BASELINE STATES OF ORGANIC CONSTITUENTS IN THE ATHABASCA RIVER SYSTEM UPSTREAM OF FORT McMURRAY

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ABSTRACT

Investigations were carried out on the Athabasca River upstream of Fort McMurray to determine the baseline quantities of organic constituents and their contribution to the organic water quality of the river system as it continues through the Athabasca Oil Sands strip mining area. Results of these investigations were evaluated to assess the fate of organic matter in this segment of the river.

Studies focussed on the natural occurrence of classes of compounds which are known to be major constituents of wastewaters from oil sands processing. Major groups of naturally occurring organic compounds and a limited number of labile compounds were also considered as a means of assessing the assimilative capacities of this river segment.

Water soluble constituents, tannins and lignins, asphaltenes, and polar constituents were the major organic components of the river system as determined from the 16 different investigations carried out.

Water samples contained an average 9 mg/ℓ of organic carbon, the majority of which was determined as dissolved organic carbon. Water soluble organics, which include the humic acids, averaged 6.9 mg/ℓ and were the largest single organic component of the river water. Also contained in this water soluble fraction were the naturally occurring tannin and lignins at 0.24 mg/ℓ. The extractable carbon fraction contained 20% asphaltenes, 33% polar constituents, and 10% hydrocarbons.

Sediment samples contained an average 11,000 to 20,000 mg/kg of total organic carbon, 6% of which occurred as extractable organic carbon. Tannins and lignins were the largest group of compounds detected in the sediments but comprised only 3% of their unextractable carbon fraction. Extractable organic carbon fractions contained 39% asphaltenes, 17% polar compounds, and 16% hydrocarbons.

On the basis of these investigations, it is concluded that organic constituents which occur in this segment of the river are mainly water soluble, naturally occurring compounds that persist consistently throughout this upstream study area. Measurements to assess the assimilative capacity of the river system indicate that minimal uptake of the majority of organic matter occurs in this river section, thus providing a constant natural input to the river system at Fort McMurray.

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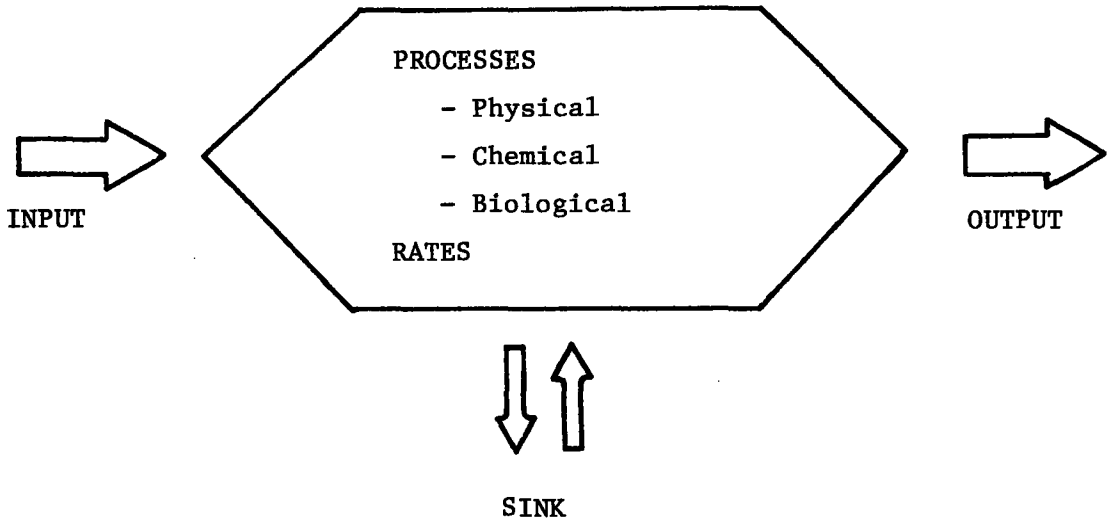
1. INTRODUCTION

The water quality of the Athabasca River is governed largely by the ability of the river to assimilate organic material from natural sources and industrial effluents. Inputs of organic material greater than the assimilative capacity of the river will result in significant environmental changes--inputs within this assimilative capacity will produce no serious environmental effects. However, assimilation of these materials may result in serious environmental side-effects such as increased productivity and oxygen depletion.

The ultimate fate of organic materials in a river system is influenced by the dilution factor, which is a function of the discharge, by the rate of degradation of organic materials, and by the supply of oxygen to support the degradative processes. Conceptually, each segment of the river has an input and an output of material dissolved or suspended in water (Figure 1). The major input of organic material is contained in river water, in flow from tributary streams, surface runoff, and ground-water discharge. These inputs may be from natural systems or may reflect inputs caused by man's activities. Material passing through the river segment experiences a number of physical, chemical and biological processes and is degraded to varying degrees depending upon the stability of the material and the severity of the process. Labile compounds such as amino acids may readily be degraded and assimilated and may not persist long; aliphatic hydrocarbons are more stable and less prone to biodegradation and may persist longer; and refractory compounds such as humic acids are even more stable and may require severe chemical or biological conditions over a longer period of time for degradation to occur. Some materials entering the river may be incorporated into the sediments which comprise the SINK (Figure 1).



Inputs

- Athabasca River water
- tributary rivers and streams
- surface runoffs
- groundwaters
- industrial effluents

Outputs

- Athabasca River water
- recharge of groundwaters

Sink

- bottom sediments

Figure 1. Model of Athabasca River system.

The natural inputs of organic material to the Athabasca River consist of water-soluble material leached from vegetation, soils, and muskeg; by surface and near-surface waters together with material extracted from the bitument deposit; and by normal near-surface and groundwater movement. This natural input occurs both upstream and downstream of Fort McMurray.

The processes occurring in each section of the river reflect the character of the river in that section which in turn can be altered by seasonal variations. The section of the river upstream of Fort McMurray, within an oil sands outcrop areas, consists of a series of major rapids resulting in turbulent conditions, sections of open water during the winter, and little opportunity for the deposition of sediments. The organic material carried by the river water as it reaches Fort McMurray is the major natural input to the next segment of the river, the stretch between Fort McMurray and Fort MacKay. In this portion of the river organic material from oil sands mining and extraction processes is an additional input to the river.

Studies on the organic water quality of the Athabasca oil sands area have been initiated in the Athabasca River system impacted by oil sands mining operation with a characterization study of the organic constituents in the industrial mining effluents (Strosher and Peaker 1976) and a further study of the organic constituents in mining effluents and their immediate contribution to the Athabasca River (Strosher and Peake in prep.). These studies are of importance in predicting the changes that may occur in the water quality of the area; however, baseline information from the upstream waters as well as studies on the river system downstream of the mining area are necessary in order to assess the overall impacts of man's activities in the mining area.

The current study was undertaken in the Alberta Oil Sands Environmental Research Program (AOSERP) study area (Figure 2) to acquire and examine baseline data from the river system as it enters the oil sands deposit area upstream of the town of Fort McMurray and to additionally examine the natural processes occurring in this

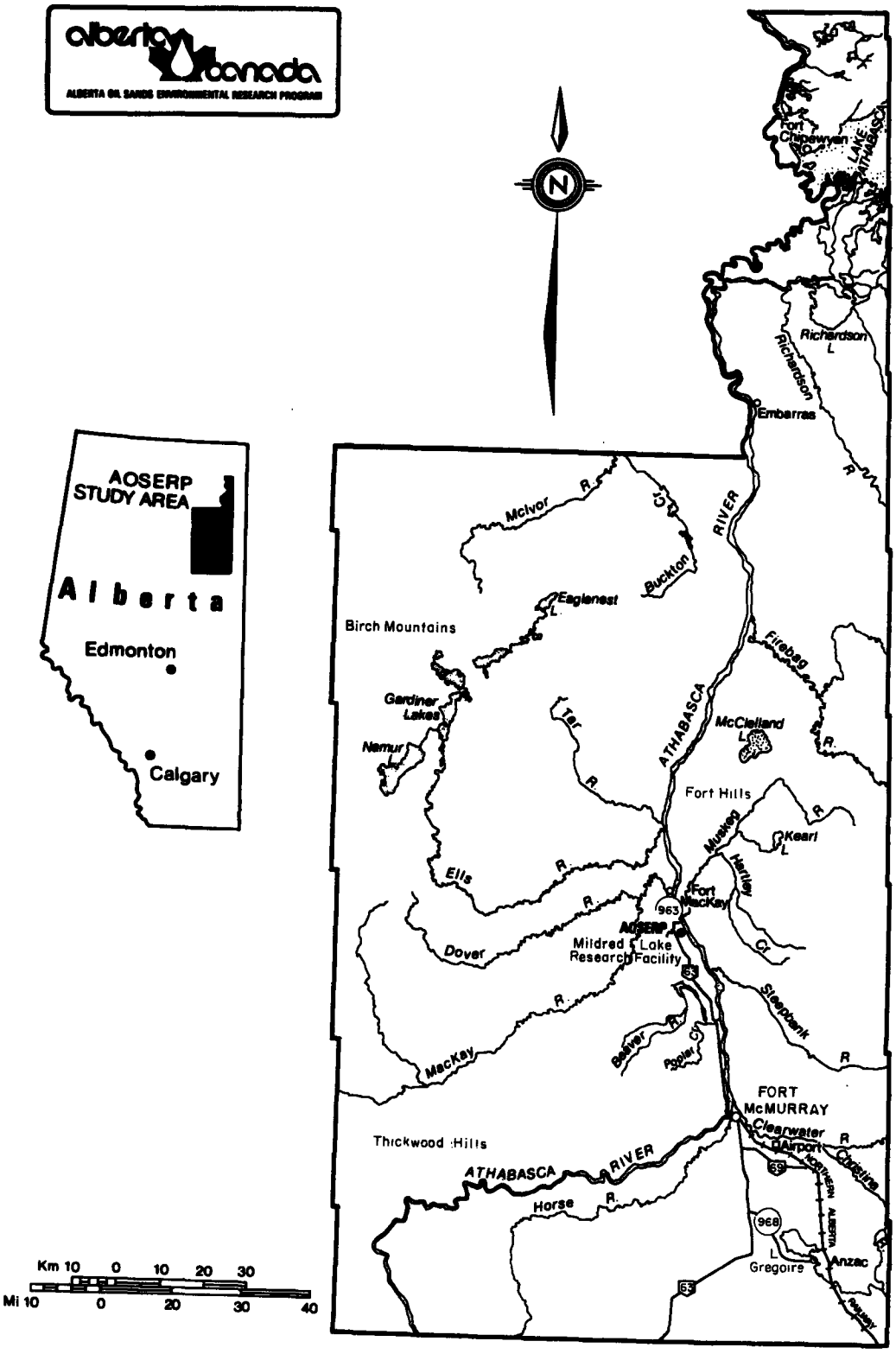


Figure 2. The AOSERP study area.

unaltered section of the river. In the three month period of the study (January to March 1978), a total of 17 organic parameters were examined in samples of water and sediment from areas upstream of Brule Point, upstream of Crooked Rapids, and just upstream of Fort McMurray. These investigations included a number of organic constituents that were found to predominate in wastewater effluents, additional investigations to determine the forms of existence of the majority of organic matter in this section of the river, and examination of some labile organic constituents to assess the fate of organic compounds and provide an overall view of the baseline states of organic water quality in the oil sands area.

Terms of reference for the study are included in Appendix 6.3.

A list of abbreviations and symbols used in this report is given in Appendix 6.1.

2. ANALYTICAL METHODOLOGY

Investigations of the current study were focused toward obtaining the baseline values for both the organic constituents that are detected in wastewater effluents and the naturally occurring organic compounds in the Athabasca River system upstream of the town of Fort McMurray. In this regard, methods and techniques developed in the previous investigations (Strosher and Peake 1976; 1977) have been modified into a more comprehensive overall investigative program which includes additional analyses developed and/or adapted for the naturally occurring organics. A general description of the overall methodology is contained in the following sections, with detailed methods contained in Appendix 6.3.

