their energy from the sun, food chains are usually based on plant and animal detritus from terrestrial sources (Hynes 1963, 1970). Algae

appear to be the dominant primary producers in the Athabasca River but the extent of their energy contribution is unknown. The main source of energy is most probably allochthonous organic matter of terrestrial origin.

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Bacteria cling to stationary submerged surfaces in a slime matrix and also colonize organic particles drifting in the current. These particles are eaten by a variety of filter feeders in the benthic community such as *Simulium* and various Trichoptera. Where light levels are high enough to support the growth of phytoplankton, these are incorporated in the slime matrix and form a rich food substrate for scrapers such as *Baetis* and *Heptagenia*. Insects and fish in turn feed upon these herbivores. Predatory fish such as northern pike may in turn eat smaller fish.

The most productive time of year in the Athabasca River seems to be the winter when flow is at a minimum, turbidity is reduced, and numbers of phytoplankton and animals are high. At this time the substrate is relatively stable, permitting increased colonization by benthic invertebrates in areas where discharge would be too violent at other times of the year. Phytoplankton also benefit from this stability and light levels are higher under conditions of reduced turbidity. Fish are generally absent from the river at this time except for pike, trout-perch, chub, shiners, and some arctic grayling. Although winter oxygen data are limited, oxygen does not appear to be critically low at this time of year (this subject will be discussed in greater detail later). With the advent of spring, discharge increases and much of the river bed becomes unstable and therefore unsuitable for many of the species which had lived there during the winter. Increased discharge increases the turbidity which further limits primary production. This trend, in combination with the return of many fish, persists into the summer and early autumn. As the autumn progresses, conditions become more stable and the cycle repeats itself.

#### 2. CHEMISTRY OF THE ATHABASCA RIVER

## 2.1 INORGANIC CHEMISTRY

A discussion of the inorganic chemistry of the Athabasca River is outside the scope of this report. The reader is referred to Seidner (1980) who discusses the water quality of the river within a regional context. This report deals only with organic water quality data and oxygen levels in the river.

#### 2.2 ORGANIC CHEMISTRY

Routine raw water quality data were provided by AOSERP for analysis under the terms of reference of this project. These data were primarily inorganic but included several organic parameters. These were tannins and lignins, humic acid (dissolved), humic acid (extracted), fulvic acid (dissolved), fulvic acid (extracted), total organic carbon, dissolved organic carbon, total kjeldahl nitrogen, phenols, oil and grease, hydrocarbons, and chemical oxygen demand. The methods used and their detection limits are summarized in Table 1.

All organic data were entered onto Memorex Minimarkette soft discs using a Cromemco Z-2D microprocessor along with the appropriate date and distance downstream of Fort McMurray. A program was developed which was capable of sorting the data according to any other parameter (such as day number or downstream distance) and graphing it on an ordinary Sony colour television. A photograph was taken directly from the screen using Kodak Plus-X film, reversed, and printed on photographic paper. Variance, standard deviation, covariance, and linear regressions were simultaneously calculated. In this manner it was possible to handle a large amount of data without recourse to tedious manual graphical techniques. All possible combinations of data which held any promise of revealing useful information were graphed. Of these approximately 100 were printed and saved. The analysis of the data provided consisted of trying to relate downstream concentration changes with mining activity and searching for relationships between parameters.

Analysis	NAQUADAT Code	Method Detect	ion Limit
Tannins & Lignins	06551L	Colourimetric	0.1
Humic Acid	06581L	Carbon Analyzer	1.0
Fulvic Acid	93050L	Carbon Analyzer	
Total Organic Carbon	06001L	Carbon analyzer	0.5
Dissolved Organic Carbon	06101L	Carbon analyzer	0.5
Total Kjeldahl Nitrogen	07015L	Steam distillation	0.02
Phenols	06532L	Colourimetric	0.001
0il & Grease	06521L	Gravimetric	0.1
Hydrocarbon	06500L		0.1
Chemical Oxygen Demand	08301L	Dichromate digestion	1.0

Table 1. Analytical methods and detection level.

Samples were taken from the Athabasca River by filling a bottle at the surface near midstream. Samples were taken in conjunction with various projects and also as part of a regular program by AOSERP workers (Akena in prep.). For this reason the number of samples taken from the Athabasca River varies from month to month and drops off sharply after 27 February 1977. It is very difficult to identify a comprehensive pattern of sampling because of this. More details of the sampling program may be found in Akena (in prep.).

Nevertheless, several groups of samples can be identified but the time required to take them varied from two to nine days. It is assumed that conditions in the river are constant over a nine day period when sampling sites along the river are compared. Although this assumption is difficult to justify, no evaluation of downstream changes is possible with these data if it is not made. Groups of samples were taken at approximately six week intervals beginning on 9 February 1976 and ending on 27 February 1977. After this date, the number of samples taken dropped off sharply and only a few samples were taken. These data are only useful for spot checks on the concentration of various compounds and they are of little significance to any detailed analysis. In addition to these problems, there are many missing data (oxygen data in particular are very sparse) and certain inconsistencies may be observed which are discussed below. Despite these difficulties some trends and generalizations are evident and will be discussed according to parameter.

# 2.2.1 <u>Total and Dissolved Organic Carbon</u>

Total and dissolved organic carbon data are very nearly equal and so will be considered together (Figure 6). The data are not only strongly correlated (r = 0.96) but are almost identical. This close relationship is unusual in comparison with smaller rivers and streams (Fisher and Likens 1973; Manny and Wetzel 1973; Lush and Hynes 1978) and even in comparison with

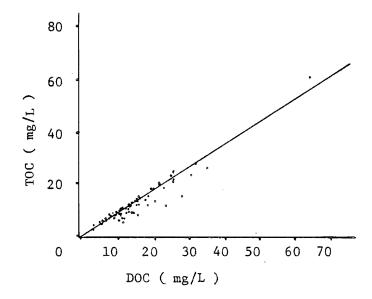
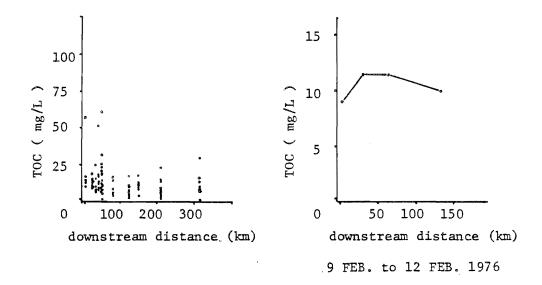


Figure 6. Dissolved organic carbon (DOC) versus total organic carbon (TOC).

lakes (Wetzel and Otsuki 1974). Analytical problems must be suspected here. According to standard NAQUADAT methods both parameters are measured with the same machine (usually a Beckman 915 Total Organic Carbon Analyzer), the only difference being that the sample is filtered through a 0.45  $\mu$ m filter for the dissolved measurement. Particulate organic carbon, which usually accounts for an increase in total organic carbon over the dissolved fraction, appears to be missing. Allochthonous inputs of terrestrial vegetation fragments might be expected to be small where the river is wide but an examination of data from tributaries reveals the same similarity between total and dissolved organic carbon. Tar particles are known to be present in tributaries and in the mainstem Athabasca. These have obviously been missed by the sample collection and analytical methods used. Another potential reason for the absence of particulate organic carbon is that the Beckman analyzer does not permit the injection of large particles because of the narrow syringe needle used (Environment Canada 1974). If samples are not properly homogenized before analysis, the particulate fraction will have settled out and may not appear in the subsample of water used.

Total organic carbon is graphed against downstream distance for various intervals of time in Figure 7. Concentrations are higher in the summer and autumn than in the winter. Spring data are not available. Concentrations tend to be higher below Fort McMurray, presumably because of sewage inputs from the town and from the effluent from Suncor and Syncrude (between 30 and 50 km downstream). In several cases, a sharp spike may be observed downstream of the two plants. Variations in effluent discharge may account for the absence of such a spike on other dates. Dissolved organic carbon follows the same trends (Figure 8).



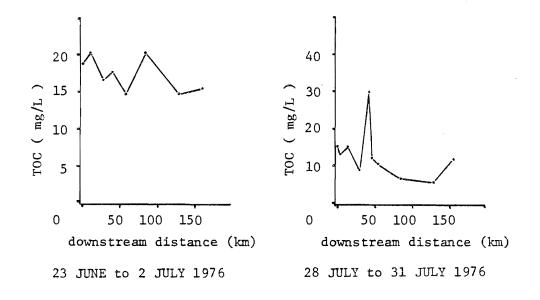
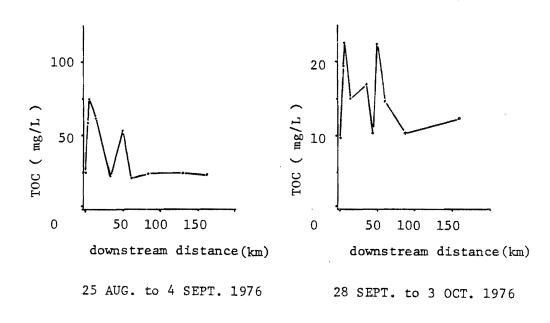
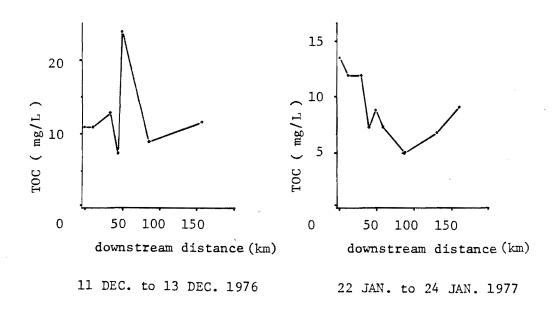
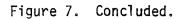
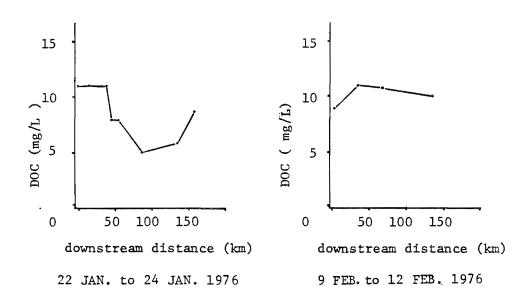


Figure 7. Total Organic Carbon (Continued).









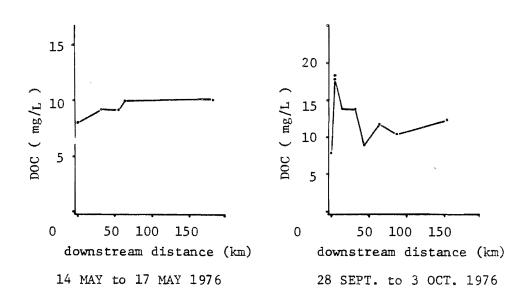
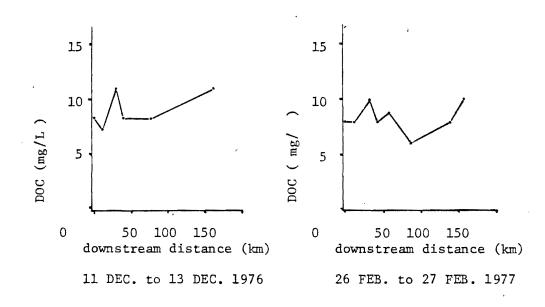


Figure 8. Dissolved organic carbon (Continued).



# Figure 8. Concluded.

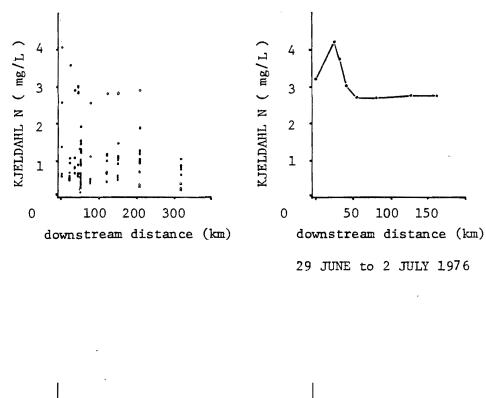
# 2.2.2 Total Kjeldahl Nitrogen

Total kjeldahl nitrogen in the Athabasca River is not significantly related to total organic carbon (r = 0.27) and does not exceed 4 mg/L. This test measures not only organic nitrogen compounds but also ammonia. Under the oxidizing conditions found in the river, however, this component would not be expected to be large. Organic nitrogen compounds include amino acids, aromatic nitrogen compounds such as nitrobenzene, and perhaps aliphatic nitrogen compounds. The analysis of specific nitrogen compounds is a complex and tedious process and has not been attempted in oil sands wastewaters. Strosher and Peake (1976, 1978, 1979) analyzed total organic nitrogen compounds in waters and wastewaters near the operating oil sands plants but did not try to identify them. In general, oil contains a wide variety of compounds which contain nitrogen but they are difficult to identify and quantify.

In the Athabasca River total kjeldahl nitrogen is often higher near the town of Fort McMurray and the extraction plants. As with total organic carbon, this parameter is more variable upstream and concentrations are higher in the summer (see Figure 9). It is impossible to distinguish oil sands compounds from natural or sewage related compounds with this test so that further analysis is not possible.

### 2.2.3 Chemical Oxygen Demand

Chemical oxygen demand is meant to measure the amount of organic matter present by causing it to be oxidized by a standard dichromate solution. In fact it is a poor measure of organic carbon because any inorganic constituent which is oxidizable, particularly chloride, will cause positive errors unless great care is taken. This problem may be the cause of the lack of correlation between chemical oxygen demand and total organic carbon (r = 0.19). Nevertheless measurements made in sequence downstream may be expected to show relative changes even though precisely what is being measured is not clear.



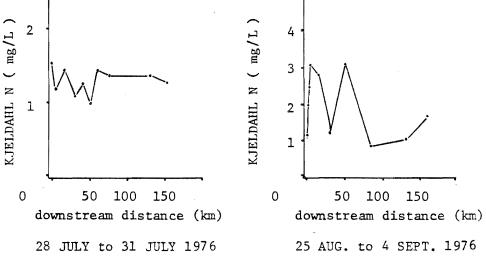
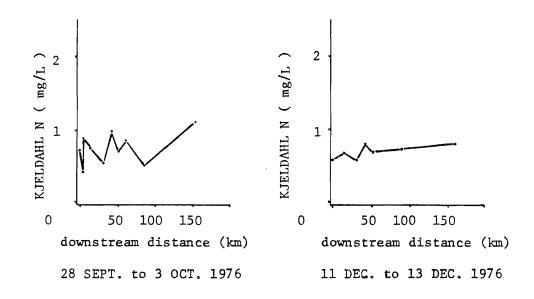


Figure 9. Total KJELDAHL N (Continued).



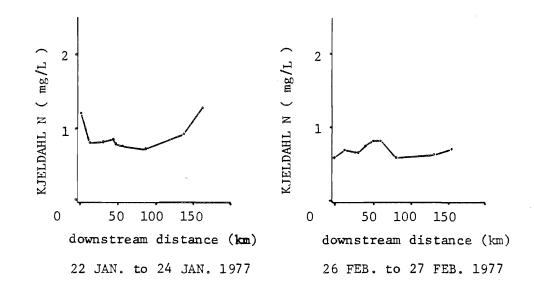


Figure 9. Concluded.

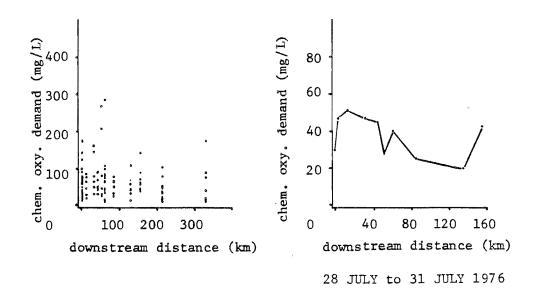
Chemical oxygen demand increases sharply at all times of the year in the vicinity of Suncor and Syncrude. Seasonal trends are not apparent (Figure 10) nor does the town of Fort McMurray seem to be exerting any influence. Increases below the Firebag River can be seen in the sampling series 28 to 31 July 1976, 28 September to 3 October 1976, and 22 to 24 January 1977. These increases remain unexplained.

#### 2.2.4 Tannins and Lignins

Tannins and lignins originate naturally from the decomposition of terrestrial vegetation in the river, from groundwater which has leached through decaying vegetation, and from pulp and paper operations upstream of Fort McMurray. They are moderately degradable under warm aerobic conditions (Wallis 1979) but tend to persist at low levels and are commonly found in ground and surface waters. Background levels of tannins and lignins rarely exceed 2 mg/L in fresh waters and this is the case in the Athabasca River (Figure 11). Several samples are higher than this in the summer and fall, however, particularly in the vicinity of the town of Fort McMurray. The tributaries to the Athabasca are generally higher in tannins and lignins and the junctions of the Horse, Hangingstone, and Clearwater rivers may be the source of higher concentrations in the summer and fall. The concentration of tannins and lignins is low and tends to decrease downstream during the winter. These naturally occurring compounds pose no threat to the quality of the river unless they are concentrated enough to impose a high oxygen demand. Their concentration is modestly related to total organic carbon (r = 0.47) and tends to follow the same seasonal trends.

### 2.2.5 Humic Acid

Humic acids are a large group of naturally occurring compounds which precipitate under acidic conditions (below pH 2). They are highly resistent to microbial attack and represent a



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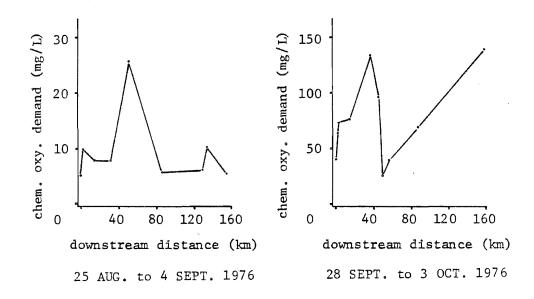
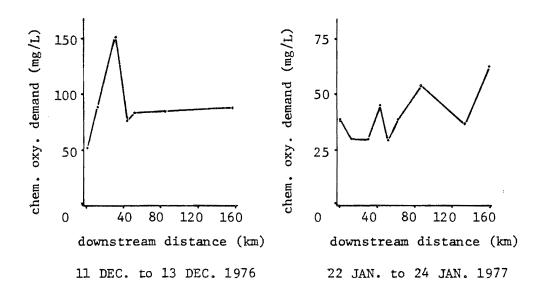
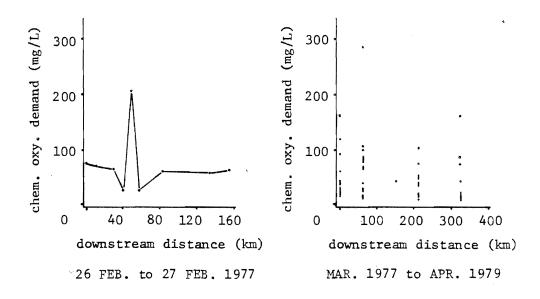


Figure 10. Chemical oxygen demand (Continued).





# Figure 10. Concluded.

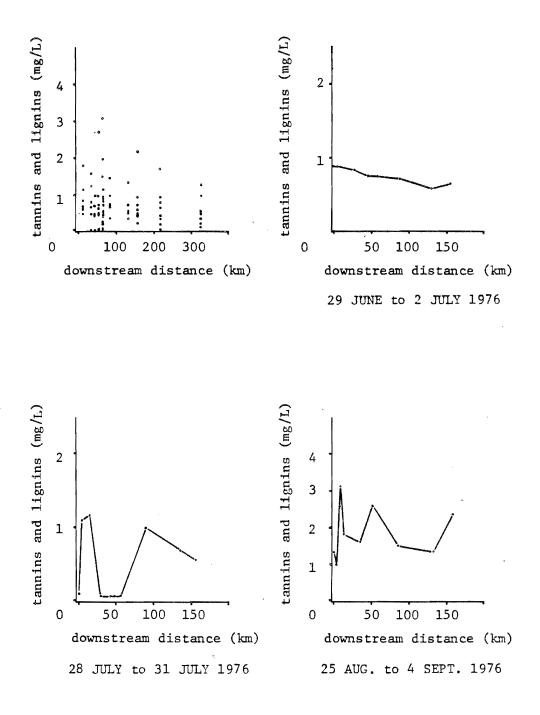
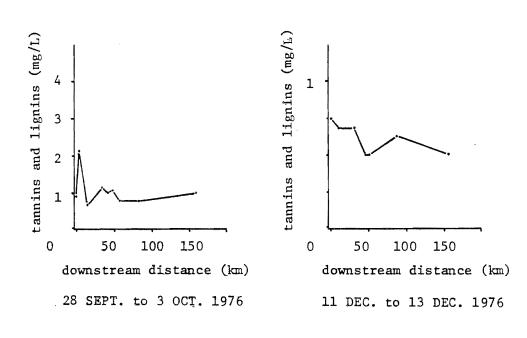


Figure 11. Tannins and lignins (Continued).



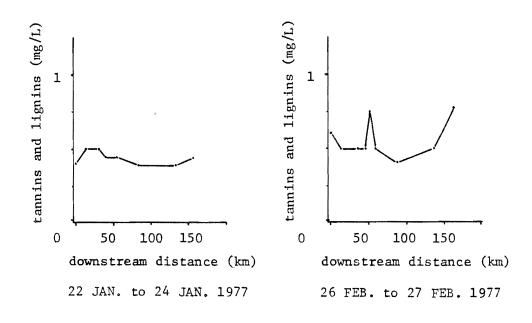
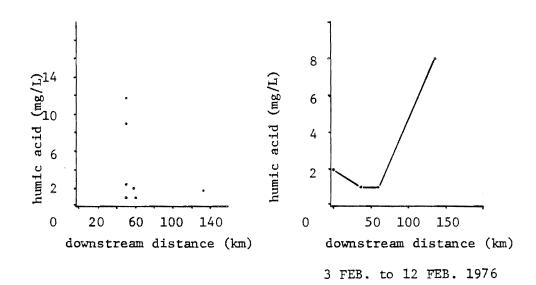


Figure 11. Concluded.

complex collection of plant degradation products. Their molecular weight may be as high as 300 000 (Lawrence 1979) but have also been reported at levels as low as 500 (Schnitzer 1965). Like fulvic acids, they are amorphous, yellow-brown or black, hydrophilic, acidic substances which have a predominantly aromatic core (Lawrence 1979; Cranwell and Haworth 1971). Humic acids have been measured in the Athabasca River in the dissolved (sample was filtered prior to analysis) and particulate (also called extractable; sample was not filtered) state. Results from the two analyses are difficult to relate as they were rarely done together on the same sample. The four samples which did receive both types of analysis are significantly related (r = 0.85) but these data are too sparse to be conclusive. Humic acids are not well correlated to total organic carbon (TOC vs. Hum. dissolved, r = 0.6; TOC vs. Hum. extracted, r = 0.26) or to fulvic acids (Ful. dissolved vs. Hum. dissolved, r = 0.53; Ful. extracted vs. Hum. extracted, r = 0.02).

Humic acids vary much more in the spring, summer, and fall than they do in the winter (Figure 12). Increases are generally apparent in the vicinity of Suncor and Syncrude but may also increase downstream. It is possible that humic acids result from the utilization of labile compounds in the river as the by-products of natural microbial activity. In general, it is believed that as the more labile organic compounds are removed from a water column by bacteria, the concentration of refractory compounds such as humic and fulvic acids increases. The amount of organic carbon, however, decreases within the system as most of the labile organic materialis mineralized to CO<sub>2</sub> (Wallis 1979). Similar results have been observed in groundwater (Wallis 1979) underneath a corn field in Ontario and would not be unexpected in a river. Certainly, there is no reason to associate humic acids with oil sand extraction although groundwater inputs in the area are an unknown quantity. The winter samples show either a constant level of



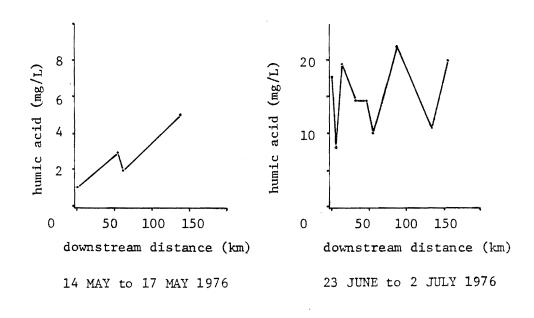
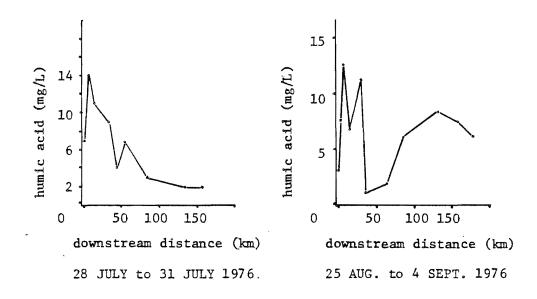
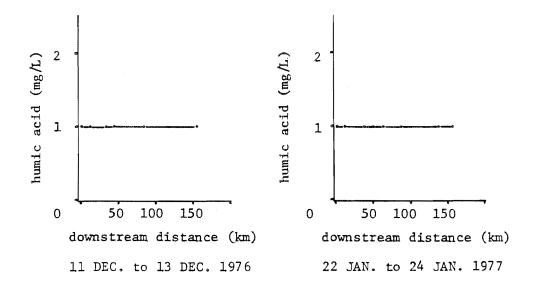


Figure 12. Humic acid (Continued).





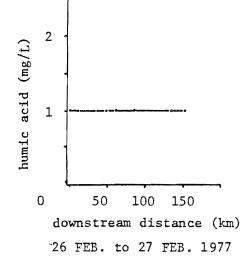


Figure 12. Concluded.