2.1 SAMPLE DESCRIPTION AND HANDLING

On 18 January 1978 the first samples were obtained from a point 2 km upstream of the Fort McMurray bridge with water samples taken in triplicate from the main channel of the river 50 m from the north shore. Sediment sampling was attempted at this location and at a series of points in a transect across the river; however, no sediments were available as the river bottom consisted of limestone and coarse gravel. Additional sampling for sediments was attempted at a number of locations downstream with a small amount of sediment being obtained from a location about 1.3 km from the Fort McMurray bridge and a distance of 10 m from the north shore. This sediment was likely contained in a small pocket on the river bottom. Sample descriptions, dates and detailed locations are listed in Table 1 and general sampling locations are shown in Figure 3.

The remaining samples were obtained on 19 January 1978 and consisted of three water samples from a location 3.5 km downstream from the Livock River confluence (approximately 100 km upstream of Fort McMurray, labeled U-100)--30 m from the south east bank, and an additional three samples 4 km upstream of Crooked Rapids

Table 1. Sample description.

Sample	General Location	Military Grid Reference	Sampling Date
Athabasca River U-100	Approximately 3.5 km downstream from Livock River confluence and 30 m from SE bank.	12VUT971583	19 Jan. 1978
Athabasca Sediment U-100	Approximately 3.5 km downstream from Livock River confluence and 20 m from NW bank.	12VUT970585	19 Jan. 1978
Athabasca River U-35	Approximately 4 km upstream of Crooked Rapids point and 20 m from south bank.	12VVT459719	19 Jan. 1978
Athabasca Sediment A U-55	Approximately 1 km downstream of Algar River confluence and 10 m from north bank.	12VVT276675	19 Jan. 1978
Athabasca Sediment B U-55	Approximately 1 km downstream of Algar River confluence and 15 m from north bank.	12VVT276675	19 Jan. 1978
Athabasca River U-2	Approximately 2 km upstream of Fort McMurray bridge on Highway 63 and 50 m from north bamk.	12VVT744861	18 Jan. 1978
Athabasca Sediment U-1	Approximately 1.3 km upstream of Fort McMurray bridge on Highway 63 and 10 m from north bank.	12VVT751861	18 Jan. 1978

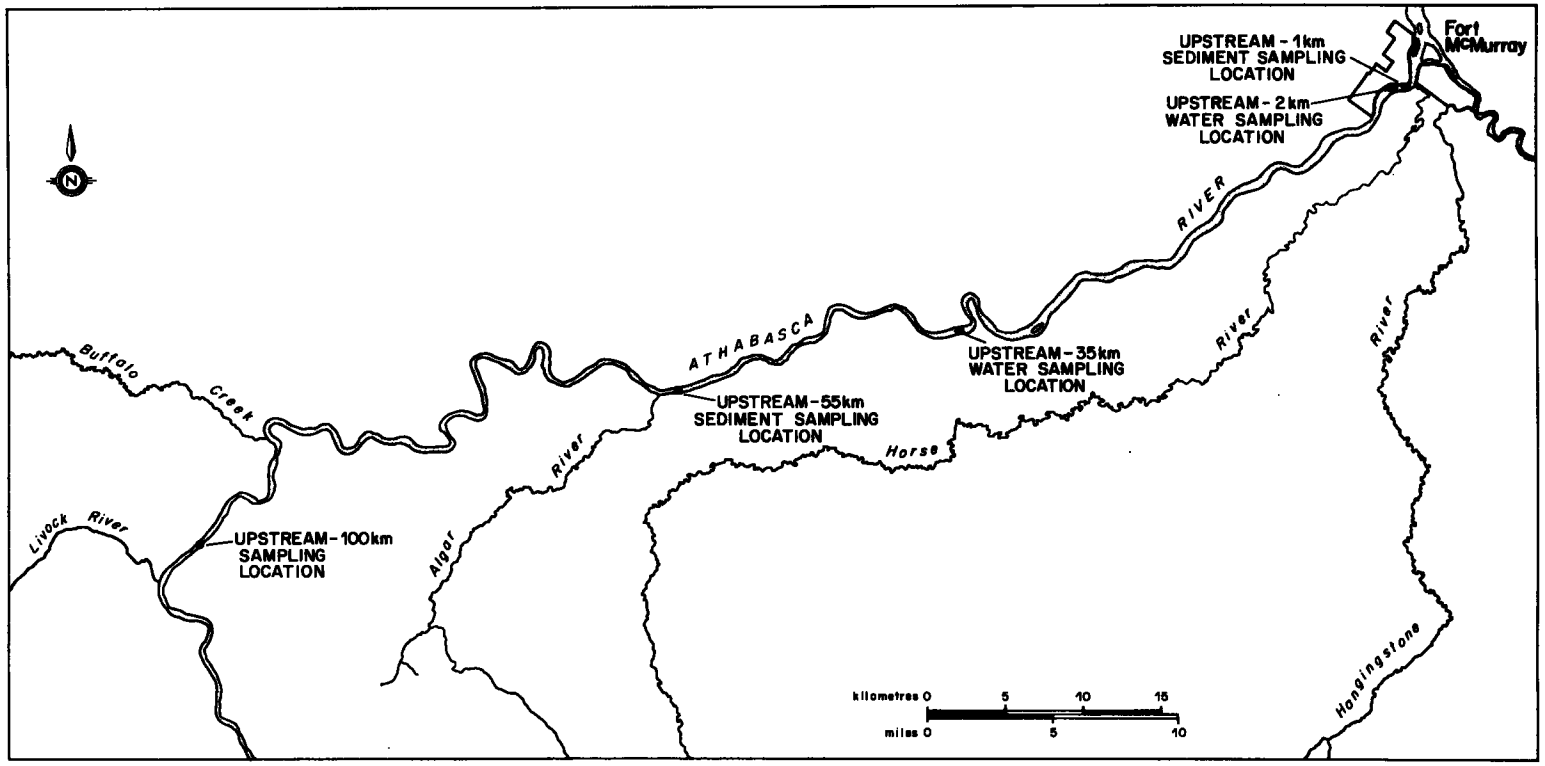


Figure 3. General locations of sampling points.

point (approximately 35 km upstream of Fort McMurray, labeled U-35) --20 m from the south bank. A sediment sample was obtained from the same distance downstream of the Livock River as the water sample but at a distance of 20 m from the northwest bank. Once again, additional attempts at obtaining sediments in a transect across the river failed to produce any further sediment at this location. At the Crooked Rapids site, no sediments were obtainable and the sampling was then attempted approximately 1 km downstream of the Algar River confluence (about 55 km upstream of Fort McMurray, labeled U-55) in less turbulent section of the river. Sampling attempts across the river at this point produced two sediment samples, one being obtained 10 m from the north bank and another approximately 15 m from the same bank.

Water sampling at each point consisted of three 40-ℓ samples to be used for the major organic analyses and three 10-ℓ samples for individual tests that did not require pre-extraction of the organic constituents. These samples were collected in acid cleaned glass containers to minimize contamination.

Extraction of the 40-ℓ water samples was achieved by using a three-step process (ASTM-D 2778). Initially the samples were acidified to pH 2 with hydrocloric acid (HCl) and extracted four times with benzene to remove acidic and neutral compounds. The pH was then changed to 11 with sodium hydroxide (NaOH) and the basic compounds were then extracted with benzene. In the third step, the pH was adjusted to 7 with HCl and extractions were carried out to remove any possible amphoteric compounds.

Sediment samples were extracted as received in a soxhlet apparatus. First the wet sediments were extracted for eight hours with acetone to remove water and some organics and then with a 9:1 V/V mixture of benzene/methanol for 24 hours to remove the bitumen material from the sediments (Murphy 1969; Evans et al. 1957).

2.2 FRACTIONATION OF ORGANIC CONSTITUENTS

The fractionation scheme used in this study was basically derived from those developed in previous investigations (Strosher and Peake 1976; in prep.) with modifications to both improve the analytical investigations and to incorporate additional analyses that would characterize the majority of the naturally occurring organic compounds. It was designed to improve the separation of various groups of organic compounds for subsequent analyses in order to insure minimal interferences and overlap in the individual analyses. These fractionation schemes are presented in the flow diagrams of Figure 4 for water samples and Figure 5 for sediment samples.

The overall schemes for both waters and sediments are very similar and differ only in the tests on unextracted samples and the general extraction methods for each. Whole water samples were analyzed for total organic carbon (TOC), amino acids, and phenols while both water samples and dispersed sediment were analyzed for amides, tannins and lignins. In the case of sediments, extractions were carried out with acetone and benzene/methanol. Both extracts were combined and transferred to benzene for subsequent fractionation, whereas water samples were fractionated during the extraction process. In each case, the initial extraction or separation was carried out at pH 2 to separate the acidic and neutral compounds from the remaining organic matter.

The aqueous portion of this separation which contained the remaining organic matter was then changed to pH 11 with NaOH and extracted with benzene to remove the basic compounds which were analyzed by gas chromatographic techniques. Once again the pH of the aqueous layer was changed this time to 7 in order to extract possible amphoteric compounds with benzene. This fraction was also analyzed by a gas chromatographic technique. The remaining aqueous solution which contained the unextractable organic matter was then acidified to less than pH 2 and passed through an ion

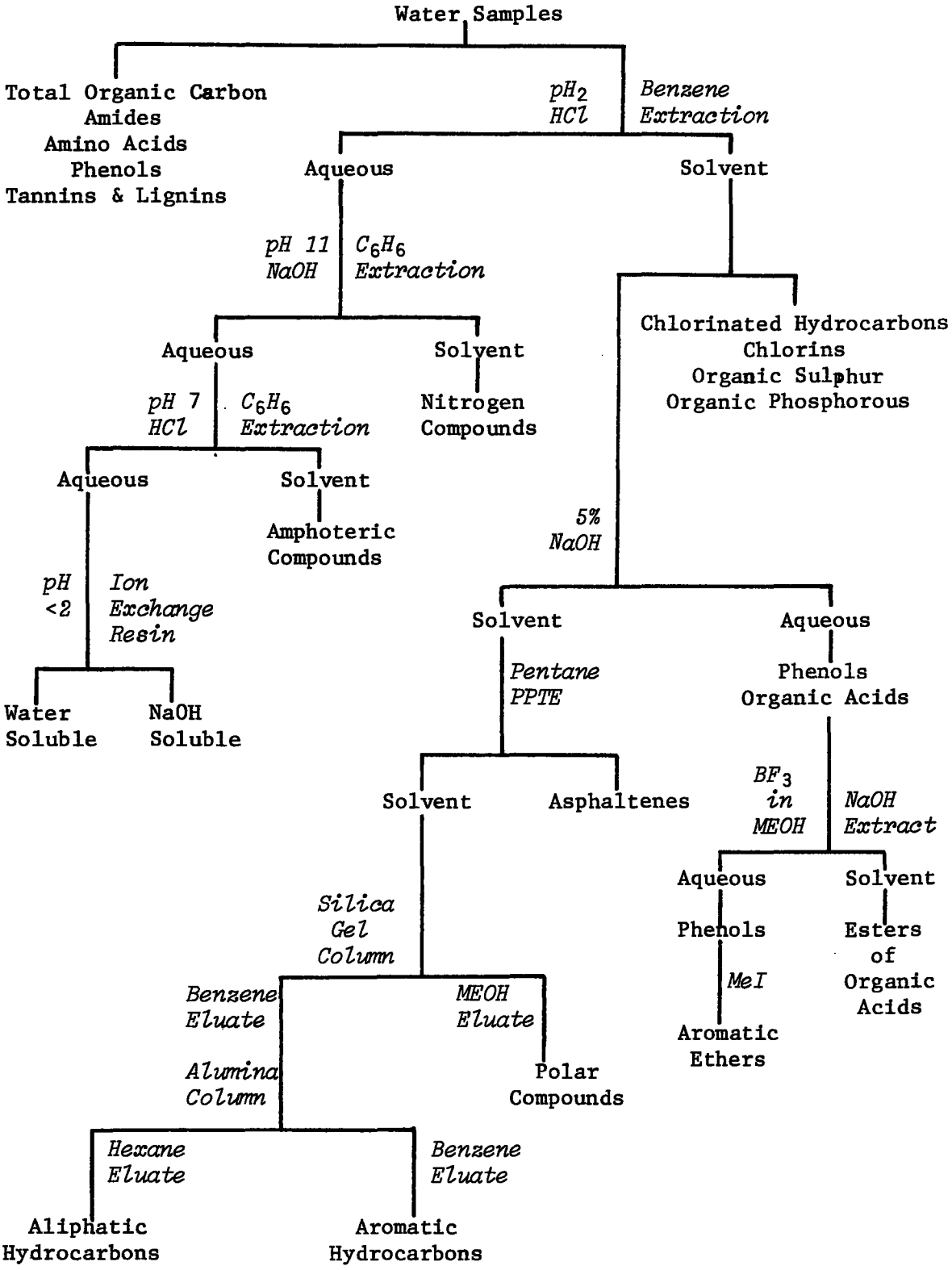


Figure 4. Flow diagram of analytical investigations on water samples.

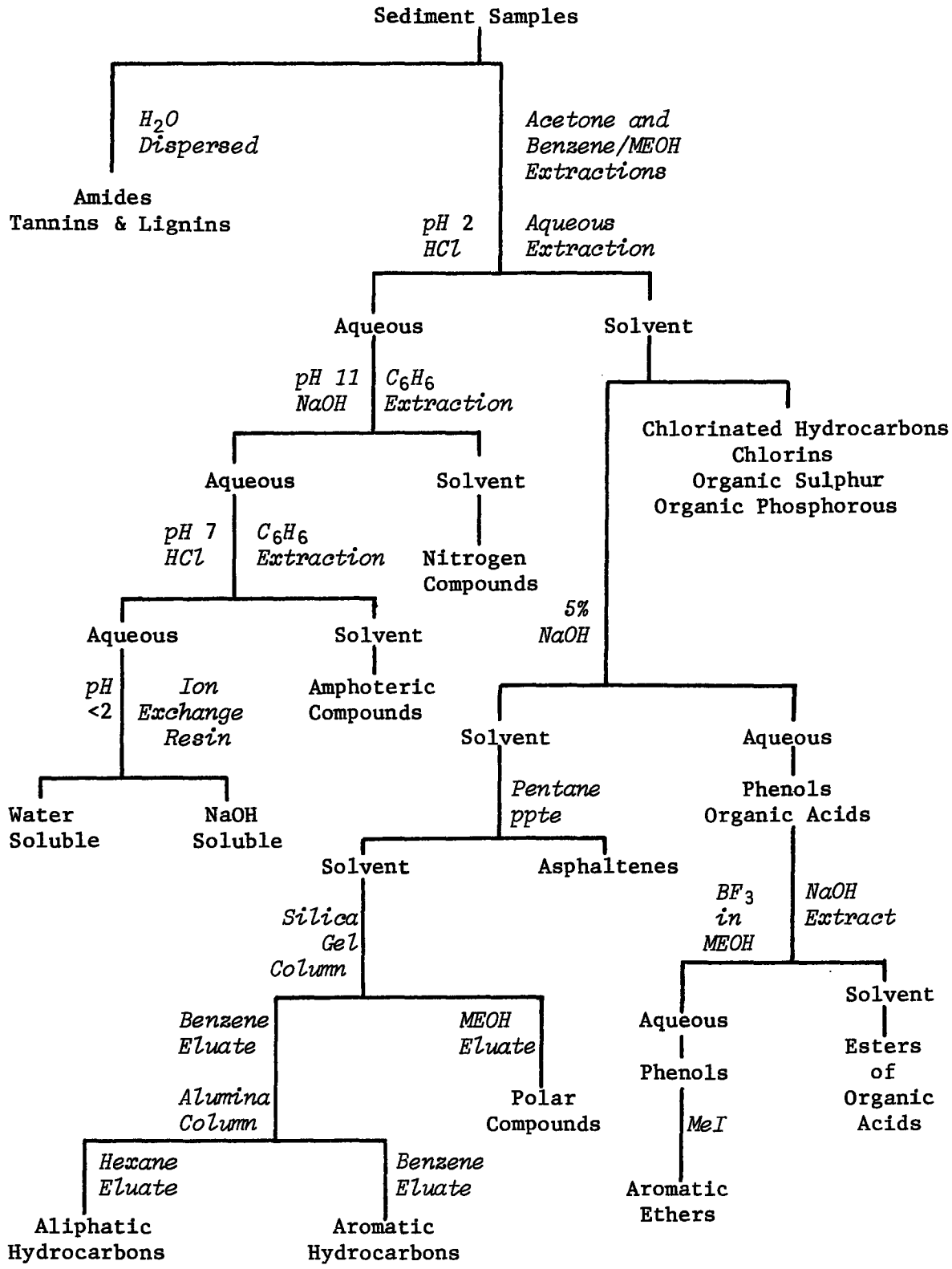


Figure 5. Flow diagram of analytical investigations on sediment samples.

exchange resin. Water soluble organics passed through the resin whereas materials such as humic and/or fulvic acids were initially retained and subsequently eluted from the column with NaOH. The resulting fractions obtained from the ion exchange resin were examined for their organic carbon content using a TOC analyzer.

The acid and neutral compounds from the initial acidic extraction were separated into two portions. One portion was analyzed for chlorinated hydrocarbons, chlorins, organic sulphur compounds, and organic phosphorous compounds by a variety of gas chromatographic (GC) and spectrofluorometric techniques. The remaining portion was extracted with a 5% NaOH solution to separate the acidic components from the neutral fraction.

The aqueous fraction which contained both organic acids and phenolic compounds was then derivitized with boron trifluoride (BF_3) in methanol (MeOH) which converted the acids to esters, thus allowing the phenols to be separated from the neutral organic acid esters by a further NaOH extraction. Phenols were then converted to aromatic ethers by heating with methyl iodide (MeI). These derivitized acids and phenols were then quantified by gas chromatography.

The neutral organic fraction was transferred to n-pentane to precipitate asphaltenes which were filtered off, dried, and weighed. The solvent soluble oily fraction was then chromatographed on a silica gel column with two solvents used to separate the hydrocarbons from polar compounds. Benzene eluted the hydrocarbons while methanol eluted polar compounds. The benzene fraction was further chromatographed on an alumina column to separate hexane eluted aliphatic hydrocarbons from benzene eluted aromatic hydrocarbons. Both hydrocarbons and the polar compounds were quantified by gas chromatographic methods.

All analyses on water samples were carried out in triplicate to determine the precision of analytical methods.

Due to the lack of sufficient quantities of sediment obtained from the U-100 and U-1 sampling locations replicate analyses were not carried out; however, analyses on the two sediments obtained from the U-55 locations were carried out in triplicate. Results of replicate analyses along with the calculated standard deviations and coefficients of variance are contained in the analytical section in Appendix 6.2. The significant calculated mean values are used in the following result sections.

3. RESULTS AND DISCUSSION

Data acquired in the current investigation are presented in the following sections according to the individual type of analysis performed and the respective results are evaluated and discussed. The summary section is used to integrate the data and provide an overview of the baseline states of organic water quality in this section of the river.

3.1 TOTAL ORGANIC CARBON

3.1.1 Waters

Total organic carbon analyses were carried out on all water samples as received, on filtered waters as a measurement of dissolved organics, and on extracted waters to provide a measurement of total extractable organic material. These analyses revealed total organic carbon levels of 9 mg/ℓ in all water samples and 9 mg/ℓ in the filtered water samples indicating that virtually the entire organic carbon content of these waters occurred in a dissolved state (Table 2). Residual organic carbon values averaged 8 mg/ℓ showing that only a small portion of the total organic carbon in the river waters was extractable. These results reveal that the majority of organic carbon occurring naturally in the water is of an unextractable, water soluble nature whereas river waters previously obtained from the surface mining area between Fort McMurray and Fort MacKay were found to contain an average of 25% extractable organic carbon (Strosher and Peak in prep.).

Particulate matter which was filtered from the waters in the analysis for dissolved organic carbon was dried and weighed. Upstream waters (U-100) contained twice as much suspended sediment in the water as did the U-35 and U-2 waters. These measured values were 6 mg/ℓ in the U-100 waters and 3 mg/ℓ in both U-35 and U-2 waters indicating that sedimentation is occurring in this portion

Table 2. Organic carbon content of waters and sediments and amounts of filtered particulate matter of waters.

Sample	Total Organic Carbon	Organic Carbon Filtered	Filtered Particulate Matter	Residual Organic Carbon	Extractable Organic Carbon
Waters (in mg/ℓ)					
Athabasca River U-100	9	9	6	8	1
Athabasca River U-35	9	9	3	8	1
Athabasca River U-2	9	9	3	8	1
Sediments (in mg/kg of dry sediment)					
Athabasca Sediment U-100	20,000				740
Athabasca Sediment U-55-A	11,000				910
Athabasca Sediment U-55-B	14,000				880
Athabasca Sediment U-1	16,000				1180

of the Athabasca River but at a very slow rate. These sediments are possibly flushed from the river system during spring runoff. Although no measurable difference was detected in the total organic carbon levels of the filtered and unfiltered water samples, some organic carbon compounds could very well be associated with the sediment material. The amount of sediment dispersed in the water is so small that contributions of any associated organic matter are negligible. The precision of the analytical method for total organic carbon in these waters is ±2% or about 0.2 mg/ℓ. In order for 6 mg of sediment to exceed the 0.2 mg level it would have to contain 30,000 mg/kg of the organic carbon, or about 30 times the amount contained in the bottom sediments.

3.1.2 Sediments

Quantitation of the organic material contained in river bottom sediments was based on the weight of the total extractable fractions and on whole sediment samples by the Leco combustion method outlined in Appendix 6.2.2. Analyses revealed that extractable organic constituents contained an average of 80% organic carbon which is similar to the organic carbon content of Athabasca bitumen, 83.3% (Berkowitz and Speight 1975).

The extreme upstream sediment (U-100) which consisted mostly of silt and fine sand contained the lowest amounts of extractable organic carbon at 740 mg/kg of dry sediment. The sediments from the U-55 locations were taken from a pocket of fine silt and clay and revealed higher levels of extractable organic carbon. The sediment collected 10 m from shore contained an average of 910 mg/kg while the sediment collected 15 m from the same shore contained an average of 880 mg/kg as organic carbon. The sediment collected nearest Fort McMurray (U-1) was similar in consistency to the U-100 sediment, i.e. silt and fine sand, but revealed the highest extractable organic carbon value at 1180 mg/kg. The precision of the gravimetric method used to obtain these values ranged from ±5 to ±8% indicating that

the variations of increasing extractable organic carbon levels found to exist from the furthest upstream to near Fort McMurray locations were real.

Total organic carbon analysis revealed 20,000 mg/kg in U-100 sediment, 11,000 mg/kg in the U-55 sediment nearest shore, 14,000 mg/kg in the other U-55 sediment, and 16,000 mg/kg in the U-1 sediment. These results indicate that an average 6% of the total organic carbon in sediments is extractable by the methods employed with 94% remaining unextractable. The following sections contain results of the study to characterize the constituents of both extractable and unextractable fractions.

Although it appears that sediments are enriched in organic carbon in the downstream samples, it must be noted that minimal sedimentation occurs in this turbulent section of the river as shown by the lack of bottom sediments available during the sampling operations. It is therefore unlikely that enrichment of organics in sediments is taking place from the water column. The higher levels of organic material found in the downstream sediments are likely due to the addition of sediments with increasing organic content as the river progresses through the oil sands deposit area.