1 mg/L (which is the lower detection limit) or an increase downstream. Downstream increases were recorded in the vicinity of the Firebag River but chemical data from that river do not include any humic acid concentrations above 1 mg/L.

### 2.2.6 Fulvic Acid

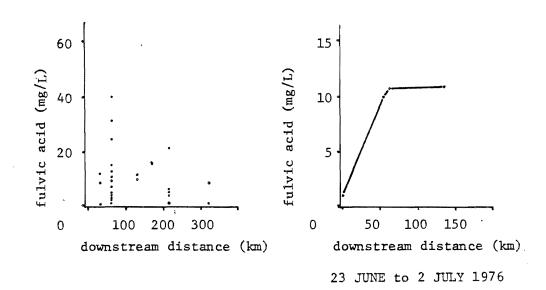
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Fulvic acids are soluble in both acid and base and are of lower molecular weight than humic acids. They are measured by difference from total organic carbon data at pH 2 and 9 (humic acids precipitate at pH 2 and are subtracted from a total organic carbon measurement made at pH 9 to obtain fulvic acids). Unless other compounds can be analyzed for separately or removed by solvent extraction, fulvic acids will be overestimated. As a result, much of what is termed "fulvic acid" here is not fulvic acid at all. A better analytical procedure would have been to identify as many other organic compounds as possible and subtract those as well.

Although humic and fulvic acids are usually measured together, fulvic acid data are much less numerous in the data provided. The data which are available are summarized in Figure 13. The highest concentrations occur in the vicinity of Suncor and Syncrude although some downstream increases are also apparent. These data suggest that "fulvic acids" are being produced in the river in the same way as humic acids, but because of the method of analysis used, they are probably only reflecting the input of oil sands effluent and municipal sewage.

## 2.2.7 Phenols

Phenolic compounds might be expected to increase downstream of Suncor and Syncrude as they are present in plant effluents (Strosher and Peake 1978). This is indeed the case except for two series of samples, one taken from 29 June to 2 July 1976 and one taken from 25 August to 4 September 1976 (Figure 14). A sharp increase by the Firebag River was also observed from 11 to 13 December 1977. As noted by Seider (1980); most of the



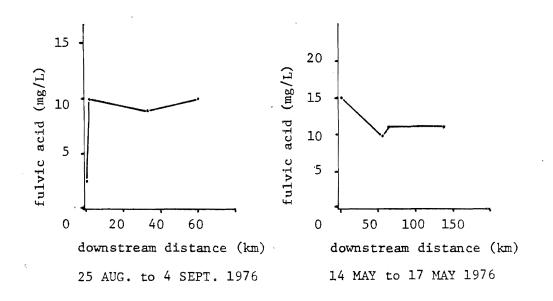
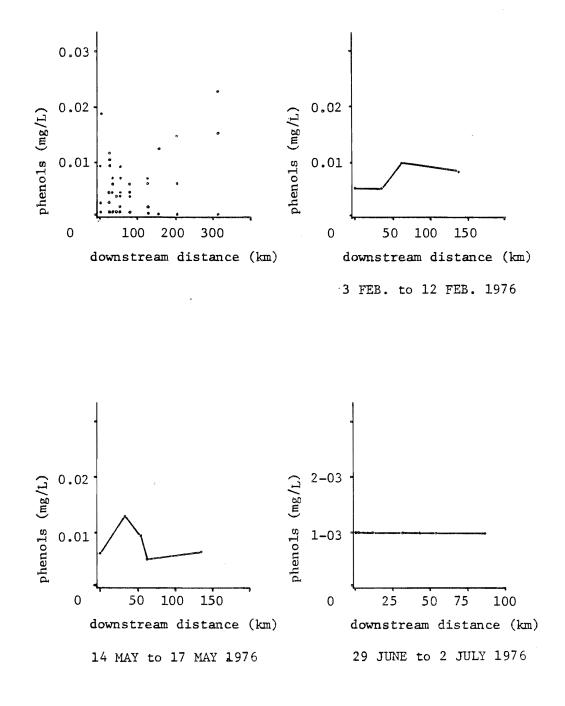
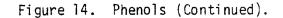
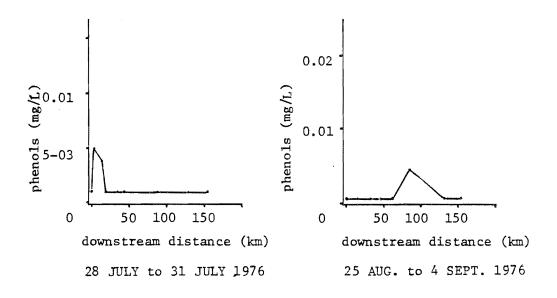


Figure 13. Fulvic acid.







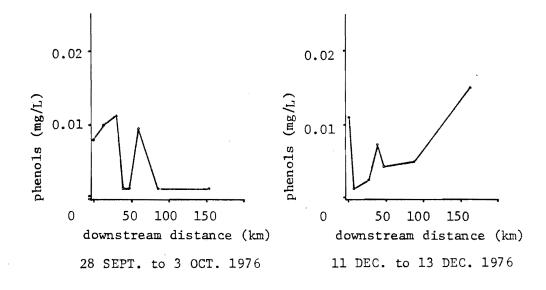


Figure 14. Continued.

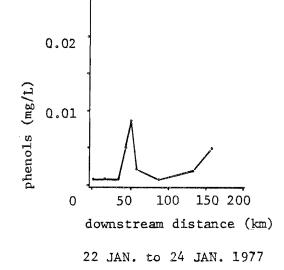
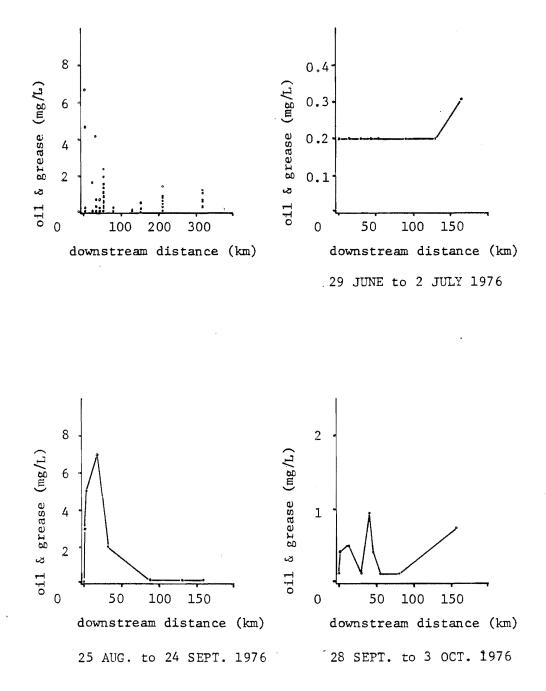


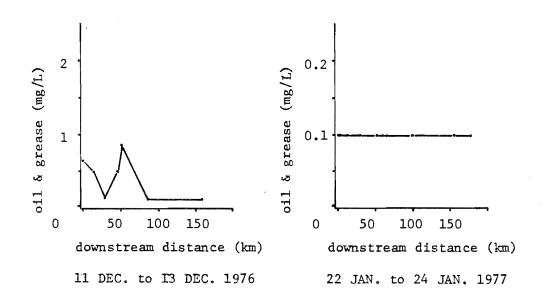
Figure 14. Concluded.

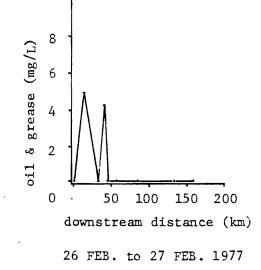
samples which exceeded the recommended limit (0.001 mg/L) were taken during the winter under ice. Assuming that the rate of input is more or less constant during the year, the greater discharge, and therefore dilution, in the spring and summer probably accounts for this. This conclusion cannot be verified on the basis of the data available. The amount of phenol detected in river water was not significantly related to the amount of total organic carbon (r = -0.13) but the breakdown of phenol by abiotic mechanisms is fairly rapid so it is difficult to establish any relationships with other parameters. Unfortunately, the test for phenols which was used only measures the simple phenols which are degradable. The more complex phenols, which are also more toxic and persistent, remain unmeasured. A more comprehensive analysis of phenols is required before definite conclusions may be made.

## 2.2.8 Oil and Grease

Increases in the concentration of oil and grease near Suncor and Syncrude were observed during all sampling series except between 29 June and 2 July 1976 and 22 to 24 July 1976 (Figure 15). High values were found in summer (25 August to 4 September 1976) and in winter (26 to 27 February 1977). As the majority of oil and grease floats on the surface, the effect of discharge would not be expected to be as important as it is with phenols. Variations in effluent discharge may cause differences in thickness on the water surface but sampling error also causes significant variability in results with oil and grease. Substances which do not freely mix with water tend to be patchy in their distribution and it is difficult to obtain a representative sample. Evaporation of the lighter oils and losses during extraction also contribute to error with this method. Oil and grease concentrations are consistently higher near Suncor and Syncrude, however, despite analytical error and sampling problems. Whether these high concentrations are contributed by plant effluent or by







drainage through the oil sands area and erosion of the McMurray Formation is unknown. Oil and grease were not measured by this method by Strosher and Peake (1978, 1979), although their more detailed analysis of hydrocarbons and asphaltenes revealed that oil by-products are present in plant effluents.

### 2.2.9 Hydrocarbons

Too few hydrocarbon data were provided to be analyzed. Of the 16 analyses performed, the highest values occur below the oil sands plants (Figure 16). Hydrocarbons are not significantly related to oil and grease (r = 0.23) although they should be. Analytical difficulties and the paucity of samples are assumed to account for this.

### 2.2.10 Methoxychlor

Although no pesticide data were provided for the Athabasca River, it is known that methoxychlor has been dumped into the river on several occasions as part of the Alberta Black Fly Program. Strosher and Peake (1978) failed to find any traces of the pesticide in the winter under ice; however, methoxychlor is added in the spring and is not persistent. Pesticides are most often found bound to sediments and so may have been present although they were not detected in the water. The input of this material is designed to control black flies well upstream of the oil sands area. The use of methoxychlor in rivers has come under criticism in the past because of its non-specificity and the use of alternatives has not been fully researched for the Athabasca River (Wallace 1979; Flannagan et al. 1979). Continued use of methoxychlor will have a detrimental influence on biomonitoring studies contemplated by AOSERP and it is only fair to point out that it is a potentially hazardous compound.

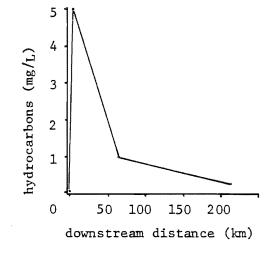


Figure 16. Hydrocarbons.

# 2.3 WATER QUALITY MONITORING IN RELATION TO ASSIMILATION CAPACITY

The monitoring of organic water quality parameters in the Athabasca River serves two purposes. The first is to check whether or not the concentration of various compounds exceeds the legal limit and the second is to determine how the river is coping with the organic load imposed upon it. The first purpose has been adequately carried out over the last three years for some compounds but not for others (such as hydrocarbons). The number of organic analyses which could be carried out is large, however, so choices must be made. The common water quality tests which are applicable in a gross sense (such as the oil and grease test) are too insensitive to yield the detailed information necessary to estimate the assimilative capacity of the river. Unfortunately, no simple established analytical routines exist for handling complex mixtures such as those from the oil sands. Ideally, a separation scheme and analytical procedure such as that used by Strosher and Peake (1978, 1979), should be used to determine the majority of compounds, however, an abbreviated procedure should suffice to assess the overall water quality. Because many organic compounds may adhere to suspended particles, experiments should also be undertaken to determine the importance of this mechanism for oil sands related compounds. This may be accomplished by filtering large volumes of samples and performing duplicate analyses on the retained particles and the filtrate. With these difficulties in mind, the following analytical scheme is suggested. It must be recognized, however, that this plan is untested and would need some development. It is put forth only as a starting point for research toward a practical working analytical procedure.

Although it is difficult to identify individual compounds without expending considerable effort, it is relatively easy to separate the majority of oil sands products (from both naturally eroding banks and from industrial processes) from naturally

occurring organic compounds resulting from plant decomposition. Many of these natural compounds such as humic and fulvic acids, tannins and lignins, and carbohydrates are water soluble and cannot be extracted by organic solvents. Oil sands products, on the other hand, can be extracted from the water and partially separated by their solubility in either polar or non-polar organic solvents at low pH. Extraction efficiency may be increased by the use of continuous extraction techniques (Goldberg and DeLong 1971) which may be adapted for field use if necessary. Naturally occurring organic compounds may be analyzed according to existing methods with the exception of fulvic acids for the reasons stated in Section 2.2.6. It is important to measure the naturally occurring compounds as well as those from artificial sources so that the total amount of organic carbon extracted and/or identified may be calculated.

Most organic compounds from oil sands sources may be separated from naturally occurring compounds by extraction with a non-polar solvent (such as benzene) at low pH (Strosher and Peake 1979). Depending on the organic compounds of interest, concentration and separation of some of these organics may also be achieved by use of adsorbent materials such as organic polymers (Simpson 1972) or polyurethane foam (Gesser et al. 1973; Bedford 1974). These methods are more specific and must be exhaustively tested to determine whether all the compounds of interest are being collected or retained before they can be used on a routine basis. Analyses at this point will give an estimate of the organic compounds from oil sands sources. Many hydrocarbons, sulphur and nitrogen containing compounds, and simple phenols in the extract can be determined directly by gas chromatography and the organic acids can be measured after esterification with  ${\rm BF}_{\rm 3}$  and methanol. Individual compounds will not be identified and high molecular weight compounds will not be detected. Nevertheless, it may be possible to measure relative changes between samples. This scheme is based on the composition of Suncor dike filter drainage and

upgrading plant effluent and should be tested on Syncrude effluent, municipal sewage effluent, and pulp plant effluents before it can be applied to Athabasca River waters comprehensively.

The second purpose of water quality monitoring is to try to determine whether or not the river is degrading compounds. This can not be done on the basis of concentration data alone because of changes in discharge downstream resulting from tributary and groundwater input. If, however, all inputs are known in terms of both volume and concentration, mass loading calculations may be made to determine whether or not compounds are disappearing from a reach of the river.

The problem, of course, is how to measure discharge in a river the size of the Athabasca. There are two gauging stations at the moment, one below Fort McMurray and one at Embarras Airport. These stations are supplemented by further gauging stations on all of the major and many of the minor tributaries to the Athabasca. This information is sufficient to estimate the discharge in the river at any one point using a simulation program developed by the U.S. Army Corps of Engineers. This program is currently being used in Alberta by the Flow Forecasting Branch of Alberta Environment and could be adapted to the Athabasca River (telephone conversation with Bill Kuhnke, Alberta Environment, 11 December 1979). This computer program should be capable of estimating the flow to within 15% which should be sufficient to detect the degradation of organic compounds. Although large analytical errors encountered in measuring organic compounds will also contribute to the total error of the method. The accuracy of the program could be tested during the mixing tests proposed in Section 3.2. Better estimates of flow would be preferable but impractical as the gauging stations in existence are scarcely more accurate and techniques such as dilution gauging are very expensive. If this program is applied to the Athabasca River and samples of water are taken for analysis above and below a test reach, it should be possible to obtain an

estimate of the assimilative capacity without spending large sums of money. It will be necessary, however, to establish the program for the Athabasca River, obtain up to date discharge information from all stations, and to sample in an organized fashion for the technique to work. This topic will be discussed further in the last chapter.

### 2.4 SUMMARY OF THE CHEMISTRY OF THE ATHABASCA RIVER

A considerable amount of data were provided by AOSERP for all water quality parameters including several organic parameters. Unfortunately many of these data are compromised by missing analyses, a random sampling program which often extended over several days, and some analytical inconsistentcies. These problems are discussed at more length in the text and the results of the data analysis are summarized below.

Total organic carbon data are very nearly equal to dissolved organic carbon data, an unusual occurrence in natural waters. Both of these chemical parameters may be observed to increase below Fort McMurray and in the vicinity of Suncor and Syncrude. Concentrations are often higher in the summer and autumn than in winter. It is not known whether this is the result of changes in effluent loading or in the assimilative capacity of the river. Total organic carbon data are not related to total kieldahl nitrogen data. The analysis of nitrogen compounds in natural waters is a complex process. The total kjeldahl nitrogen test is too general to use for any measurement of the assimilative capacity as it cannot tell the difference between a simple amino acid and a toxic nitrogen compound. Although total kjeldahl nitrogen was observed to increase near the existing oil sands plants, it is impossible to interpret the data further because of the general nature of the test.

The chemical oxygen demand test suffers from the same lack of specificity. Although COD is higher near oil sands plants and below Fort McMurray, it is not significantly related to total organic carbon as it should be. No significant conclusions may

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be made from these data. Tannins and lignins are produced by pulp and paper operations as well as from the natural decomposition of plant material. The concentration of tannins and lignins is higher in the tributaries than in the Athabasca River, possibly reflecting the closer contact with decaying vegetation characteristic of headwater regions. No significantly high concentrations of tannins and lignins were found. Humic acids are more refractory compounds which result from the degradation of plant material. Some increases in concentration were observed near Fort McMurray but the reason for this is unclear. It is possible that they represent the end products of the degradation of municipal wastes but this has not been proven. Fulvic acid data are unreliable because more than fulvic acids are measured by this method.

Phenols are known to be present in oil sands effluents and appear in the Athabasca River in higher concentrations by Suncor and Syncrude. Unfortunately the analytical method used only detects the simple phenols which are readily degradable by abiotic mechanisms. No data are available on more dangerous polymerized phenolic compounds in the Athabasca River. Many phenol analyses were found to be over the guidelines, especially in the winter under ice conditions. Oil and grease concentrations were also higher in the vicinity of the oil sands plants but the data are variable. This may have been the result of sampling difficulties. This test is not sufficiently specific to detect the presence of organic compounds from industrial sources as it is unable to distinguish between these and naturally occurring erosion (of the McMurray Formation) products. Hydrocarbon data are not significantly related to oil and grease data although they should be. This observation supports the contention that the standard chemical tests are inadequate for the analysis of the complex organic effluents which are known to enter the Athabasca River.

The monitoring of organic water quality parameters should serve to check for compliance to water quality standards and also to examine the capacity of the river to take up organic compounds. The problems described above with existing analytical methods show that they are not sufficiently comprehensive to accurately describe and quantify the complicated assemblage of organic compounds in the river. If possible it would be desireable to keep the simpler water quality tests such as for residue, chemical oxygen demand and total kjeldahl nitrogen. Unfortunately, there is a need to distinguish between organic compounds which are hazardous to the river and those which are not. For this reason a refinement in analytical technique is necessary. Although some research is required to work out the details of a new analytical scheme, a starting point is suggested in the text. Once a standard analytical procedure has been established, mass fluctuation calculations may be made in the field by combining a comprehensive sampling plan with discharge measurements calculated by a computer program. These data permit the calculation of a chemical budget over a selected test reach of the river so that net losses of different chemicals may be detected. These data are essential for modelling purposes as both rates and amounts lost may be calculated if the mass loading calculations work.

#### 3. THE ASSIMILATION PROBLEM

### 3.1 SOURCES OF ORGANIC COMPOUNDS

The major sources of organic compounds to the Athabasca River below Fort McMurray are listed in Table 2. Some of these inputs are continuous with which the river must deal on a day to day basis. Mine depressurization waters are somewhat more variable both temporally and spatially. The other inputs are sporadic or may not happen at all. Each of these three main groups is discussed below.

# 3.1.1 Plant and Animal Degradation Products

This class of compounds includes natural degradation products such as humic and fulvic acids, tannins and lignins, carbohydrates and amino acids. The more labile compounds are always very low in concentration (such as carbohydrates and amino acids) because of microbial mineralization. The more persistent compounds such as humic and fulvic acids represent a complex conglomeration of molecules more resistent to degradation. All of these compounds occur naturally in the river. If flow prediction in the Athabasca River indicates that groundwater inputs may be important, samples should be taken from wells on the banks of the river after the method of Lock and Wallace (1979). The role of these compounds is discussed further in Section 2.2.5 and 2.2.6.

#### 3.1.2 Oil Sands Related Compounds

This class of materials includes chemical compounds from mine depressurization waters, accidental spills of tailings sludge, dike seepage from tailings ponds, upgrading plant effluents, spills of crude and fuels, and erosion products from the McMurray Formation. In order for any estimations of assimilative capacity to be made, the amount, timing, and chemical composition of each input must be known as well as possible. Without this information it will be impossible to either calculate rates of

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Table 2.	Sources	01	organic	compounds	to	the	Athabasca	River.

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	Plant and Animal Degradation Products	Oil Sands Related Compounds	Municipal Effluents
Continuous	Naturally occurring organic compounds from upstream	Groundwater inputs including dike drainage and in situ residue Upgrading plant effluents eroding McMurray Formation	Sewage
	· · · · · · · · ·	· · · · · · · · · · · ·	
Discontinuous		Mine depressurization waters Accidental spills of tailings sludge Spills of crude and fuels	Pesticides

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uptake or to predict the concentration of contaminants downstream. These inputs may be expected to be similar chemically but their magnitude and rate will vary considerably. Andreychuk (1980) has quantified and described as many of these effluents as possible. Some difficulties were encountered in obtaining information, as many companies and agencies responded to the request for information sent out, but several others did not.

It is clear that it would be difficult and expensive to measure all the inputs of organic matter from these sources along the river. On the other hand at least some data are essential to predictions of assimilative capacity. Many of the smaller sources are not gauged at all and dike seepage is a difficult thing to estimate. Some of the larger inputs, however, such as the Beaver River, are gauged, and if samples are taken for analysis according to the scheme outlined in Section 2.3, useful information may be gathered. Input rates, location of effluent channels and pipes, and timing of discharges are not well documented and need to be organized and compiled into a data management system as suggested by Andreychuk (1980). Chemical analysis should include the inorganic parameters already measured, as well as a more detailed organic analysis such as the scheme outlined in Section 2.3.

#### 3.1.3 Municipal Effluents Including Pesticides

The only municipal effluent information available according to Andreychuk (1980) was from the Town of Fort McMurray. Chemical and biological oxygen demand were reported to be 147.2 and 36.0 mg/L, respectively, by Andreychuk. Beier (1979) found that the sewage effluent contained 77 mg/L COD and 21 mg/L BOD during a spot check in the summer of 1979. This information indicates that a demand for oxygen will be placed on the river but more data are required for modelling purposes. Pesticides may be a component of municipal effluent along with other toxic organic compounds such as some herbicides. Although the amounts of these which reach the river will most probably be very small, the methoxychlor added as part of the Alberta Blackfly Control Program will not. The effects of this program on the river could be built into a scheme designed to measure the effects of organic compounds in general (see Section 4). At the very least, more work needs to be done to identify pesticides and other organic chemical components in municipal effluent.

# 3.2 TRANSPORT OF ORGANIC COMPOUNDS IN THE ATHABASCA RIVER

Organic compounds will be carried by the river at different rates and in different concentrations (assuming constant input from a source) during the year because of large fluctuations in discharge. In the winter when flow is low, the velocity is reduced and mixing will not proceed as efficiently as in summer. Mixing experiments carried out by Beltaos (1979) indicate that complete mixing would not take place for 94 km under winter conditions if the slug is injected at the side of the channel. If the slug is injected closer to the centroid of the flow pattern, complete mixing will occur within only 25 km. Almost all inputs are injected at the side of the channel so that the effluent plume will spread out only slowly across the river. No experiments have been carried out in spring or summer so that the mixing characteristics at higher discharges are unknown. At least one more experiment should be undertaken in the spring at high discharge. An additional experiment would be desireable in the late summer or early fall when discharge is declining. At these two times fish are spawning in the Athabasca River and its tributaries and the behavior of dissolved constituents on these occasions is not well understood.

Higher volumes of water will reduce the concentration of organic compounds which come into contact with the benthic community. This may be favorable from the point of view of toxicity but microbial degradation will also be reduced by decreased contact (if compounds can be degraded at all). Winter low flow conditions will cause an increased contact with the benthos. These complications will affect any calculation of assimilative capacity based on in situ measurements as the mass loading method assumes that dissolved constituents are completely mined. For this reason the reach chosen for measurement should be well downstream of the major sources, perhaps in the vicinity of the Firebag River. These measurements should be made under different discharge conditions for comparison. Although the winter months under ice cover may be a time of high productivity (see Section 1.4), the river may be able to degrade the more labile organic compounds most efficiently under these conditions. The problem of increased oxygen consumption will be discussed in Section 3.3.2.

#### 3.3 DECOMPOSITION OF ORGANIC COMPOUNDS

If a compound can be degraded in the river, its rate of decomposition is fundamental to the problem of assimilative capacity. Some chemicals such as simple hydrocarbons can be utilized by bacteria and others, such as simple phenols, are degradable by abiotic mechanisms. More complex compounds may be partially degradable or be toxic to some organisms. Still others may release toxic by-products during degradation. As a typical effluent probably contains all of these possibilities, the net effect is difficult to predict. If calculations of mass loading are possible in the Athabasca River, some rates may be applied to these processes by keeping close tabs on the organic constituents within a test reach. Laboratory experiments carried out with whole effluent will also aid in the determination of rates if field conditions can be simulated.

# 3.3.1 Degradative Potential for Organic Compounds

The ability of the Athabasca River to decompose organic compounds may be estimated by field measurements and by laboratory experiments. The field measurements are the mass loading calculations discussed in Section 2.3 and involve a co-ordinated series of chemical and discharge measurements. This method will not be able to resolve small changes because of the 15% error associated with discharge measurements but large changes should be apparent. The accuracy of the discharge measurements may be checked during future mixing experiments. Problems will occur with the estimation of groundwater inputs and the difficulty of measuring discharge under ice conditions. Chemical analysis will also present difficulties and a working scheme, such as the one outlined in Section 2.3, should be established in advance of field work.