3.2 ASPHALTENES

Fractionation of oil or bitumen on the basis of normal pentane solubility produces two fractions; a pentane soluble oily fraction called maltenes and a pentane insoluble fraction which precipitates from pentane and is called asphaltenes. Quantitation is based on the weight of precipitated asphaltenes.

Fractionations were carried out both on extractable material from the 40 ℓ water samples and on extracts of bottom sediments. Occurrences in the water samples averaged 0.25 mg/ℓ in both U-100 and U-2 samples and 0.22 mg/ℓ in the U-35 water sample (Table 3). These values represent 18 to 21% of the extractable

Table 3. Organic constituents of waters and sediments.

Sample	Asphaltenes	Aliphatics	Aromatics	Polar Compounds	Amphoteric Compounds
Waters (in mg/ℓ)					
Athabasca River U-100	0.25	0.004	0.002	0.004	0.001
Athabasca River U-35	0.22	0.014	0.002	0.004	0.001
Athabasca River U-2	0.25	0.012	0.002	0.003	0.002
Sediments (in mg/kg of dry sediment)					
Athabasca Sediment U-100	320	12.2 (23)[a]	5.6 (21)	4.2 (187)	0.005
Athabasca Sediment U-55-A	370	40.3 (147)	42.6 (127)	4.8 (152)	0.006
Athabasca Sediment U-55-B	480	6.4 (44)	2.6 (22)	1.8 (84)	0.002
Athabasca Sediment U-1	542	51.8 (90)	51.2 (180)	10.4 (390)	0.009

[a]Measured by weight.

organic carbon in the river waters and compares with the 17 to 25% asphaltenes measured in crude bitumen (Strosher and Peake 1976; Berkowitz and Speight 1975).

River bottom sediments collected at the U-100 location contained 320 mg/kg as an asphaltene fraction. The more clayey sediments obtained from the U-55 locations contained 370 and 480 mg/kg asphaltenes respectively in the sediments 10 m and 15 m from the north shore. The U-1 sediment contained 540 mg/kg as asphaltenes. These asphaltene values, in terms of organic carbon, represent 34 to 46% of the extracted organic carbon from the sediments.

3.3 ALIPHATIC HYDROCARBONS

The pentane soluble oily fraction which resulted from the asphaltene fractionation technique was further fractionated into various components by column chromatography techniques. One fraction which eluted from an alumina column in n-hexane contained the aliphatic hydrocarbons which were measured by gas chromatography. The amounts of these aliphatic hydrocarbons found in river waters ranged from an average of 0.004 mg/ℓ in the U-100 sample to 0.014 and 0.012 mg/ℓ in the U-35 and U-2 water samples respectively (Table 3). A total of 12.2 mg/kg were detected in the U-100 sediment increasing to a high of 51.8 mg/kg in the U-1 sediment. The U-55 sediments varied from 40.3 mg/kg nearest the shore to 6.4 mg/kg at a distance 5 m greater from the shore.

River water fractions consisted mainly of a mixture of unresolved, extremely complex, branched and cyclic saturated compounds as were evidenced in previous investigations (Strosher and Peake 1976; in prep.). Normal straight chain alkanes in the range of nC15 to nC31 were also detected by GC, but in much lesser abundance. Sediment samples contained a somewhat similar display of aliphatic hydrocarbons however the overall average molecular weight (as determined by GC retention time) of these compounds in

sediments is slightly higher--approximately 380 atomic mass units (amu)--than those found in waters at 300 amu.

Accuracy of the gas chromatographic methods for the measurement of hydrocarbons and polar compounds is limited by the ability of some compounds to elute from the GC column under the conditions employed during the analyses. For instance, high molecular weight hydrocarbons may not be eluted from the column at the temperature limitation of column packing material and polar compounds are likely to be retained on the GC column at even lower molecular weight due to the interactions of the polar functional groups with the column packing material. In order to assess the accuracy of the GC results on the components of oily fractions, a further examination of aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds was carried out to determine the total amounts of these constituents as eluted from the liquid chromatography columns.

Aliphatic hydrocarbons eluted from the alumina chromatography with hexane were evaporated to remove traces of solvent and weighed to determine the total amount of extractable aliphatic hydrocarbons in samples. Due to the small amount of materials in the water extracts, only sediment fractions could be quantitated in this manner. The U-100 sediment revealed a total 23 mg/kg of the aliphatic hydrocarbons by weight. Sediments from U-55 locations contained 147 mg/kg from samples nearest shore and 44 mg/kg at a distance 5 m further from shore. U-1 sediment values were 90 mg/kg of the aliphatic hydrocarbons by this method. These results show that an average of only 38% of the aliphatic hydrocarbons were being detected by the gas chromatographic methods indicating that 62% of this fraction occurs at even higher molecular weights than the estimated average of 300 amu obtained by gas chromatography.

Although the accuracy of the gas chromatographic methods appear limited by the type of compounds found in this fraction, the precision of the data obtained on sediments is excellent (±4 to 7%). This indicates that the higher molecular weight compounds are consistently retained on the GC column.

3.4 AROMATIC HYDROCARBONS

Aromatic hydrocarbons were the second group of compounds obtained from the alumina chromatography separation and were eluted with benzene. These compounds, also analyzed by gas chromatography, ranged from substituted nathphalenes (142 amu) to multi-ringed compounds (300 amu) with an average molecular weight of about 200 amu in waters and 230 amu in sediments. The majority of these compounds, however, were unresolved due to the complex variety of substituted and unsubstituted aromatics present.

Results of gas chromatographic analysis revealed the river waters contained an average of 0.002 mg/ℓ throughout this section of the river (Table 3). River bottom sediments which generally contained the higher molecular weight aromatics also contained considerably larger amounts of them. U-100 sediment revealed 5.6 mg/kg of these aromatics, U-55 sediments contained an average 42.6 mg/kg in deposits 10 m from shore decreasing to 2.6 mg/kg at 15 m from shore, and U-1 sediment had the highest levels of 51.2 mg/kg.

Aromatic hydrocarbon fractions from sediments were also measured by weight to determine the total amount of these compounds in the extractable material. U-100 sediment revealed a total of 21 mg/kg of the aromatics by weight. U-55 sediments contained 127 mg/kg in samples taken 10 m from shore and 22 mg/kg at 15 m from shore. The aromatic hydrocarbon content of U-1 sediment was 180 mg/kg. On the average, gas chromatographic methods detected only 24% of the total aromatic hydrocarbon content as measured by weight. The fact that average aromatic compounds were found to elute at higher temperatures than the average aliphatic compounds substantiates the findings whereby only 24% of the total aromatics were detected by GC as compared to 38% of the total aliphatic hydrocarbons by the GC methods. Although accuracy of the GC methods as they apply to the aromatic hydrocarbons found in these sediments is considerably lacking, precision of the GC analytical data still appears excellent ranging from ± 9 to 11%, once again indicating that the higher molecular weight compounds are consistently

retained on the GC column.

3.5 POLAR COMPOUNDS

A third component of the oily fraction was separated from the hydrocarbons by liquid chromatography on silica gel. These polar compounds were eluted with methanol and measured by gas chromatography.

The measurable polar compounds by GC were found in amounts which averaged 0.004 mg/ℓ in the river waters (Table 3). U-100 sediments contained 4.2 mg/kg of the polar materials while U-55 sediments showed 4.8 mg/kg in samples taken closest to shore and 1.8 mg/kg in the U-55-B sample. The U-1 sediment contained the highest amount of polar compounds--10.4 mg/kg of dry sediment.

Sediment fractions containing polar compounds, were additionally weighed in order to more accurately assess the total amounts of these compounds as a contributor to the extractable carbon fraction. U-100 sediment revealed 187 mg/kg of the polar compounds by weight. U-55 sediment contained 152 mg/kg in deposits nearest shore and 84 mg/kg in the sample further from the same shore. These polar compounds measured 390 mg/kg by weight in the U-1 sediment. The results of this additional investigation reveal that polar compounds are a considerable contributor to the extractable carbon fraction of sediments and that only an average of 2.6% of the total polar compounds were detectable by GC.

In order to assess various inputs of these oily materials to the river system and their fate as they progress through any section of the river, comparison of the relative amounts of the three oily components must be evaluated. Aliphatic hydrocarbons are the least stable of the three components and are most easily biologically degraded or lost by evaporation processes. On the other hand, polar compounds are the most complex of the three components, are degraded the slowest, and are more soluble in water. Therefore depletion of the lower molecular weight aliphatic or aromatic hydrocarbons would produce an increase in the relative

amounts of polar compounds, especially in the water.

In this respect, the oily fraction of both waters and sediments was evaluated to determine if possible losses of the lighter hydrocarbons in respect to the polar compounds occurs. In the case of river waters, GC results show that U-100 samples contained 40% aliphatic hydrocarbons, 20% aromatic hydrocarbons, and 40% polar compounds. In contrast, U-35 and U-2 waters revealed about 70% aliphatic hydrocarbons, 11% aromatics, and 19% polar compounds in their oily fractions thus indicating an enrichment of aliphatic hydrocarbons as the river progressed through the bitumen deposit area. This increase in the aliphatic fraction, possibly by groundwater and/or tributary flow, masks any possible measurement of degradative processes which may be occurring in this section of the river.

Comparison of the relative amounts (by weight) of these oily components in the sediment samples revealed considerable differences in their overall composition in this section of the river. U-100 sediment contained 11% aliphatic hydrocarbons, 10% aromatic hydrocarbons, and 79% polar constituents. The U-55 and U-1 sediments deposits which occurred further into the oil sands deposit area displayed considerably different compositions of oily components. The U-55 sample collected nearest shore contained 34% aliphatics, 33% aromatics, and 33% polar compounds. Another sediment sample obtained from the same location but 5 m further from shore contained 27% aliphatics, 25% aromatics, and 48% polar compounds. U-1 sediment revealed 14% aliphatic hydrocarbons, 30% aromatic hydrocarbons, and 56% polar compounds. Although caution must be taken in interpreting this small amount of data on the limited amount of sediments available in this upstream segment of the Athabasca River, it appears that once the river enters the oil sands deposit area, hydrocarbon content of the oily constituents progressively decreases, leaving an increased amount of polar constituents in downstream samples. This phenomenon may either be due to degradative processes of the lighter hydrocarbons or to weathering of the lighter materials.

Evidence of the second process is supported by the increased aliphatic hydrocarbon content found in the U-35 and U-2 water samples.

3.6 AMPHOTERIC ORGANIC COMPOUNDS

In order to more fully examine the composition of the total organic content of river waters and bottom sediments, especially the extractable component, an additional extract or separation procedure was carried out at pH 7 to determine the amount of amphoteric organic compounds in this system. Amphoteric compounds which have characteristics of both acid and base functions are therefore soluble in both acidic or basic solutions and require extraction at neutral pH.

Analysis by gas chromatography revealed that these compounds comprise a relatively small portion of the extractable carbon fractions. Levels contained in river waters were 0.001 to 0.002 mg/ℓ or about 0.1% of the extractable carbon (Table 3). Amounts found in sediment extracts were slightly higher ranging from 0.002 to 0.009 mg/kg; however, they represented only 0.001% of the extractable carbon in these sediments.

3.7 PHENOLS

Phenols are one of the two components that are measured as the acidic organic fraction of the river system. They were analyzed by two methods, the standard colorimetric method and the gas chromatographic method developed in a previous investigation (Strosher and Peake 1976). The two investigative methods provide a comparison of amounts of simple phenols as measured by the colorimetric method to the more complete phenolic content as measured by the gas chromatographic method.

Amounts of phenols in river waters as determined by the colorimetric method were below detectable limits (less than 0.001 mg/ℓ, Table 4). In comparison, GC results showed that phenolic compounds were present at levels of about 0.002 mg/ℓ. Examination of the gas chromatographic retention times of these

Table 4. Phenols, organic acids, and amino acids in waters and sediments.