Laboratory uptake experiments have the advantage of control over experimental conditions. A major drawback, however, is that the choice of substrate, physical conditions, and innoculants is crucial to the results of the experiment. If individual compounds are to be tested the experimental matrix can rapidly get out of hand. For this reason experiments with whole effluents have a much better chance to provide data which are comparable to those from field experiments.

If individual compounds are to be tested, they should be selected on the basis of analyses of effluent from various sources. The work of Strosher and Peake (1978, 1979) indicates that representatives from the following classes of compounds should be tested: organic sulphur compounds, organic acids and esters, phenols, aldehydes, ketones, quinones, hydrocarbons, asphaltenes, and nitrogen containing compounds. Nix (in prep.) states that ' initial laboratory work indicated that five substrates could be extracted and analyzed by GC/MS. These were;

meta-cresol, methyl salicylate, beta-pinene, hexadecane, and dibenzothiophene' (page 2). These compounds were extracted from river water but it was found that hexadecane, beta-pinene, and dibenzothiophene could not be dissolved in water at the desired concentration so these were dropped from the list and camphor was added in their place. When choices such as these must be made it is hard to see how these laboratory experiments can be related to the field situation.

The early experiments described in this interim report (in prep.) showed that all substrates were biodegradable. In the future further experiments with whole effluents should be carried out as Strosher and Peake (1978, 1979) have shown that many other important compounds are being discharged into the river. Flasks are simple but cannot be thought to duplicate river conditions. An artificial stream channel might be more useful to test the effects of various substrates brought in from the river (eg. mud, sand, gravel, etc.). This would add sessile bacteria to the experiment as well as providing a potential sediment sink for degradation products and compounds of marginal solubility. Despite experimental difficulties, this approach may yield useful information about the degradation potential for organic compounds entering the Athabasca River.

### 3.3.2 Oxygen Demand

One of the problems associated with degradable organic compounds in the river is the oxygen demand which they exert. During the ice-free months replenishment of oxygen from the atmosphere is probably not a limiting factor, although no oxygen depth profiles appear to be available. Although very few oxygen data have been collected, its concentration has not been observed to drop below 5.2 mg/L in the study area (Table 3) at any time of the year. Oxygen concentration does seem to decrease downstream and in July and August to a certain extent. The lowest levels were found in the delta by Big Point Channel but even these were

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Downstream Distance from Fort McMurray	(km) Date	Oxygen (mg/L)
321 10 Jan. 1979 5.2 321 12 Feb. 1979 5.3	$\begin{array}{c} 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ $	28 Aug. 1976 1 Oct. 1976 22 Nov. 1976 14 June 1977 8 July 1977 23 July 1977 17 Aug. 1977 19 Aug. 1977 19 Aug. 1977 19 Oct. 1977 15 Oct. 1977 18 Oct. 1976 13 Dec. 1976 23 Nov. 1976 23 Nov. 1976 23 Nov. 1976 23 Sep. 1976 13 Dec. 1977 15 Oct. 1977 19 Aug. 1977 19 Aug. 1977 15 Oct. 1977 15 Oct. 1977 11 May 1978 23 Aug. 1978 28 Sep. 1978 28 Sep. 1978 28 Sep. 1977 28 Sep. 1977 26 July 1977 26 June 1978 9 Aug. 1978	9.6 10.4 10.8 9.1 10.3 9.6 8.9 13.0 8.2 13.6 9.8 13.4 12.0 10.0 9.9 13.4 12.0 9.3 10.6 9.4 12.2 9.0 13.2 9.4 11.0 7.4 8.3 8.0 9.4 10.0 8.9 9.3 9.4 10.0 8.5

Table 3. Oxygen concentration in the Athabasca River.

all over 5 mg/L. These values are all above the minimum oxygen requirements quoted for fish and invertebrates by Davies (1975).

The data which are available now indicate (but are too few to prove) that the Athabasca River is not suffering from lack of oxygen, even in the winter. Further development of pulp and paper mills is expected upstream which will place an additional load upon the river. Hsueh (1979) has developed a computer model designed to predict the amount of organic waste which may be discharged from pulp and paper operations without reducing the oxygen concentration in the river below 5 mg/L. Unless oxygen recharge occurs before the river enters the oil sands region, further reductions which will take place below Fort McMurray will cause the concentration to fall below this level. The sinuous meanders and rapids upstream of Fort McMurray should, however, permit this recharge to take place. Andreychuk (1980) reports an average BOD of 3.7 mg/L for Syncrude mine depressurization water, 41.3 mg/L for Suncor effluent water, and 87 mg/L for municipal sewage from Fort McMurray. Industrial effluent and municipal sewage effluent from Suncor, Syncrude, and the town of Fort McMurray account for about 0.7% of the 20 year return minimum daily flow in the Athabasca River (Andreychuk 1980). Although this amount appears to be small, the low oxygen levels which may occur under ice require that more BOD and oxygen data need to be collected for all effluents and for the Athabasca River itself before the extent of this threat can be determined accurately. The model developed by Hsueh (1979) would be useful in this regard. This model assumes that 5 mg/L of oxygen is a safe lower limit, but if water containing only this amount enters the AOSERP study area, the additional BOD loading could reduce the concentration still further. It is also possible that the rapids above Fort McMurray will add enough oxygen to make this unimportant. More work needs to be done to ensure that enough oxygen is present in the river right down to the Delta at all times of the year.

#### 3.5 IMPORTANCE OF SEDIMENTS

The sediments of the Athabasca River support extensive colonies of sessile bacteria (Nix et al. 1979). This means that they represent a reactive layer at the bottom of the stream which has the capability of removing organic and inorganic material from water which passes through it or over it. Compounds in effluents and degradation products which become insoluble may also be precipitated into the bottom sediments. If groundwater is discharging through the stream bed, the sediments are probably capable of removing part of its organic load (Wallis 1979). Organic material in the river water column will also be subjected to this removal process if it is passing through the stream bed as groundwater recharge. Organic compounds are known to bind metals such as vanadium and nickel in the Athabasca River (Allan and Jackson 1978) and this interaction represents as important sink for these otherwise harmful trace elements.

The rate of water transfer through the sediments, the uptake rate of chemicals by the sediments (by biological or chemical processes) and the interaction of freely passing surface water with the bottom sediments all need to be known before an effective model of the assimilative capacity of the Athabasca River can be completed. These can be discovered by sinking shallow wells through the sediments and sampling the water above and below the sediment surface. Careful organic analysis will reveal the losses of organic compounds. The amount of water which is entering the river from groundwater sources may be estimated using seepage meters according to the method of Lee and Cherry (1978). If water is being lost through the sediments the amount may be calculated by changes in discharge if these can be measured with sufficient accuracy. Laboratory experiments which involve passing water containing organic compounds through columns of sediment or allowing water to pass over sediments in bowls may be carried out according to the methods of Wallis (1979) and Lock and Hynes (1976). Both

field and laboratory experiments may be required in order to fully investigate the processes of degradation and precipitation associated with sediments.

#### 3.5 TOXICITY OF ORGANIC COMPOUNDS

Although some organic compounds are safely biodegradable, many others are not and some may be toxic. Those compounds which are toxic will impair the ability of the bacteria in the river to degrade others and will pose a direct threat to plants and animals living in the river. Some toxic compounds such as phenols may be degraded by chemical processes or be precipitated into the sediments. Jantzie et al. (1979) have assembled information from the AOSERP study area in all four systems (Land, Air, Water, and Human). With regard to organic compounds in water they recommend that more research be done in order to characterize the organic compounds found in the effluents of each oil sands plant, that a standard method of organic analysis be developed to do this, that the toxicity of each major group of compounds be investigated in the literature and in the laboratory, and that mass balances be constructed for the flow of each toxic compound identified in the study area. Jantzie et al. (1979) have gone further than this and have described a number of projects which pertain to organic compounds which have been listed in Table 4 by title. The reader is referred to their report for more details. Many of the concepts developed in this report also appear in these projects. The relationship of toxicological research to the fundamental problem of the assimilative capacity of the Athabasca River for organic compounds is discussed further in Section 4.

### 3.6 BIOMONITORING

The concept of biomonitoring as developed by McCart (1980) includes both the biodegradation of organic compounds and their toxicity. The selection and monitoring of indicator and sensitive species of algae, bacteria, benthic invertebrates, and

Table 4. Projects described by Jantzie et al. (1979) which pertain wholly or in part to the toxicology of organic compounds in water.

Project Nu	mber	Title
		· ·
2		Analysis of organic compounds in air, water, sediment/soil and biota
2.1		Literature review of methods used to extract organic compounds from various samples
2.2		A comparative study of the methods of extracting organic compounds from water
2.3		Monitoring of organic compounds in water samples and sediments
12		Inventory of effluent and wastewaters
14		Characterization of organic emissions and effluents from an oil sands plant
19		Effects of industrial effluents on aquatic organisms
19.1		Long term effects of groundwater to fish and inver- tebrates - laboratory studies
20		Biomonitoring of the effects of industrial effluents on aquatic organisms
20.1		Biomonitoring of Syncrude mine depressurization water discharge
20.2		Biomonitoring of Suncor process effluent

fish can effectively describe changes of aquatic communities in response to organic loading. Routine monitoring of chemical compounds in effluents and water courses is also a useful tool, unless the timing of the sample collection is exactly right, important events might be missed altogether. Biomonitoring can integrate the effects of many small events in a cost effective manner and provide an indication of the general health of the Athabasca River. As discussed in the introduction, the measurement of assimilative capacity is really keeping track of changes which are occurring in response to organic loading and deciding what extent of change is acceptable. Biological monitoring can provide quantitative description which will define the magnitude of changes in aquatic community structure.

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The implementation of biomonitoring in the AOSERP study area should include the development of a detailed sampling strategy, selection of indicator organisms, and the establishment of a routine monitoring program which can operate at minimum cost as outlined by McCart (1980). In combination with the chemical data collected under the revised program suggested in Section 4, the field and laboratory measurements of the uptake of organic compounds, and the measurement of their toxicity, the assimilative capacity of the Athabasca River may be described in some detail. This information will allow predictions to be made of the effects of future loading stress and will permit the establishment of effluent regulations based on the best information available. A description of a program which could reasonably expect to achieve this result is outlined in Section 4.

3.7 SUMMARY OF THE INVESTIGATION OF ASSIMILATIVE CAPACITY

Organic compounds enter the Athabasca River from several sources. Plant and animal degradation products are natural organic compounds which come from upstream, groundwater and tributary sources and some of the more refractory compounds (such as

humic acids) may be generated in situ. Oil sands related compounds include mine depressurization waters, groundwater containing dike seepage and the by-products of in situ work, upgrading plant effluents, erosion products (of the McMurray Formation), and spills of crude, sludge, or refined oils. It is of great importance to know the volume of effluent discharges as well as their chemistry for modelling purposes and it is noted that many data of this sort are not available at this time. Municipal effluents from the town of Fort McMurray and the oil sands plants have an appreciable biological oxygen demand. More data are required regarding both the volume and chemistry of municipal effluent discharges for modelling purposes. The addition of methoxychlor and the possible presence of pesticides in municipal effluent may adversely affect any future biomonitoring studies which are carried out.

The mixing characteristics of the Athabasca River have been investigated in the winter and indicate that complete mixing of bank discharges will not occur in less than 94 km under ice. Further mixing experiments need to be carried out under different discharge conditions, in the spring and early fall. Effluents which are injected closer to the centroid of flow will be mixed much more rapidly than those which enter the river along the banks.

The decomposition of organic compounds is complicated by toxic effects. Toxic by-products may result from the chemical degradation of initially harmless chemicals and compounds which are degradable to one organism may be toxic to another. The gross degradative potential of organic compounds may be estimated by the chemical budget/mass loading calculations described in Section 2.3. Laboratory work with individual compounds is under way. This work should be extended to the uptake of whole effluents under various environmental conditions and by different substrates.

Insufficient oxygen and biological oyxgen demand data are available at present for winter conditions under ice. Future oxygen modelling for upstream regions should include the AOSERP study area as well. The data which are available indicate that oxygen conditions under ice are not critically low.

Losses of organic compounds to sediments may occur by biological uptake or chemical precipitation. The rate of water transfer and of uptake should be investigated. The toxicity of organic compounds should be investigated within the larger context of toxicity in all four systems according to the plan outlined by Jantzie et al. (1979). This work will be aided by the results of biomonitoring and the calculation of chemical budgets.

Biomonitoring should be undertaken according to the plan put forward by McCart (1980). This consists of a preliminary consolidation of background information, the selection of suitable test organisms, and the establishment of a routine biomonitoring program. The results from biomonitoring will serve to integrate the cumulative effects of many effluent discharges on the aquatic flora and fauna and demonstrate any changes in community structure which may occur.

### 4. PROPOSED RESEARCH PLAN

### 4.1 LABORATORY WORK

#### 4.1.1 Organic Analysis

The analysis of samples for organic compounds must be made more relevant and standardized before any field program is undertaken. Each sample must receive all of the analyses in the standard program. The exact analytical procedure employed must be worked out in the laboratory before field sampling occurs, perhaps along the following lines.

Oil sands related organic compounds may be separated from naturally occurring organic compounds by solvent extraction and/or polymeric adsorbants (see Section 2.3). The naturally occurring compounds such as tannins and lignins, humic acid, carbohydrates, and total organic carbon may be measured using existing techniques and should present no special problems. The oil sands related compounds are much more difficult to measure and a simple analytical technique needs to be developed. The measurement of organic compounds by gas chromatography is suggested as a starting point for this investigation. If this method works satisfactorily, it may be sufficient by itself. The objective of the laboratory investigation is to establish a standard scheme which will identify and quantify all major classes of compounds by inexpensive, readily available means, without worrying about individual chemicals. This investigation presents a major analytical challenge and should be undertaken by qualified organic chemists.

# 4.1.2 <u>Computerized Discharge Measurements in the Athabasca</u> River

The measurement of the uptake capacity of the river by mass loading techniques requires a knowledge of the discharge above and below the test reach. This may be done as outlined in Section 2.3 by obtaining the flow forecasting program from

Alberta Environment and adapting it to the Athabasca River. If the volume of tributary discharge to the river is accurately known, this method should work reasonably well. It may be tested for accuracy during the mixing experiments described in Section 4.2.1.

### 4.1.3 Uptake Measurements in the Laboratory

It is important to be able to compare field uptake measurements with laboratory experiments under controlled conditions. This work is underway as AOSERP project WS 2.3.1 under the direction of P. Nix of Chemical and Geological Laboratories Ltd. If the project succeeds in providing uptake rates for individual compounds and for whole effluents, it will provide much useful information to the problem under investigation. These data will be especially useful if they can be related to substrate type in the river and typical environmental conditions. It may be desireable to do more work in this area if field measurements are successfully made in the future. The use of recirculating stream channels with varying substrates may prove useful in this regard.

# 4.1.4 Toxicity of Organic Compounds

As discussed in Section 3.4, some organic compounds may be toxic to aquatic flora and fauna. The investigation of this problem should be undertaken within the context of a more comprehensive toxicity program as discussed by Jantzie et al. (1979). The investigation of toxicity will benefit from the results of uptake measurements of organic compounds in the laboratory (Section 4.1.3), field uptake measurements of organic compounds (to be discussed in Section 4.2.2), and from the results of biomonitoring (to be discussed in Section 4.2.3). Unless it can be shown that toxic organic compounds are not being introduced to the river in significant quantities, or that harmful breakdown products are not being produced, any measurement of the assimilative capacity of the Athabasca River could be misleading. Although some compounds may be taken up at measureable rates, others may be causing severe damage to some aquatic organisms. If this turns out to be the case a decision will have to be made with regard to the ecological significance of the organisms which are adversely affected. This possibility may not be readily apparent in the consideration of field and laboratory uptake data alone as a compound which is toxic to one organism may be degraded by another. Biomonitoring information is very valuable if this is the case as it provides information on how community structure may be changing. Assimilative capacity and toxicity measurements can identify mechanisms and biomonitoring can keep track of community changes.

# 4.1.5 Oxygen Modelling

Considerably more information is needed regarding the oxygen concentration under ice in the Athabasca River. This will become even more critical if pulp and paper developments and further oil sands development are allowed as discussed in Section 3.3.2. Hsueh (1979) assumed that a minimum concentration of 5 mg/L was permissible below the pulp and paper plants and based his BOD loading estimates on this assumption. This assumption is supported by data recieved by Davis (1975) for freshwater fish and invertebrate species. It is most probable that the rapids and turbulence above Fort McMurray would allow for a considerable recharge of oxygen. If water containing this amount of oxygen (under ice) is allowed to enter the study area, however, it is possible that the BOD load exerted upon the Athabasca River by oil sands effluents will reduce the oxygen level in the river to critically low levels. Modelling of oxygen in the Athabasca River under ice should consider the oil sands region as well and this will require that the amount of effluent as well as its BOD be known. These data may be acquired during the procedure outlined in Section 4.2.2. In addition it will be necessary to measure the concentrations of oxygen in the river under ice at several locations ranging from Fort McMurray to the Peace-Athabasca Delta to determine existing conditions. If field measurements of

the uptake of organic compounds are carried out, (see Section 4.2.2) oxygen and biological oxygen demand samples may be taken at the same time, and the modelling of oxygen in the river may be carried out in conjunction with the discharge calculations in the same manner as other chemical constituents. If the river is allowed to become anaerobic during the winter, its productivity will be severly reduced. In Section 1.3.2.5 it is suggested that the winter may be the most productive time of the year and migrating fish populations depend upon a stable food resource in the river during the spring movement upstream. If the Athabasca is allowed to become anaerobic, problems such as those encountered in the Red Deer River will occur.

4.2 FIELD WORK

#### 4.2.1 Mixing Experiments

The mixing experiments carried out by Beltaos (1979) under winter conditions indicate that complete mixing would not take place for more than 94 km downstream if the effluent is injected at the side of the channel. Under the higher discharge conditions encountered in the spring this figure may be considerably reduced. The mixing conditions encountered in the river will strongly influence the concentrations of organic effluents and therefore their potential for degradation or toxicity. If organic compounds are not uniformly mixed, whole sections of the river bottom or water column may not be exposed to the effluent plume at all. This will also affect the depletion of oxygen in the river. For these reasons it is important to know how efficiently effluents will be mixed under typical conditions which occur at all times of the year. If this is not known, toxic effects will be difficult to assess and the calculations of uptake described in Section 4.2.2 may be grossly overestimated.

Further mixing experiments should be carried out during the spring when discharge is high and preferably also during the late summer or early autumn when discharge is at an intermediate level. The autumn measurement would be useful to help understand the behavior of dissolved constituents during the fall spawning season. If this is not practical, then an intermediate value between spring and winter will have to be assumed. If enough mixing measurements are made, a relationship between mixing and discharge may be developed. Although this relationship cannot be expected to be very accurate based on only three measurements, some useful information will be gained. If more measurements can be made, all of the modelling attempts which may be made of the river will be greatly benefited. More information in particular is needed below the effluent discharges of Syncrude and Suncor. A further benefit to be gained is the testing of the computer calculation of discharge described in Section 4.1.2. Once full mixing has been achieved in the river, the discharge may be calculated by a simple formula and compared with the computed values. This could be done at very little extra expense and would provide an independent test of the accuracy of the program. This in turn would allow confidence limits to be placed on the uptake measurements described in Section 4.1.2.

# 4.2.2 <u>Monitoring Organic Water Quality and Measuring the</u> <u>Uptake of Organic Compounds in the Athabasca River</u>

The first step in the establishment of a rational organic water quality monitoring program is the identification of all major sources of organic compounds to the Athabasca River. These include the river upstream of Fort McMurray, sewage effluent from both Suncor and Syncrude, dike seepage from the Suncor tailings pond, all mine depressurization waters, major tributaries, and the Athabasca River itself. All existing chemical and discharge information for these various sources should be compiled and a permanent ongoing record should be maintained for each as recommended by Andreychuk (1980).

The assessment of the uptake of organic compounds in the Athabasca River requires measurements of discharge volume as well as chemistry. If the amount of discharge is not known, the data cannot be used for mass loading calculations and the error of the method is increased. Some value judgements will have to be made as it would be prohibitively expensive to monitor every small effluent pipe. At the moment, however, the discharge volumes of some of the most important sources are unknown.

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After the major sources have been identified, initial samples taken for chemical analysis, and methods of discharge measurement established, a schedule for routine sampling may be decided upon. These data, in combination with discharge measurements computed for the Athabasca River will allow calculations of the uptake capacity of the river for organic compounds. If chemical analysis and discharge measurements are co-ordinated, the uptake capacity may be calculated for each set of routine samples. The more sets of samples which are taken, the better our understanding of the uptake capacity will be but costs will limit these. At least three sets of samples should be taken each year; in the early spring during high discharge, in the late summer or early autumn, and during the winter under ice. The selection of test reaches for measurements of uptake capacity will depend upon the results of further mixing experiments. The sites chosen will encompass a reach where mixing is reasonable complete and the discharge in the river may be computed with an error of less than 15%. Once the routine is established, uptake measurements may be made as often as desired.

#### 4.2.3 Interactions of Organic Compounds with Sediments

Organic compounds may become associated with sediments as water passes through them or river water passes over them. Water may pass through the sediments from below as groundwater discharge or from above as river recharge. Organic compounds may be lost because of biological uptake or chemical precipitation (for example with metals). Organic matter may also be occluded in precipitating minerals such as  $CaCO_3$  (Otsuki and Wetzel 1973). Losses which occur as river water passes over the sediments may be measured according to the procedure outlined in Section 4.2.2.

Losses of organic matter which occur as water passes through the sediments may be measured by the use of shallow wells according to the methods of Lee and Cherry (1978) or Lock and Wallace (1979). This involves sinking a length of perforated tubing into the shallow sediments and withdrawing water slowly. If this method does not yield enough water, larger bore pipe may be required. By sampling groundwater at different depths and river water just above the sediments, a loss of organic matter may be measured. Seepage meters (Lee and Cherry 1978) may also be used to sample groundwater after it has passed through the sediments (without contaminating the sample with river water) and for measuring the discharge rate.

# 4.2.4 Biomonitoring

An integral part of the measurement of the assimilative capacity of the Athabasca River is the monitoring of selected indicator organisms in the river. While the calculation of the uptake capacity of the river for organic compounds will yield much useful information to the management of the river, it will not describe the changes in community structure which may be taking place. If the general health of the river is to be understood and managed, it is essential to know how the populations of the various aquatic organisms are reacting to the organic (and other) loads placed upon them.

Assimilative capacity has been defined as the ability of the river to respond to external stresses. The calculation of uptake capacities by mass loading techniques is useful to describe responses to effluent loading over a short period of time. Biomonitoring, on the other hand, integrates the effects of many loading events by expressing them as a change in community structure. Neither technique is sufficient to describe the changes

taking place in the river in direct relation to effluent loading but together a convincing relationship may be developed.

The establishment of a biomonitoring program has been described in detail by McCart (1980). This plan consists of a consolidation of background information, the selection of suitable test organisms, and the inauguration of a routine biomonitoring program. The routine sampling program should be a long term project, operating at low cost, and should be given equal status with the chemical sampling program. These two programs, in conjunction with toxicity testing, laboratory and field uptake experiments, oxygen modelling, and discharge and mixing measurements, will make a comprehensive estimate of the assimilative capacity of the Athabasca River for organic compounds possible.

### 4.3 IMPLEMENTATION OF THE RESEARCH PROGRAM

The measurement of the assimilative capacity of the Athabasca River is a complex subject requiring input from several scientific disciplines and co-ordination between several monitoring programs. The research plan outlined in this section requires the co-operation of chemists, biologists, and hydrologists and the results must be interpreted for scientists and laymen alike. Above all the research effort must be directed by a central co-ordinating authority. If these diverse research efforts are not controlled by some sort of management committee with the ultimate objective of determining the assimilative capacity as their mandate, the results will not be satisfactory. In addition to this, research progress should be evaluated at the end of each year and strategy reconsidered. Communication between scientists will be difficult to maintain and so all individual research plans should be discussed as fully as possible by all project participants.

At least three years of work have been recommended in this section exclusive of the routine monitoring which will continue after the groundwork has been completed. The following tentative schedule might be considered in this regard:

- Year 1 1. Biomonitoring including consolidation of background biological data base;
  - Establishment of standard organic analysis of samples for use wherever organic analysis is required;
  - Identification of major effluent sources and initial sampling;
  - Continuation of laboratory uptake studies (AOSERP Project WS 2.3.1);
  - 5. Commencement of toxicity testing; and
  - 6. Establishment of a data base management program.
- Year 2
- Finish consolidating background biological data and select suitable indicator organisms for biomonitoring.
- Mixing experiments under different conditions in conjunction with the testing of the river discharge estimation project;
- 3. Sediment studies in the Athabasca River;
- Elaboration of the data management scheme to keep track of all experimental data pertaining to the project;
- Monitoring of oxygen in the river and modelling of BOD loading;
- 6. Continuation of laboratory uptake experiments;
- 7. Continuation of toxicity testing; and
- 8. Co-ordinated sampling, analysis, and discharge measurements for field measurements of uptake capacity.
- Year 3 1. Biomonitoring on a routine basis;
  - Continuation of field measurements of uptake capacity as a routine chemical sampling program;

- 3. Continuation of oxygen and BOD modelling;
- 4. Compilation of field uptake and biomonitoring data;
- 5. Compilation of laboratory uptake and toxicity data;
- 6. Continuation of sediment uptake studies; and
- 7. Report writing.