Sample	Phenols Colorimetric	Phenols by GC	Organic Acids	Amino Acids
Waters (in mg/ℓ)				
Athabasca River U-100	<0.001	0.003	0.002	0.00007
Athabasca River U-35	<0.001	0.002	0.002	0.00005
Athabasca River U-2	<0.001	0.002	0.002	0.00004
Sediments (in mg/kg of dry sediment)				
Athabasca Sediment U-100		1.5	5.2	
Athabasca Sediment U-55-A		0.6	10.5	
Athabasca Sediment U-55-B		0.5	2.8	
Athabasca Sediment U-1		2.5	4.9	

phenolics confirmed the presence of the more complex variety of compounds which are undetectable by colorimetric analysis.

Sediments contained phenolic compounds at levels of 1.5 mg/kg in the U-100 sediment, about 0.6 mg/kg in U-55 sediments, and 2.5 mg/kg in the U-1 sediment. Once again, these phenolics were the more complex variety.

3.8 ORGANIC ACIDS

The second component of the acidic fraction was the organic acid fraction. These organic acids were analyzed by gas chromatography as their respective methyl ester derivatives. The GC analysis revealed the presence of a mixture of high molecular weight compounds which are probably aromatic in structure as found in previous investigations (Strosher and Peake 1976;

Amounts of these organic acids extracted from water samples averaged 0.002 mg/ℓ (Table 4). Organic acids comprised the largest amount of the acidic component in sediment samples. The U-100 sediment contained 5.2 mg/kg of the acids; U-55 sediments, 10.5 mg/kg in the sample nearest shore and 2.8 mg/kg in the sample 15 m from shore; and the U-1 sediment contained 4.9 mg/kg.

3.9 AMINO ACIDS

Amino acids were investigated in the river water as a natural labile material that could provide a measurement of degradative processes that might be occurring within this section of the river. Depletion rates were based on the total amount of amino acids.

The levels of amino acids became progressively less from upstream to downstream sampling locations. U-100 waters contained an average of 7×10^{-5} mg/ℓ of these acids, U-35 waters revealed 5×10^{-5} mg/ℓ, and U-2 waters were slightly less at 4×10^{-5} mg/ℓ (Table 4). In order to assess the degree of degradation if any, one must assume that inputs are uniform throughout this section of the river and that analytical methods are precise. The precision

of these methods averaged ±9% and accounts for some of the marginal differences in amino acid content in the waters. Degradation processes may account for the remaining differences of 2×10^{-5} mg/ℓ from upstream to downstream locations.

3.10 SULPHUR COMPOUNDS

Organic sulphur compounds and elemental sulphur were detected in solvent extracts of waters and sediments with a flame photometric detector coupled to a gas chromatograph. River waters contained an average of 0.002 to 0.002 mg/ℓ of the organic sulphur compounds and 0.0001 to 0.0005 mg/ℓ of elemental sulphur (Table 5). Sediment samples revealed greater amounts of these compounds, generally increasing in value from upstream to downstream locations. U-100 sediments had 0.4 mg/kg of the organic sulphur compounds and 0.2 mg/kg of elemental sulphur. The two U-55 sediments varied considerably in their respective amounts of these compounds. Sediment obtained 10 m from shore revealed 6.0 mg/kg of organic sulphur compounds and 0.5 mg/kg of elemental sulphur while the sediment collected 5 m further from shore contained only 2.2 mg/kg of the organic sulphur compounds but a considerably higher value of elemental sulphur at 3.9 mg/kg. U-1 sediment values for these compounds measured 16.0 mg/kg for the organic sulphur compounds and less than 0.1 mg/kg for the elemental sulphur.

Sulphur responses for both waters and sediments revealed a complex mixture of high molecular weight sulphur compounds (averaging 250 amu) which are mainly unresolved by gas chromatography. These compounds are similar to the organic sulphur compounds in bitumen as determined in a previous investigation (Strosher and Peak 1976).

3.11 ORGANIC PHOSPHOROUS COMPOUNDS

Organic phosphorous compounds were also measured by gas chromatography using a flame photometric detector. Amounts of these compounds in water samples averaged 0.00003 to 0.00005 mg/ℓ (Table 5). Sediments contained considerably larger amounts of the phosphorous

Table 5. Organic sulphur and phosphorous compounds and elemental sulfur in waters and sediments.

Sample	Sulphur Compounds	Elemental Sulphur	Phosphorous Compounds
Waters (in mg/ℓ)			
Athabasca River U-100	0.003	0.0005	0.00005
Athabasca River U-35	0.002	0.0001	0.00003
Athabasca River U-2	0.002	0.0003	0.00005
Sediments (in mg/kg of dry sediment)			
Athabasca Sediment U-100	0.4	0.2	0.03
Athabasca Sediment U-55-A	6.0	0.5	0.02
Athabasca Sediment U-55-B	2.2	3.9	0.01
Athabasca Sediment U-1	16.0	<0.1	0.02

compounds, averaging 0.03 mg/kg in U-100 sediment, 0.01 to 0.02 mg/kg in U-55 sediments, and 0.02 mg/kg in the U-1 sediment.

These organic phosphorous responses, although present in much lower quantities than the organic sulphur compounds, contained more individually resolved compounds as displayed in the gas chromatograms.

3.12 ORGANIC NITROGEN COMPOUNDS

Extracts of waters and sediments were analyzed for nitrogen containing organic compounds by electrolytic conductivity detection of the gas chromatographic effluent. Because of the polar nature of some organic nitrogen compounds, only those extractable from samples by the extraction methods used and eluted from the gas chromatographic column are measured by this method. Compounds such as the amides or amino acids are not measured by this method without prior derivatization.

Nitrogen compounds detected in waters ranged from 0.0006 mg/ℓ in U-100 water samples to 0.0010 mg/ℓ in U-35 waters and 0.0008 mg/ℓ in U-2 waters (Table 6). Sediment samples contained similar levels of these organic nitrogen compounds with U-100 sediment levels of 0.0002 mg/kg and U-55 and U-1 sediments averaging 0.0009 to 0.0010 mg/kg.

3.13 CHLORINATED HYDROCARBONS

Chlorinated hydrocarbons were also determined by electrical conductivity detection of the gas chromatographic effluent. Amounts detected in U-100 water samples averaged 0.0012 mg/ℓ while U-35 waters were 0.0009 mg/ℓ and U-2 waters were 0.0012 mg/ℓ (Table 6). Sediment samples revealed values of 0.25 mg/kg in the U-100 sediment and 0.28 mg/kg in U-1 sediment with lower values found in U-55 sediments at 0.14 to 0.16 mg/kg.

The detected responses of chlorinated hydrocarbons revealed distinct resolved compounds similar in character to responses obtained for a variety of pesticides; however, further examination

Table 6. Organic nitrogen compounds and chlorinated hydrocarbons in waters and sediments.

Sample	Organic Nitrogen Compounds	Chlorinated Hydrocarbons
Waters (in mg/ℓ)		
Athabasca River U-100	0.0006	0.0012
Athabasca River U-35	0.0010	0.0009
Athabasca River U-2	0.0008	0.0012
Sediments (in mg/kg of dry sediment)		
Athabasca Sediment U-100	0.0002	0.25
Athabasca Sediment U-55-A	0.0009	0.16
Athabasca Sediment U-55-B	0.0010	0.14
Athabasca Sediment U-1	0.0009	0.28

by an electron capture detector has failed to identify them as any of the more commonly used pesticides.

3.14 CHLORINS

Chlorin analysis were carried out on water and bottom sediment samples to assess the contribution of biomass or phytoplankton to the total organic carbon load of the river system. Levels of these plant pigments vary throughout river systems which is a function of the varying degrees of productivity in lakes and rivers. Generally, degradation of these pigments would occur in the course of transport down a river with turbulent water flow and oxidation conditions. This would possibly be offset by the photosynthetic activity of organisms producing chlorophyll within the river segment.

Spectrofluorometric analysis revealed little degradation of these pigments in the water samples from upstream to downstream locations. U-100 water samples contained an average 0.0011 mg/ℓ of the chlorins, U-35 waters had 0.0009 mg/ℓ, and U-2 waters revealed 0.0010 mg/ℓ (Table 7). With a variation in analytical precision of ±10%, the differences in chlorin content in water samples represent neither a net gain or loss from the two competing processes. Sediment concentrations of chlorins were 0.66 mg/kg in U-100 sediments, an average of 0.05 mg/kg in U-55 sediments, and 2.50 mg/kg in U-1 sediments.

3.15 AMIDES

Amides were detected as their corresponding hydroxamate by a colorimetric method. River waters contained levels of amides varying from 0.56 mg/ℓ in U-100 water samples to 0.39 mg/ℓ in U-35 waters and 0.45 mg/ℓ in U-2 waters (Table 7). Analysis for amides were also performed on sediments dispersed in distilled water with removal of the sediment material prior to spectrophotometric investigations. Upstream-100 sediment contained the highest levels of amides at 2.3 mg/kg with U-1 sediment slightly lower

Table 7. Chlorines, amides, and tannins and lignins in waters and sediments.

Sample	Chlorins	Amides	Tannins and Lignins
Waters (in mg/ℓ)			
Athabasca River U-100	0.0011	0.56	0.47
Athabasca River U-35	0.0009	0.39	0.40
Athabasca River U-2	0.0010	0.45	0.44
Sediments (in mg/kg of dry sediment)			
Athabasca Sediment U-100	0.66	2.3	580
Athabasca Sediment U-55-A	0.05	1.0	780
Athabasca Sediment U-55-B	0.05	1.3	570
Athabasca Sediment U-1	2.50	2.1	870

at 2.1 mg/kg. U-55 sediments averaged about half these values at 1.0 to 1.3 mg/kg.

In order to determine the contribution of amides to either the total organic carbon content or extractable carbon content of samples, additional analyses were carried out on the extracted samples. Results revealed that amides were completely extracted from waters and sediments; however, organic nitrogen analysis by GC failed to account for these compounds and therefore present no duplication of results by the two methods. To detect these compounds by GC, derivatization of the polar functional group is required.

3.16 TANNINS AND LIGNINS

In order to more fully investigate the total natural organic carbon loading of the upstream Athabasca River system, further analyses additional to those contained in the contract terms of reference were carried out. One of these analytical investigations was on the levels of tannins and lignins in both waters and sediments. Tannins and lignins are major constituents of most plants that may enter a water system through the process of vegetative degradation. These compounds are composed of complex polycyclic aromatic compounds which are considered highly resistant to biodegradation thus contributing to the background amounts of natural organic matter in a river system.

Levels detected in water samples averaged 0.47 mg/ℓ in U-100 samples, 0.40 mg/ℓ in U-35 samples, and 0.44 mg/ℓ in the U-2 water samples (Table 7). Additionally, the colorimetric test was adapted to continue investigations into the river bottom sediments. Sediment samples were dispersed in water, reagents added, then upon completion of the color complexing sediments were removed to enable spectrophotometric analysis. Amounts detected in upstream-100 sediment averaged 580 mg/kg. U-55 sediments contained 780 mg/kg of these compounds in samples taken 10 m from shore and 570 mg/kg in samples collected 15 m from shore. U-1 sediment revealed the highest level at 780 mg/kg.

Investigations on extracted samples revealed that tannins and lignins were not extracted from waters or sediments but were completely contained in the unextractable carbon fractions. Results for sediments therefore do not represent any portion of the extractable organic carbon as measured. They do however, provide a partial measurement of the total organic carbon content of sediments.

3.17 WATER SOLUBLE ORGANIC COMPOUNDS

Upon examination of the extractable amounts of organic carbon and their constituents in water samples, it was found that only an average of about 10% of the organic carbon was being accounted for. This meant that roughly 90% of the total organic carbon was presumably still associated with the water in a soluble form. Investigations were then carried out to determine the character of this water soluble component based on retention characteristics when applied to a strongly acidic cation exchange resin. Water soluble non-extractable components such as humic acids are retained by the ion exchange resin and are removed only with highly basic solutions. The water soluble components were fractionated on the basis of either being completely water soluble and passing through the column, or being retained and eluted with sodium hydroxide.