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The research plan above is flexible and the amount of time required for each segment of the project may vary. The experiments carried out in the latter two years should be influenced by the findings of the first year. The program manager should have the responsibility for maintaining continuity and for fulfilling the ultimate objective.

The calculations of the loading and uptake of organic compounds will lend themselves very well to other chemical budgets which may be required. For example, it would only be necessary to extend the analysis of samples taken to inorganic parameters in order to determine the budgets of trace elements over a test reach. The adoption of this plan should result in sufficient data to model the behavior of any element or compound in the Athabasca River subject to experimental limitation.

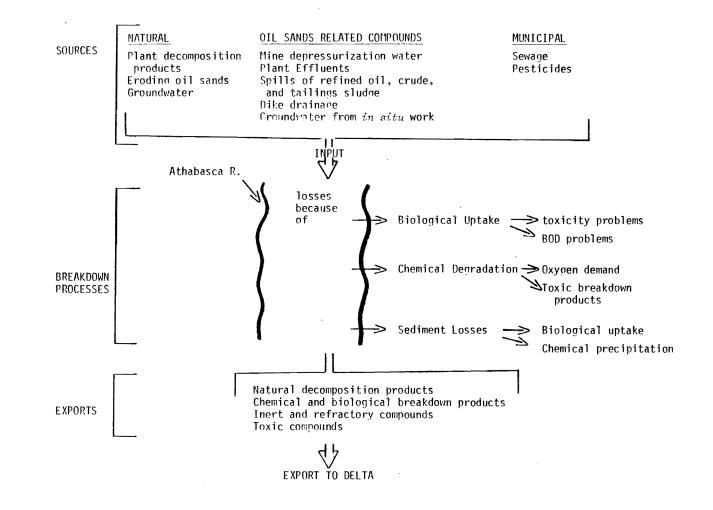
All data resulting from this research plan should be kept in a central computing facility. A data management system such as the EQUIS program used by the Waste Management Branch of the British Columbia Provincial Government might be considered in this regard. If modelling of the Athabasca River is attempted, the process will be greatly aided if all experimental data have been entered according to a standard format and may be obtained from one computer. If text editing is available, the writing of the final report will be facilitated.

# 4.4 APPLICATION OF SUGGESTED RESEARCH TO MODELLING

A model of the processes which are occurring in the Athabasca River will be an important tool for the task of understanding the assimilative capacity of the river. The work outlined in the preceeding research plan is designed to measure the amounts and composition of all inputs, the rates of degradation of organic compounds, the rates of loss of organic compounds to sediments, the effects of toxins on aquatic organisms, oxygen demand, and the nature of the water which reaches the delta. These factors are summarized in a simple conceptual model in Figure 17.

In order to understand the fate of organic compounds it is necessary to model not only the amounts of chemicals which participate in various processes but also the rates of transfer. Successful modelling must also include physical factors such as discharge, water temperature, mixing characteristics, and substrate changes. As the model becomes more refined it may be desirable to add other parameters such as bacterial populations and suspended sediment load. The depth of modelling eventually achieved will depend very much on the quality of the data on which it is based. If it proves to be impossible to collect detailed information for a realistic range of environmental conditions, a mathematical simulation may not be possible. In this case, the eventual model would not be much more complex than that shown in Figure 17. If a sufficient quantity of information can be collected, a mathematical simulation with predictive capability may be developed. This promises to be a difficult task and would require the services of expert programmers and statisticians as well as input from regular project scientists. Large scale models of this kind are only rarely developed because of the difficulties involved. If a model can be produced by this and other research, it will represent a unique and valuable management tool.

- 5. RECOMMENDATIONS
  - Mixing measurements should be carried out under spring discharge conditions and, if possible, in the late summer or early autumn;
  - 2. All of the organic analyses presently employed should be discontinued with the exception of



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Figure 17. Conceptual model of sources, mixing, and degradation of organic compounds.

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dissolved organic carbon, humic acid, and tannins and lignins. They should be replaced with a more comprehensive analytical procedure such as the one outlined in the text;

- 3. The flow forecasting computer program should be obtained from Alberta Environment and applied to the Athabasca River in order to calculate discharge at chemical sampling points;
- 4. Samples for chemical analysis should be taken from the Athabasca River, its tributaries, and from all major effluent sources simultaneously so that chemical budgets may be calculated for test reaches of the river. Samples should be analyzed according to a standard analytical procedure developed in the laboratory before field sampling commences;
- 5. The discharge rate of all major effluent sources should be measured as well as the amount, timing, and chemical composition whenever a chemical budget is to be computed;
- More oxygen data need to be collected from the Athabasca River under ice in the winter for oxygen modelling;
- Degradation rates and rates of water transfer through the sediments of the Athabasca River should be investigated;
- The toxicity of the organic compounds discharged into the river need to be investigated within the context of a larger regional toxicity program as outlined by Jantzie et al. (1979);
- A biomonitoring program should be instigated with particular attention paid to the bacteria and the benthic invertebrates in the river;
- Laboratory uptake experiments should be continued with different substrates, whole effluents, and comprehensive organic analysis;

11. All data collected in the course of monitoring and experimental work should be kept in accessible computer files; and

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12. Research directed toward measuring the assimilative capacity of the Athabasca River for organic compounds should be carried out according to plan such as the one suggested in Section 4 and be managed by a central committee capable of integrating the diverse elements and disciplines required. This committee should also be responsible for any modelling of the data and results collected.

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# 7. APPENDIX--WORKSHOP HELD AT KANANASKIS ON 14 AND 15 FEBRUARY 1980 TO DISCUSS THE ISSUES RAISED BY THIS REPORT

7.1 PURPOSE OF THE WORKSHOP

This workshop was convened to obtain advice, criticisms, and ideas from all user groups interested in this problem. Although the workshop served to evaluate the report, its main purpose was to provide a forum for the expression of differing points of view. These sometimes took the form of criticism of the report itself but more often were simply part of a debate of the issues surrounding the topic of assimilative capacity.

The question of what assimilative capacity really is and how it can be measured was discussed at great length. Because people representing many different points of view were present, it was not possible to obtain agreement on all questions. This summary will outline the items which were generally agreed upon and present some differing views on those which were not.

#### 7.2 WORKSHOP PARTICIPANTS

Representatives from industry, government, consulting firms, and the University of Calgary were present. A list of participants and their affiliations is provided in Table 5. General points of view are summarized below.

7.2.1 Industry

Industry representatives were primarily interested in establishing whether or not a problem existed and, if so, how to solve it. They were also concerned with regulations which might result and how their engineering processes would be affected by it.

## 7.2.2 Government

Government officials were also interested in the extent of any problem which might be identified but wanted to be able to model the system so that they could effectively regulate

February 1980.		
NAME	ORGANIZATION	
Peter Wallis	Kananaskis Centre	
Allan Legge	Kananaskis Centre	
Tim Ladd	University of Calgary	
R. Martin	Suncor	
C. Wyndham	University of Calgary	
D.R. Shaw	E.R.C.B.	
Read Seidner	AOSERP	
Les Johnston	Alberta Environment	
Peter Nix	Chemical and Geological Laboratories	
Bill Lake	Alberta Environmental Center	
Anne Avramenko	AOSERP	
Bruce Baker	Kananaskis Centre	
Bill Cary	Suncor	
Eric Peake	Kananaskis Centre	
John Retallack	Syncrude	
Terry Antoniuk	Gulf Canada Resources Inc.	
John Wuite	Alberta Environment, Edmonton	
Paul Hsueh	Alberta Environment, Edmonton	
Mel Strosher	Kananaskis Centre	
Bob More	Alberta Environment (Systems & Computing)	
Al Andreychuk	Stanley Associates Engineering Ltd.	
Jay Nagendran	Alberta Environment (S & A Div.)	
Trefor Reynoldson	Alberta Environment	
David Robinson	Environment Canada E.P.S.	
Paul Shewchuk	Alberta Environment	
Ken Crutchfield	Energy & Natural Resources (Fish. & Wildlife Div.)	
S.A. Telang	Kananaskis Centre	
Hans Boerger	Dept. of Biol University of Calgary	
Mike MacKinnon	Syncrude Canada Ltd.	
A. Mark Akena	Alberta Environment	
Harold Thimm	E.R.C.B.	
Gordon Hodgson	Kananaskis Centre	

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Table 5. List of participants for the AOSERP workshop 14 and 15 February 1980.

it. The lack of guidelines, knowledge, and previous experience have hampered them in the past. As managers, they need to know the answers to their questions immediately and are not interested in long involved research projects unless they are absolutely necessary.

## 7.2.3 Consulting Firms

The consulting industry has carried out a considerable amount of research in the oil sands area. They are interested in seeing the results of this work put to use and also in undertaking more work on a contractual basis in the future.

## 7.2.4 Universities

The universities have a mandate to carry out both pure and applied research. Both industry and government stand to benefit from both of these and have supported all of the research in this area. Because the carrying out of research is the primary objective of the universities, they can also provide a common ground for the meeting of industry and government representatives to deal with problems such as this.

# 7.3 TOPICS DISCUSSED

The agenda of the workshop is included as Table 6. These topics were not adhered to rigidly but served as a focus for the discussion. A brief presentation on the topic prefaced each discussion.

7.4 MAJOR TOPICS OF DISCUSSION

#### 7.4.1 Definition of Assimilative Capacity

The definition of assimilative capacity presented in the report was accepted by most participants. This definition states that assimilative capacity is the ability of the river to respond to changes imposed upon it by man's activities and still maintain its productivity and diversity. This definition admits the possibility of the existence of a level of loading which will not have any effect upon the river but assumes it to be very small. Table 6. Agenda of the workshop on the Assimilative Capacity of the Athabasca River for Organic Compounds.

Chairman: Peter Wallis The report will be evaluated within the context of the following discussion topics: Thursday February 14, 1980 7:00 - 10:00 Introduction - terms of reference (P. Wallis) - brief summary of report What is assimilative capacity? How do we measure it and what are the implications for industry and government? Friday February 15 9:00 - 12:00 Methods of measuring assimilative capacity. (P. Wallis). 1:00 - 3:00 Changes in analytical procedure and monitoring programmes for organic compounds. (E. Peake).

Other discussion topics can be included if desired.

Given the magnitude of development in the area and the diversity of effluents which may be expected to reach it, it is improbable that no changes will occur in the Athabasca River.

Representatives from the university, consulting firms, and, to a lesser extent, government, were interested in understanding the processes which are occurring in the river. Industry was less receptive to the idea, being more concerned with identifying and quantifying potential problems. It was generally agreed, however, that this was impossible to do unless some understanding of the processes which are occurring in the river was achieved.

# 7.4.2 Modelling

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Some government representatives suggested that the modelling of simple parameters such as oxygen might prove adequate for effective regulation of industrial and municipal effluents. While all admitted the desirability of this simplistic approach it was not generally felt that it would be inadequate. Unfortunately the toxicity of many oil sands by products cannot be measured by oxygen modelling and so important effects could be overlooked by this technique.

It was generally recognized that a detailed model which would allow accurate, comprehensive predictions was not possible. On the other hand, an evaluation of changes which might be occurring in the river would be very difficult without some kind of a model. Clearly something between simplistic oxygen modelling and very detailed ecological modelling is desirable in this instance. Both Bill Cary (Suncor) and Ken Crutchfield (Energy and Natural Resources - Fish and Wildlife) felt that biomonitoring would be particularly useful in this regard. While others agreed that this would indeed be useful, the question of toxicity and degradative potential of various effluents remains to be answered. The comprehensive approach outlined in this report received some support but concern was expressed over the amount of work which was proposed. While all agreed that the existing data were inadequate for regulatory purposes, no firm consensus of opinion could be reached regarding what new information needed to be collected. Several people, notably Ken Crutchfield, expressed the belief that the plan outlined in this report was adequate to begin with. If adopted, many changes would be required as the work went along. The information generated by the plan suggested here should provide enough data for some gross modelling of processes occurring in the Athabasca River. If this is achieved, the changes occurring in the river can be identified and decisions made with regard to their regulation.

## 7.4.3 Characterization and Quantification of Effluents

It was generally agreed that before any assessment of the assimilative capacity of the river could be made, it would be necessary to measure the amounts of all major effluent discharges to the river. It was also recognized that more information regarding the chemical nature of the effluents was required but exactly how much effort should be expended in this direction was the subject of much discussion. This report contends that the standard analytical procedures which have worked well in the past under different conditions are not adequate to describe the behavior of the effluents which reach the Athabasca River. It is recommended that a more comprehensive analytical plan be developed and a starting point is suggested in Section 2.3.

Some government and industry participants were sympathetic to this approach but others were reluctant to contribute their support to the development of a scheme which they thought was more comprehensive than necessary. If the plan suggested in this report proves feasible, however, and the old tests (for organic parameters) are dropped, then very little extra expense or effort should be incurred. Unfortunately this new approach would mean that it would be difficult to compare data between the oil sands areas and other programs in different locations. The unique problems associated with the development of the oil sands, however, require a

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comprehensive and flexible analytical scheme. As standard techniques capable of handling such a complex assemblage of chemicals do not exist, it is necessary to develop them.