Results indicate that the majority of the water soluble component was retained on the ion exchange resin and removed with the sodium hydroxide. Upstream-100 and U-2 water samples contained 4.9 mg/ℓ as organic carbon in this fraction while U-35 waters had 5.1 mg/ℓ (Table 8). The water soluble fractions that were not retained on the resin measured 2.0 mg/ℓ in U-100 samples, 1.8 mg/ℓ in U-35 samples, and 1.9 mg/ℓ in U-2 waters.

In light of the tannin and lignin investigations, whereby it was found that these compounds were unextractable, additional analyses were carried out on the two fractions obtained from the ion exchange resin to determine whether tannins and lignins were present. Results indicated that an average of 40% of the tannins and lignins or 0.18 mg/ℓ were completely water soluble and not

Table 8. Water soluble organic compounds in waters (mg/ℓ).

Sample	Fractions from Ion Exchange Resin as TOC		
	Eluted with Water	Eluted with Sodium Hydroxide	Total Water Soluble
Athabasca River U-100	2.0	4.9	6.9
Athabasca River U-35	1.8	5.1	6.9
Athabasca River U-2	1.9	4.9	6.8

retained by the resins. The sodium hydroxide fractions contained the remaining 60% of the tannins and lignins (0.28 mg/ℓ). In terms of organic carbon however, these findings represented only 5% of the water soluble fraction obtained from the resin and 3% of the sodium hydroxide fraction.

4. SUMMARY AND CONCLUSIONS

4.1 RIVER WATERS

Athabasca River water samples were collected from three locations in the oil sands deposit area upstream of Fort McMurray. This segment of the river system is characterized by turbulent water flow and was examined in winter under ice conditions to determine baseline states of organic constituents as a contribution to the organic load of the river system through the Athabasca mining area. Analyses were conducted for a number of organic components that are found in industrial effluents (as well as for naturally occurring organic compounds). Additional investigations to determine the forms of existence of the majority of naturally occurring organic matter were made and some labile organic constituents were examined to assess the fate of organic compounds in this section of the river.

Water samples consistently contained 9 mg/ℓ total organic matter the majority of which was in the form of dissolved, unextractable organic carbon. Measurement of the total organic carbon content of extracted waters showed that 1 mg/ℓ of the organic carbon was extracted leaving 8 mg/ℓ in the form of water soluble non-extractable carbon.

Non-extractable carbon compounds were separated into two classifications on the basis of retention by ion exchange resins. An average 1.9 mg/ℓ as organic carbon was eluted with water from the resin column while 5 mg/ℓ was characterized as humic like materials which were retained by the acidic resin and eluted with sodium hydroxide solution. This combined water soluble material which averaged 6.9 mg/ℓ was the largest single component representing 77% of the organic carbon content of the waters.

Contained in this water soluble fraction were the naturally occurring tannin and lignin compounds. They accounted for a total of 0.24 mg/ℓ as measured by the organic carbon content. Tannins and lignins occur in both fractions obtained from the resin and represent 5% of the water soluble fraction and 3% of the

sodium hydroxide fraction.

Nitrogen containing compounds were the next largest group of organic compounds found in waters. The majority of this fraction was determined as extractable amides which occurred at levels ranging from 0.27 to 0.39 mg/ℓ. These nitrogen compounds along with the sulphur and oxygen contining compounds which comprise the polar compounds account for an average 3.5% of the total organic carbon or 33% of the extractable organic carbon in water samples.

Asphaltenes, probably contributed by the oil sands deposits, accounted for 0.20 mg/ℓ of the organic carbon in waters. This amount of asphaltenes, although low in terms of total organic carbon content of waters, accounts for 20% of the extractable organic carbon.

Hydrocarbon contribution to the river waters as measured by GC occurs at considerably lower values in terms of organic carbon with 0.005 mg/ℓ found in upstream-100 waters. A 3-fold increase in hydrocarbon content does occur however, between the upstream-100 km and upstream-35 km locations (0.016 mg/ℓ), the majority of which is due to an increase in aliphatic hydrocarbon content. The total hydrocarbon content is upstream-2 km waters was found to be 0.012 mg/ℓ as organic carbon. This increase in aliphatic hydrocarbon content along with the uniform measurements of aromatic hydrocarbons and polar compounds in these waters precluded any degradative measurement of the more liable aliphatic hydrocarbon fractions.

Amino acids were measured as a naturally occurring group of labile compounds in order to assess the degree of degradative processes that occur in this segment of the river. Amounts of total combined amino acids declined from 7×10^{-5} mg/ℓ in upstream-100 water samples to 5×10^{-5} and 4×10^{-5} mg/ℓ in U-35 and U-2 waters respectively. Analytical error may account for approximately 30% of these differences in the total amino acid content from upstream to downstream locations; therefore, degradative losses may be 2×10^{-5} mg/ℓ or 29% of the upstream value.

Of the total 9 mg/ℓ of organic carbon which occurs in water samples, an average 7.7 mg/ℓ was measured as organic carbon in the various investigations, which represents 86% of the organic carbon content of water samples. A mass balance of these constituents in terms of organic carbon is contained in Table 9.

4.2 RIVER BOTTOM SEDIMENTS

Bottom sediments from the Athabasca River were also obtained from three different locations in the study area upstream from Fort McMurray. Sampling locations varied from water sampling points due to the lack of bottom sediments in this segment of the river. The majority of analytical investigations carried out on water samples were also performed on sediment samples.

Total organic carbon content of the sediments ranged from 20,000 mg/kg in upstream-100 km sediment to 11,000 and 14,000 mg/kg in upstream-55 km sediments, and 16,000 mg/kg in upstream-1 km sediment. Extractable organic carbon content was also determined and the sediment extracts revealed that only 6% of the total organic carbon was in an extractable form. Amounts of this extractable carbon generally increased from the furthest upstream samples with 740 mg/kg in U-100 sediment, 880 to 910 mg/kg in U-55 samples and 1180 mg/kg in U-1. The U-100 sediment, which location occurs on the outer edge of the oil sands deposit, contained the highest total organic carbon content and the lowest extractable organic carbon content, indicating a higher percentage of the more naturally occurring organics such as humic acids and kerogen or possibly particulate carbon.

Tannins and lignins were one of the largest groups of compounds as detected in the sediments. These compounds were part of the non-extractable organic carbon containing fraction and were found at levels averaging 380 mg/kg or 3% of the non-extractable carbon fractions.

The majority of the investigations were focused to the extractable organic carbon fractions of sediments in order to measure baseline states of bitumen constituents and their contribution to

Table 9. Mass balance of organic constituents of waters (mg/ℓ) and sediments (mg/kg) as organic carbon.

Sample	Total Organic Carbon	Extracted Organic Carbon	Recovered Organic Constituents					Percentage of Carbon Analyzed		
			Water Soluble	Asphaltenes	Hydrocarbons	Polar Compounds	Tannins & Lignins	Extractable Carbon	Non-Extractable Carbon	Total Carbon
Water U-100	9	1	6.9	0.21	0.005	0.40	0.31	62	86	83
Water U-35	9	1	6.9	0.18	0.016	0.28	0.22	48	86	82
Water U-2	9	1	6.8	0.21	0.012	0.32	0.25	54	85	82
Sediment U-100	20,000	740		267	41	150	308	62	2	4
Sediment A U-55	11,000	910		311	245	122	421	75	4	10
Sediment B U-55	14,000	880		403	71	67	335	61	3	6
Sediment U-1	16,000	1,180		454	240	312	470	85	3	9

this segment of the river system. Asphaltenes were the largest single contribution to the extractable fraction, averaging 39% or double the asphaltic content of oil sands bitumen (17-19%). It is apparent that considerable weathering of the bitumen takes place either before or after entering the bottom sediments of the river.

Oily constituents, as measured by weight, comprised an average 33% of the extractable organic carbon in sediments. The components of this oily fraction consist of aliphatic and aromatic hydrocarbons and the O, N, and S containing polar compounds. Because of the nature of these oily compounds that exist in the sediments of this river segment, gas chromatographic analysis could not detect the majority of these high molecular weight constituents; therefore gravimetric determinations were considered to be a more accurate measurement of these components. On the average, both hydrocarbons and polar compounds contributed equally to the extractable carbon fractions; however, considerable variations occurred in the relative amounts of the various constituents that comprise the oily fractions. Upstream-100 sediment collected at the outer edge of the oil sands deposit area contained 11% aliphatic hydrocarbons, 10% aromatic hydrocarbons, and 79% polar constituents. The remaining sediment deposits which occurred downstream from this sampling point and deeper into the deposit area displayed considerably different compositions of oily components. The U-55 sediments contained 27 to 34% aliphatic hydrocarbons, 25 to 33% aromatic hydrocarbons, and 33 to 48% polar compounds. The U-1 sediment revealed only 14% aliphatic hydrocarbons, 30% aromatic hydrocarbons, and 56% polar compounds. On the basis of the limited data available, it appears that after the river progresses through the bitumen deposit area, hydrocarbon content of the oily constituents (especially aliphatic hydrocarbons) is reduced considerably in sediments closer to Fort McMurray. These results are substantiated by the increased aliphatic hydrocarbon content found in the U-35 and U-2 water samples and reduces the possibility that degradative processes might be occurring on these lighter aliphatic hydrocarbons in the sediments. A mass

balance of analyzed organic carbon constituents versus extractable and total organic carbon is given in Table 9.

4.3 RIVER SYSTEM

In order to assess the contribution of this upstream segment of the Athabasca River in terms of organic constituents, to the overall water quality of the Athabasca River system through the mining area, the results of this investigation have been evaluated in terms of the river model as previously described. Dilution factors and degradative processes influence the ability of a river to assimilate organic material, however, assessment of inputs versus outputs must also be evaluated in order to arrive at the overall organic carbon load and the various constituents which the river carries.

The concentration of organic material in the river water is controlled by opposing factors. The factors which decrease concentration of organic materials are: dilution by waters with lesser amounts of organics than previously existed in the river, degradation of organic matter by chemical and biological processes, losses by evaporation to the atmosphere and incorporation into the sediments. Factors which increase the concentration of organics in the river waters include: inputs of water with a greater amount of organic materials than previously existed in the river, generation by biological processes, and release by the sediments.

The majority of organic carbon carried by the river is of a water soluble nature and does not vary in total content from upstream to downstream sampling points. Water soluble organic material in the river is complex and is likely generated over a long time period by chemical and biological processes occurring in soils, muskeg, and decaying terrestrial vegetation and is evidenced by the presence of tannins and lignins. It is unlikely that material of this complexity is generated in the flowing river system where residence times are short. Sediment deposits in this

segment of the river were found to be sparse and therefore probably do not play a major role as a sink or as a source of organics in the flowing water. As the concentration of water soluble organics in river water does not change from the upstream to the downstream sampling locations, no major dilution of the organic materials occurs, implying that tributary streams and groundwaters either contribute little flow or that they contain similar amounts of organic material to that found in the Athabasca River waters. There is no evidence that the water soluble organics in the river are being degraded. This is in keeping with their origin as material which has previously been biodegraded over long time periods and which are now refractory.

In order to assess any degradative processes that might be occurring in this river segment, two groups of labile compounds were investigated, amino acids and chlorins. The amino acids showed an overall decline from 100 km upstream to the Fort McMurray locations, whereas the chlorin concentration was constant. This is in keeping with the unstable nature of amino acids, some of which are susceptible to chemical oxidation and to utilization by micro-organisms; conversely aquatic organisms also produce and release amino acids to the water. Chlorins may also be degraded chemically, particularly under acidic conditions in the presence of light. Conditions during the winter season apparently do not favor this degradation in the short period (about 1 day) of residence in this segment of this river system. Any degradation which may occur is balanced by photosynthetic production of chlorophyll.