# 7.4.4 Research Management

One major point of agreement was that the research required to investigate the assililative capacity of the river should be managed by a central authority. Instead of a number of unrelated projects proceeding independently of each other, a comprehensive plan should be developed and implemented. This overall plan should be subject to review every year and allowed to evolve within the context of the final objectives.

The data which are generated by all facets of the research plan should be integrated as far as possible and stored in a central computing facility. One reviewer suggested the EQUIS system used for similar purposes by the British Columbia government. Standardized formats for data entry and easy access should be employed in order to ensure maximum usefulness.

# 7.5 CONCLUSION

Whatever results finally come out of the investigation of the assimilative capacity of the Athabasca River, they will be of great significance to Alberta. The decision making process has been hampered by the lack of precedents in this field so that very little continuity can be established with past development projects. The procedure used to research the problem will be just as important to future development projects in Alberta as the eventual management decisions which are taken. If the effect of man's activities upon the river can be measured and modelled, an accomplishment of major scientific importance will have been achieved. Furthermore a benchmark will have been established to which all future projects will be referred to for some time to come. A problem of this complexity rarely admits of easy solutions and it is very difficult to obtain agreement between people representing opposing user groups and different academic disciplines. Some people felt that the approach taken by this report was too narrow while others felt that it was too broad. This summary has dwelt upon the points about which some agreement was reached and has also outlined other areas of conflict.

The only point which was agreed upon unanimously was that this type of workshop was a very valuable contribution towards understanding the problem. Many people commented that they were glad of the opportunity to hear other opinions and meet researchers and managers from different academic backgrounds. It is not surprising that engineers, biologists, and chemists can find many topics to disagree upon. It is heartening, however, to see such a diverse group work out some areas of agreement. Whatever work is undertaken in the future should include workshops of this nature to review progress and continue the communication between researchers, industry, and government managers.

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8.		LIST OF AOSERP RESEARCH REPORTS
1. 2.	AF 4.1.1	AOSERP First Annual Report, 1975 Walleye and Goldeye Fisheries Investigations in the Peace-Athabasca Delta1975
3. 4.	HE 1.1.1 VE 2.2	Structure of a Traditional Baseline Data System A Preliminary Vegetation Survey of the Alberta Oil Sands Environmental Research Program Study Area
5.	HY 3.1	The Evaluation of Wastewaters from an Oil Sand Extraction Plant
6. 7.	AF 3.1.1	Housing for the NorthThe Stackwall System A Synopsis of the Physical and Biological Limnology and Fisheries Programs within the Alberta Oil Sands Area
8.	AF 1.2.1	The Impact of Saline Waters upon Freshwater Biota (A Literature Review and Bibliography)
9.	ME 3.3	Preliminary Investigations into the Magnitude of Fog Occurrence and Associated Problems in the Oil Sands Area
10.	HE 2.1	Development of a Research Design Related to Archaeological Studies in the Athabasca Oil Sands Area
• 11.	AF 2.2.1	Life Cycles of Some Common Aquatic Insects of the Athabasca River, Alberta
12.	ME 1.7	Very High Resolution Meteorological Satellite Study of Oil Sands Weather: "A Feasibility Study"
13.	ME 2.3.1	Plume Dispersion Measurements from an Oil Sands Extraction Plant, March 1976
14. 15.	ME 3.4	A Climatology of Low Level Air Trajectories in the Alberta Oil Sands Area
16.	ME 1.6	The Feasibility of a Weather Radar near Fort McMurray, Alberta
17.	AF 2.1.1	A Survey of Baseline Levels of Contaminants in Aquatic Biota of the AOSERP Study Area
18.	HY 1.1	Interim Compilation of Stream Gauging Data to December 1976 for the Alberta Oil Sands Environmental Research Program
19.	ME 4.1	Calculations of Annual Averaged Sulphur Dioxide Concentrations at Ground Level in the AOSERP Study Area
20.	HY 3.1.1	Characterization of Organic Constituents in Waters and Wastewaters of the Athabasca Oil Sands Mining Area
21. 22.		AOSERP Second Annual Report, 1976-77 Alberta Oil Sands Environmental Research Program Interim Report to 1978 covering the period April 1975 to November 1978
23.	AF 1.1.2	Acute Lethality of Mine Depressurization Water on Trout Perch and Rainbow Trout
24.	ME 1.5.2	Air System Winter Field Study in the AOSERP Study Area, February 1977.
25.	ME 3.5.1	Review of Pollutant Transformation Processes Relevant to the Alberta Oil Sands Area

26.	AF 4.5.1	Interim Report on an Intensive Study of the Fish Fauna of the Muskeg River Watershed of Northeastern
		Alberta
27.	ME 1.5.1	Meteorology and Air Quality Winter Field Study in
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28.	VE 2.1	the AOSERP Study Area, March 1976
20.	VE Z.I	Interim Report on a Soils Inventory in the Athabasca
		Oil Sands Area
29.	ME 2.2	An Inventory System for Atmospheric Emissions in the
		AOSERP Study Area
30.	ME 2.1	Ambient Air Quality in the AOSERP Study Area, 1977
31.	VE 2.3	Ecological Habitat Mapping of the AOSERP Study Area:
		Phase I
32.		AOSERP Third Annual Report, 1977-78
33.	TF 1.2	Relationships Between Habitats, Forages, and Carrying
		Capacity of Moose Range in northern Alberta. Part I:
		Moose Preferences for Habitat Strata and Forages.
34.	HY 2.4	Heavy Metals in Bottom Sediments of the Mainstem
		Athabasca River System in the AOSERP Study Area
· 35.	AF 4.9.1	The Effects of Sedimentation on the Aquatic Biota
36.	AF 4.8.1	Fall Fisheries Investigations in the Athabasca and
		Clearwater Rivers Upstream of Fort McMurray: Volume 1
37.	HE 2.2.2	Community Studies: Fort McMurray, Anzac, Fort MacKay
38.	VE 7.1.1	Techniques for the Control of Small Mammals: A Review
39.	ME 1.0	The Climatology of the Alberta Oil Sands Environmental
		Research Program Study Area
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		Fort McMurray - Winter Conditions
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ч <b>ј</b> .	11 0.1	and Wildlife Resources in Alberta, with Particular
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	VC 3.1	Interim Report on Symptomology and Threshold Levels of
45.	VE 3.3	Air Pollutant Injury to Vegetation, 1975 to 1978
72.	VE 3.5	Interim Report on Physiology and Mechanisms of Air-Borne
1.0		Pollutant Injury to Vegetation, 1975 to 1978
46.	VE 3.4	Interim Report on Ecological Benchmarking and Biomonitoring
		for Detection of Air-Borne Pollutant Effects on Vegetation
1.7	<b>TC</b> 1 1 1	and Soils, 1975 to 1978.
47.	TF 1.1.1	A Visibility Bias Model for Aerial Surveys for Moose on
1.0		the AOSERP Study Area
48.	HG 1.1	Interim Report on a Hydrogeological Investigation of
10		the Muskeg River Basin, Alberta
× 49.	WS 1.3.3	The Ecology of Macrobenthic Invertebrate Communities
		in Hartley Creek, Northeastern Alberta
50.	ME 3.6	Literature Review on Pollution Deposition Processes
51.	HY 1.3	Interim Compilation of 1976 Suspended Sediment Date
-		in the AOSERP Study Area
52.	ME 2.3.2	Plume Dispersion Measurements from an Oil Sands
		Extraction Plan, June 1977

53.	HY 3.1.2	Baseline States of Organic Constituents in the
<sup>'</sup> 54.	WS 2.3	Athabasca River System Upstream of Fort McMurray A Preliminary Study of Chemical and Microbial Characteristics of the Athabasca River in the
55.	HY 2.6	Athabasca Oil Sands Area of Northeastern Alberta Microbial Populations in the Athabasca River
56.	AF 3.2.1	The Acute Toxicity of Saline Groundwater and of Vanadium to Fish and Aquatic Invertebrates
57.	LS 2.3.1	Ecological Habitat Mapping of the AOSERP Study Area (Supplement): Phase I
58.	AF 2.0.2	Interim Report on Ecological Studies on the Lower Trophic Levels of Muskeg Rivers Within the Alberta Oil Sands Environmental Research Program Study Area
59.	TF 3.1	Semi-Aquatic Mammals: Annotated Bibliography
60.	WS 1.1.1	Synthesis of Surface Water Hydrology
61.	AF 4.5.2	An Intensive Study of the Fish Fauna of the Steepbank River Watershed of Northeastern Alberta
62.	TF 5.1	Amphibians and Reptiles in the AOSERP Study Area
63.	ME 3.8.3	Analysis of AOSERP Plume Sigma Data
64.	LS 21.6.1	A Review and Assessment of the Baseline Data Relevant to the Impacts of OII Sands Development on Large Mammals in the AOSERP Study Area
65.	LS 21.6.2	A Review and Assessment of the Baseline Data Relevant to the Impacts of Oil Sands Development on Black Bears in the AOSERP Study Area
66.	AS 4.3.2	An Assessment of the Models LIRAQ and ADPIC for Application to the Athabasca Oil Sands Area
67.	WS 1.3.2	Aquatic Biological Investigations of the Muskeg River Watershed
68.	AS 1.5.3	Air System Summer Field Study in the AOSERP Study Area,
	AS 3.5.2	June 1977
69.	HS 40.1	Native Employment Patterns in Alberta's Athabasca Oil Sands Region
70.	LS 28.1.2	An Interim Report on the Insectivorous Animals in the AOSERP Study Area
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72.	LS 7.1.2	The Ecology of Five Major Species of Small Mammals in the AOSERP Study Area: A Review
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•	AS 4.5	Air Quality Modelling and User Needs
75.	WS 1.3.4	Interim Report on a Comparative Study of Benthic Algal Primary Productivity in the AOSERP Study Area
76.	AF 4.5.1	An Intensive Study of the Fish Fauna of the Muskeg River Watershed of Northeastern Alberta
77.	HS 20.1	Overview of Local Economic Development in the Athabasca Oil Sands Region Since 1961.
78.	LS 22.1.1	Habitat Relationships and Management of Terrestrial Birds in Northeastern Alberta

79.	AF 3.6.1	The Multiple Toxicity of Vanadium, Nickel, and
80.	HS 10.2 & HS 10.1	Phenol to Fish. History of the Athabasca Oil Sands Region, 1980 to 1960's. Volumes I and II.
81.	LS 22.1.2	Species Distribution and Habitat Relationships of Waterfowl in Northeastern Alberta.
82.	LS 22.2	Breeding Distribution and Behaviour of the White Pelican in the Athabasca Oil Sands Area.
83.	LS 22.2	The Distribution, Foraging Behaviour, and Allied Activities of the White Pelican in the Athabasca
84.	WS 1.6.1	Oil Sands Area. Investigations of the Spring Spawning Fish Populations in the Athabasca and Clearwater Rivers Upstream from
85.	HY 2.5	Fort McMurray; Volume I. An intensive Surface Water Quality Study of the Muskeg River Watershed. Volume I: Water Chemistry.
86.	AS 3.7	An Observational Study of Fog in the AOSERP Study Area.
87.	WS 2.2	Hydrogeological Investigation of Muskeg River Basin, Alberta
88.	AF 2.0.1	Ecological Studies of the Aquatic Invertebrates of the Alberta Oil Sands Environmental Research Program Study
89.	AF 4.3.2	Area of Northeastern Alberta Fishery Resources of the Athabasca River Downstream of Fort McMurray, Alberta. Volume 1
90.	AS 3.2	A Wintertime Investigation of the Deposition of Pollutants around an Isolated Power Plant in Northern Alberta
91.	LS 5.2	Characterization of Stored Peat in the Alberta Oil Sands Area
92.	WS 1.6.2	Fisheries and Habitat Investigations of Tributary Streams in the Southern Portion of the AOSERP Study Area. Volume 1: Summary and Conclusions
93.	WS 1.3.1	Fisheries and Aquatic Habitat Investigations in the MacKay River Watershed of Northeastern Alberta
94.	WS 1.4.1	A Fisheries and Water Quality Survey of Ten Lakes in the Richardson Tower Area, Northeastern Alberta.
		Volume 1: Methodology, Summary, and Discussion.
95.	AS 4.2.6	Evaluation of the Effects of Convection on Plume Behaviour in the AOSERP Study Area
96.	HS 20.3	Service Delivery in the Athabasca Oil Sands Region Since 1961
97.	LS 3.4.1	Differences in the Composition of Soils Under Open and
		Canopy Conditions at Two Sites Close-in to the Great
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101. 102.	LS 21.1.3 LS 21.1.4	bution in the AOSERP Study Area Woodland Caribou Population Dynamics in Northeastern Alberta Wolf Population Dynamics and Prov Polationships in North
•		Wolf Population Dynamics and Prey Relationships in North- eastern Alberta

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