Levels of oxygen required to support degradative processes are more than sufficient in this section of the river especially to support degradation of organic matter by micro-organisms. Even under winter conditions, waters in this river segment are saturated in dissolved oxygen at 12.5 mg/ℓ Environment Canada, Inland Waters Directorate, Calgary (Personal Communication, 15 March 1978). These oxygen levels are a function of the steep gradient of the river that result in many open turbulent sections. This high oxygen content is in agreement with the occurrence of mainly refactory

compounds in this river segment which undergo minimal microbial degradation. Since the natural demand for oxygen is low because of the minimal degradation which takes place and the river therefore saturated with oxygen, this section of the river is likely capable of accepting and assimilating considerable amounts of non-toxic labile organic materials. In terms of oxygen depletion it is calculated that the river at this point could handle the introduction of 20,000 kg/day of labile organic material and still remain at acceptable levels of about 8 mg/ℓ. These also are the conditions which exist in the Athabasca River through the strip mining area, as the gradient of the river is much less than upstream resulting in less turbulence, no open water, and therefore no additional supply of oxygen.

Organic material constituting the natural organic load of the river during winter (120,000 kg/day) is not labile and has little effect upon dissolved oxygen levels. Similarly the organic material contributed to the river by the GCOS extraction plant is mainly material which is not readily degradable (Strosher and Peake 1976) and therefore does not affect the amount of dissolved oxygen in the river.

The amount of naturally occurring organic material which is extractable in these river waters is low (1 mg/ℓ) in contrast to the wastewaters from the GCOS plant, which contained 13 to 89 mg/ℓ. This illustrates the fundamental difference in the composition of the natural organic materials occurring in the river system and those which are introduced by oil sands mining and extraction processes. Occurrences of organic acids, phenolic compounds and sulphur compounds, which are major compound classes of the wastewater effluents (Strosher and Peake 1976; in prep.), total less than 0.01 mg/ℓ in the undisturbed river waters. The introduction of these materials, which are not labile, into the river is not likely to reduce dissolved oxygen levels directly; however, they may have undesirable toxic effects upon aquatic biota and may indirectly

reduce dissolved oxygen levels.

Hydrocarbons presumably derived from the oil sands deposit by natural leaching occur in small quantities in the river waters, 0.005 to 0.016 mg/ℓ. These hydrocarbons are generally higher molecular weight than the hydrocarbons found in the GCOS upgrading plant wastewaters or some components found in the river downstream of the GCOS plant. The toxicity of these higher molecular weight compounds is low or undetermined as compared with the known toxicity of low molecular weight hydrocarbons.

It is apparent from this and previous studies on water quality in the Athabasca River that the naturally occurring organics carried by the river provide a background level which can only be increased by the addition of wastewater effluents unless dilution rates or degradative processes are more prevalent in the downstream sections of the river system. Only studies of these processes in the section of the river leading into Lake Athabasca will determine whether degradation or concentration of these materials will occur.

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6. APPENDICES

6.1 LIST OF ABBREVIATIONS AND SYMBOLS

amu	atomic mass units
ASTM	American Society for Testing and Materials
BF_3	boron trifluoride
^oC	degrees Celsius (centigrade)
cm^3	cubic centimetres
C_6H_6	benzene
g	gram
GC	gas chromatograph
HCl	hydrochloric acid
i.e.	example
kg	kilogram (10^3 gram)
km	kilometre (10^3 metre)
ℓ	litre
m	metre
MeI	methyl iodide
MeOH	methanol (methylalcohol
mg	milligram (10^{-3} gram)
min	minutes
mℓ	millilitre (10^{-3} litre)
mm	millimetre (10^{-3} metre)
N	nitrogen
NaOH	sodium hydroxide
ng	(nanogram (10^{-9} gram)
NH_4OH	ammonium hydroxide
nm	nanometre (10^{-9} metre)
n-TFA	n-Butyltrifluoroacetyl
O	oxygen
pH	hydrogen-ion exponent
ppte	precipitate
S	sulphur
TFAA	trifluoroacetic anhydride

TOC	total organic carbon
µg	microgram (10^{-6} gram)
V/V	volume/volume
%	percent
<	less than

6.2 ANALYTICAL METHODS

6.2.1 Accuracy and Precision of Analytical Investigations

A variety of methods have been used throughout this investigation including standard colorimetric tests, analyses by a commercial carbon analyzer, and gas chromatographic analyses on groups of compounds previously separated by techniques developed or modified for this study. The accuracy and precision of standard tests has been established while analyses by carbon analyzers are governed by the precision of the instrument. All analytical investigations were carried out in triplicate with procedural and analytical blanks used throughout the investigations. These steps along with the care taken in sampling operations ensure the accuracy of the various methods. Instrumental accuracy, however, is limited by the ability of the equipment to analyze the entire range of compounds contained in each investigation and the standards upon which instruments are calibrated. Precision is calculated on the basis of replicate analyses and is expressed as the coefficient of variation. These values along with the standard deviation and mean values for the three water samples and two sediment samples in terms of each analyses are given in Table 10. The overall results of these precision measurements are incorporated in the following detailed analytical sections. In general, the precision of analyses for compounds occurring in amounts above 0.1 mg/ℓ were less than ±10% while values for trace quantities of organic materials reached a high value of ±60%, however, in terms of their respective standard deviations, the reliability of data obtained was considered acceptable.

6.2.2 Total Organic Carbon

Total organic carbon analyses were carried out on all water samples with the use of a commercial carbon analyzer. A Dorhman Model DC52 organic carbon analyzer was used to directly measure the organic carbon content of the water samples. The principle of

Table 10a. Mean values, standard deviation and coefficient of variance of analytical results.

Sample	Total Organic Carbon	Dissolved Organic Carbon	Extractable Organic Carbon	Asphal-tenes	Aliphatic Hydro-carbons	Aromatic Hydro-carbons	Polar Compounds
Upstream Water-100							
Mean	9.1	8.9		0.25	0.004	0.002	0.004
Standard Deviation	0.12	0.21		0.032	0.001	0	0.0006
Coefficient of Variance ±%	1	2		13	25	0	15
Upstream Water-35							
Mean	9.3	9.1		0.22	0.014	0.002	0.004
Standard Deviation	0.15	0.25		0.027	0.003	0.0006	0
Coefficient of Variance ±%	2	3		12	21	30	0
Upstream Water-2							
Mean	9.1	8.9		0.25	0.012	0.002	0.003
Standard Deviation	0.21	0.15		0.025	0.001	0.0006	0.0006
Coefficient of Variance ±%	2	2		10	8	30	20
Upstream Sediment-55-A							
Mean			912	368	40.3	42.6	4.8
Standard Deviation			45.6	12.2	2.95	3.82	1.09
Coefficient of Variance ±%			5	3	7	9	23
Upstream Sediment-55-B							
Mean			877	476	6.4	2.6	1.8
Standard Deviation			69.9	27.4	0.27	0.29	0.46
Coefficient of Variance ±%			8	6	4	11	25

Table 10b. Mean values, standard deviation, and coefficient of variance of analytical results.

Sample	Amphoteric Compounds	Phenols	Organic Acids	Amino Acids	Organic Sulphur Compounds	Elemental Sulphur	Organic Phosphorous Compounds
Upstream Water-100							
Mean	0.001	0.003	0.002	0.00007	0.003	0.0005	0.00005
Standard Deviation	0.0006	0.001	0.0006	0.00001	0.0006	0.00006	0
Coefficient of Variance ±%	60	33	30	14	20	12	0
Upstream Water-35							
Mean	0.001	0.002	0.002	0.00005	0.002	0.0001	0.00003
Standard Deviation	0.0006	0.0006	0.001	0.000004	0.0006	0.00006	0.000006
Coefficient of Variance ±%	60	30	50	8	30	60	20
Upstream Water-2							
Mean	0.002	0.002	0.002	0.00004	0.002	0.0003	0.00005
Standard Deviation	0.0006	0.0006	0.001	0.000001	0.0006	0.0001	0.000006
Coefficient of Variance ±%	30	30	50	3	30	33	12
Upstream Sediment-55-A							
Mean	0.006	0.6	10.5		6.0	0.5	0.02
Standard Deviation	0.001	0.02	0.61		0.37	0.05	0.004
Coefficient of Variance ±%	17	3	6		6	10	19
Upstream Sediment-55-B							
Mean	0.002	0.5	2.8		2.2	3.9	0.01
Standard Deviation	0.0006	0.05	0.07		0.28	0.41	0.001
Coefficient of Variance ±%	30	10	3		13	11	10

Table 10c. Mean values, standard deviation, and coefficient of variance of analytical results.

Sample	Organic Nitrogen Compounds	Chlorinated Hydrocarbons	Chlorins	Amides	Tannins and Lignins	Water Soluble Compounds	Sodium Hydroxide Soluble
Upstream Water-100							
Mean	0.0006	0.0012	0.0011	0.56	0.47	2.0	4.9
Standard Deviation	0.00006	0.00015	0.00006	0.029	0.026	0.15	0.27
Coefficient of Variance ±%	10	13	5	5	6	8	6
Upstream Water-35							
Mean	0.0010	0.0009	0.0009	0.39	0.40	1.8	5.1
Standard Deviation	0.00005	0.0002	0.0001	0.036	0.029	0.20	0.38
Coefficient of Variance ±%	5	22	11	9	7	11	7
Upstream Water-2							
Mean	0.0008	0.0012	0.0010	0.45	0.44	1.9	4.9
Standard Deviation	0.00006	0.0002	0.0001	0.046	0.021	0.15	0.27
Coefficient of Variance ±%	7	17	10	10	5	8	5
Upstream Sediment-55-A							
Mean	0.0009	0.16	0.05				
Standard Deviation	0.0001	0.020	0.008				
Coefficient of Variance ±%	11	13	16				
Upstream Sediment-55-B							
Mean	0.0010	0.14	0.05				
Standard Deviation	0.0001	0.016	0.008				
Coefficient of Variance ±%	10	11	16				

detection is the conversion of organic carbon in the presence of hydrogen and a nickel catalyst to methane which is quantified by flame ionization detection. Pre-acidification of the water samples converts inorganic carbon to carbon dioxide which in turn is completely vented off in the analytical cycle. Instrumental precision in the detectable range is ±2% or 1 mg/ℓ.

These analytical investigations were carried out on water samples as received and on waters filtered through Whatman GF/C glass microfibre filters previously heated at 500°C for 24 h in order to measure amounts of dissolved organics. Samples were then extracted with benzene at pH 2, pH 11, and pH 7, evaporated with a rotary vacuum apparatus to remove traces of benzene, the volume measured and the sample analyzed for amounts of non-extractable organic carbon. Thus the amount of organic carbon extracted with benzene could be determined by difference and used as a basis for the analytical investigations carried out on the extractable portion of water samples. The mean values for whole and filtered water samples ranged from 8.9 to 9.3 mg/ℓ with a precision of ±1 to 3% or ±0.3 mg/ℓ. This precision is somewhat better than the minimum precision of the instrument at 1 mg/ℓ; however, since the instrumental error is calculated at these levels, analytical results were expressed to the nearest whole number value.

Total organic carbon analysis were also carried out on sediment samples. A Leco Model WR-12 induction furnace carbon analyzer was used to determine the organic carbon content. This is accomplished by oxidizing the organic carbon in sediments pretreated with HCl to remove inorganic carbon, to carbon dioxide which is collected on molecular seive then removed and measured by a thermal conductivity detector. Precision of the instrument is determined at 1% of the carbon value; however sediment sample consistency reduced this precision to ±10%.

The amount of extractable organic compounds in sediment was obtained by weighing a portion of the combined acetone and benzene/methanol extracts and relating this to the dry weights of

sediments. Organic carbon analysis of this extractable fraction revealed that 80% of the organic material occurred as organic carbon; thus the total organic carbon content of sediments were calculated on this basis. Replicate analysis were carried out on both upstream-55 sediment samples and produced calculated mean values of 912 and 877 mg/kg. Precision of these analyses calculated as the coefficient of variance ranged from ±5 to 8%.

6.2.3 Asphaltenes

The organic matter extracted with solvents from each of the river waters and bottom sediments from acidic aqueous solutions and subsequent removal of acidic organic components was then separated into two fractions on the basis of solubility in normal pentane. By definition, the insoluble organic matter of petroleum extracts is known as asphaltenes. The precipitated asphaltenes were removed by filtration through a fine sintered glass disc, after which they were washed with pentane, air dried, and weighed. Mean values obtained for water samples ranged from 0.22 to 0.25 mg/ℓ with a precision of ±10 to 13%. Sediment samples revealed higher levels with mean values of the two upstream sediments at 368 and 476 mg/kg. Precision of these higher values were ±3 and 6%.

6.2.4 Aliphatic Hydrocarbons

Oily fractions of each benzene extract were chromatographed on neutral Brockman activity I alumina to separate groups of compounds for further analysis (Peake et al. 1972a; 1972b). The first group of compounds eluted from the alumina with n-hexane was the aliphatic hydrocarbons which were subsequently analyzed by gas chromatography (GC). A Varian Aerograph Model 2100 gas chromatograph equipped with dual flame ionization detectors was operated under the following conditions: glass columns were 3.6 m long and 2 mm inside diameter, packed with 3% SE 30 Ultraphase coated on 60-80 mesh high performance Chromosorb W, and oven temperature programmed from 60° to 265°C at a rate of 10°C per minute. Injection

port and detector temperatures were 260°C; helium carrier gas flow rates were 50 cm^3/min; hydrogen rates were 30 cm^3/min and air flow was adjusted to give maximum detector sensitivity. Quantitation was based on the gas chromatographic responses to normal straight chain aliphatic hydrocarbons in the range of nC^8-nC^{30}.

Analytical results by GC for water samples were low with average responses varying from 0.004 to 0.014 mg/ℓ in the three different samples. The coefficient of variance for these mean values ranged from ±8 to 25%; however, in terms of calculated standard deviations this range represents only 0.001 to 0.003 mg/ℓ, thus confirming the reliability of results obtained. Sediment samples contained levels of aliphatic hydrocarbons varying from 6.4 to 40.3 mg/kg in the two upstream sediments with a precision of ±4 to 7%.

Due to the high molecular weight compounds found in fraction containing aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds, it was found that gas chromatographic responses were not measuring the entire amounts of these compounds especially those obtained from sediments. A further analysis of these fractions was carried out to more accurately determine the total amounts of these compounds that constitute the oily fractions of the sediments. These various fractions which eluted from the silica gel and alumina chromatography were evaporated under nitrogen to eliminate traces of solvent and weighed to determine the total amounts of both aliphatic and aromatic hydrocarbons, and polar compounds. As in the gravimetric analysis for asphaltenes, precision was determined to be within ±10%.

6.2.5 Aromatic Hydrocarbons

The second group of organic compounds to be separated on the alumina column was the aromatic hydrocarbons which were eluted from the column with benzene. Analysis were conducted by gas chromatography as described in 6.2.4 above. Gas chromatographic responses were calibrated to the detection of anthracene (Strosher and Hodgson 1975).

These aromatic responses averaged 0.002 mg/ℓ for all replicate water samples from the three sampling locations. As in the aliphatic hydrocarbon analyses the coefficient of variance for these small amounts was relatively high ranging from 0 to ±30%; however, in terms of standard deviation they amount to only 0.0006 mg/ℓ, however; fractions containing aromatic hydrocarbons revealed mean values of 2.6 and 42.5 mg/kg in the two upstream samples with precision values of ±9 to 11%.

6.2.6 Polar Compounds

Oily fractions of river waters and sediments, upon separation from asphaltenes, were introduced to a chromatography column containing Baker reagent silica gel (40-140 mesh) to separate hydrocarbons from polar compounds. The hydrocarbons were eluted first in benzene and were then chromatographed on alumina as previously described in sections 6.2.4 and 6.2.5. The second eluant from the silica gel column was methanol which contained the designated O, N, and S polar compounds. These polar compounds, however, do not comprise the total amount of O, N, and S containing compounds in water samples and also may not be entirely detectable by the gas chromatography method (6.2.4) used to quantify them. The values thus obtained in this investigation have not been used in the overall measurement of organic constituents in the water and sediment extracts. The polar compound results merely constitute a measurement of these detectable compounds by classical organic separation techniques and have been used to provide a comparison of the various constituents of oily fractions in water samples in order to assess possible degradative processes that might be taking place (section 3.4). Quantitation was based on the GC response to anthracene.

Analytical investigations of the polar compounds were also carried out in triplicate on all water samples and the two upstream sediment samples. Mean values for water samples were 0.003 to 0.004 mg/ℓ with a precision of 0 to ±20%. The averaged values

for sediment samples were 1.8 and 4.8 mg/kg which were obtained from a range of ±23 to 25% thus confirming the variability of results obtained by this method.

6.2.7 Amphoteric Compounds

Amphoteric compounds which have characteristics of both acid and base functions are soluble in both acidic and basic solutions are therefore non-extractable at pH 2 and pH 11 levels which are used to extract the acidic, neutral, and basic compounds. Thus an additional extract at pH 7 was carried out to investigate the possible occurrence of the amphoteric compounds. Analysis of these benzene extracts was achieved by the gas chromatographic method described in section 6.2.4 with the GC calibrated to the anthracene response.

Water samples contained an average 0.001 to 0.002 mg/ℓ of the amphoteric compounds while sediment samples contained slightly higher levels of 0.002 and 0.006 mg/kg. Coefficients of variance for these trace quantities were considerably high ranging from ±17 to 60% revealing considerable variation in results; however, reliability of data obtained is still considered acceptable in light of the standard deviation values calculated (0.0006 to 0.001).

6.2.8 Phenols

Initially the standard water quality test for phenols--the 4-aminoantipyrene colorimetric test--was utilized. This test, as it is sensitive only to simple phenols and some substituted phenolics, produced a very inaccurate measurement of the large number of compounds which are classed as phenols. Accordingly, the following method for the separation and analysis of phenols was developed.

Phenolic compounds and organic acids were extracted from the bulk of the organic material with sodium hydroxide and transferred to a suitable solvent. The organic acids were then separated

from phenols on the basis of their chemical reactivity. Organic acids are alkylated at 60°C by reaction with boron trifluoride in methanol but phenols are not; thus, the unreacted acidic phenols could be separated from the neutral organic acid esters by sodium hydroxide extraction. A methyl iodide alkylation was then employed to convert phenols to aromatic ethers for analysis by gas chromatography as described in section 6.2.7 with detector response calibrated to anthracene.

Values obtained for water samples averaged 0.002 to 0.003 mg/ℓ with a precision of about ±30% to 0.0006 deviation from the mean values. Sediment samples contained mean values of 0.5 and 0.6 mg/kg with a variance of ±3 to 10%.

6.2.9 Organic Acids

Organic acids were separated, derivatized and measured by gas chromatography as was described in the previous phenol analysis section. Reliability of results on trace quantities as measured in water samples was considered marginal with coefficients of variance ranging from ±30 to ±50% of mean values of 0.002 mg/ℓ. Reliability of results on sediment samples, however, shows a considerable improvement with ±3 to 6% variation from mean values to 2.8 and 10.5 mg/kg respectively. These results indicate that the lower amounts of organic acids found in the water samples are approaching detectable limits of the method.

6.2.10 Amino Acids

Amino acids were determined on the water samples as received. The method of river water concentration, hydrolysis and deionization were similar to those of Degens and Reuter (1964) and the amino acid analysis was by gas chromatography using the techniques of Roach and Gehrke (1969a).

One liter water samples were concentrated to a few milliliters with a rotary evaporator and the amino acids hydrolysed by heating for 16 h at 100°C with 6N HCl. Any precipitate in the

hydrolysate was removed by centrifugation. The hydrolysate was reduced to dryness in a rotary evaporator, a few millilitres of water were added and the sample was repeatedly taken to dryness until a pH of ≈4 was obtained. The solution was deionized by passing through a column of GCG 240 ion exchange resin from which the amino acids were eluted with 2N NH_4OH. The solution was reduced to dryness in a rotary evaporator and the resulting solids dissolved in about 1 ml of 0.1N HCl. n-Butyltrifluoroacetyl derivatives were then prepared by the direct esterification method of Roach and Gehrke (1969b), with reactions conducted in a 1 ml REACTIVIAL sealed with a Teflon-lined cap. To reduce damage to syringes and to facilitate gas chromatography, the corrosive trifluoroacetic anhydride was removed by evaporation with a stream of nitrogen and the N-TFA amino acids dissolved in methylene chloride.

Gas chromatography columns 6 ft. (1.8 m) by 2 mm i.d. were packed with Regis Company TABSORB and were temperature programmed from 60°C to 210°C at 4°C per minute.

The entire analytical procedure, including hydrolysis and ion exchange chromatography was tested a number of times using standard mixtures containing from 1.4 to 7 μg of each of 17 amino acids. Reproducible results were obtained for all the 17 amino acids with the exception of cysteine, which is sensitive to oxidation, but great care was needed in all phases of derivatization, particularly the final evaporation of the TFAA-methylene chloride solution. Values for the molar response relative to glutamic acid were calculated and found to be consistent with those found by Gehrke et al. (1968). The response of the gas chromatograph was sufficient to detect as little as 0.2 ng of each derivatized amino acid, but it is doubtful if quantities less than 1 ng could be quantitatively separated from samples and derivatized.

Contamination is a continual problem in microanalysis, and previous investigators have found it impossible to eliminate completely, the contamination by amino acids from chemicals and distilled water. In order to reduce contamination to a minimum,

all glassware was washed with detergent and water, rinsed with tap water and distilled water, soaked overnight in chromic acid and washed with tap water, distilled water, and finally double distilled water. Care was taken to avoid fingerprint contamination (Hamilton 1965; Oro and Skewes 1964). A typical blank run, including hydrolysis, showed 0.0024 µg of contamination per sample.

Analytical precision was found to vary from ±3 to 14% on mean values of 0.0004 to 0.00007 mg/ℓ as with a standard deviation of 0.000001 to 0.0001.

6.2.11 Sulphur Compounds

Samples were analyzed for organic sulphur compounds and elemental sulphur by a gas chromatograph equipped with a flame photometric detector (Martin and Hodsgon 1973). A Tracor Model 560 gas chromatograph equipped with a flame photometric detector and linearizer was used to analyze the organic sulphur compounds plus elemental sulphur. The chromatographic column used was a 1.8 m by 2 mm inside diameter glass column packed with 3% SE 30 Ultraphase coated on 60-80 mesh Chromosorb W. The oven temperature was programed from 50° to 250°C at 10°C/min, the injection port temperature was 210°C, and the detector temperature was 210°C. The flow rate of helium carrier gas was 80 cm^3/min, hydrogen flow rate was 65 cm^3/ min, and air at 165 cm^3/min.

The analyses were carried out on the initial benzene extracts at pH 2. In this manner it was possible to measure and quantify the total range of sulphur compounds and extractable elemental sulphur in all sample with responses based on the gas chromatographic detection of parathion and elemental sulphur.

Analytical precision was found to vary from ±20 to 30% on mean values of 0.002 to 0.003 mg/ℓ of organic sulphur compounds in water samples. In comparison the precision of elemental sulphur in the water samples ranged from ±12 to 60% of the 0.001 to 0.0005 mg/ℓ levels recorded indicating once again that detectable limits are being approached. Precision levels of organic sulphur compounds

and elemental sulphur in sediment samples were considerably higher and measured ±6 to 13% on values of 2.2 and 6.0 mg/kg of organic sulphur compounds and ±10 to 11% on 0.5 to 3.9 mg/kg of elemental sulphur.

6.2.12 Organic Phosphorous Compounds

Examination of extracts for the possible occurrences of organic phosphorous compounds were carried out in much the same manner as were investigations of the organic sulphur compounds. Gross extracts were analyzed by the gas chromatographic technique, utilizing the flame photometric detector with a phosphorous filter. Once again, parathion was used to calibrate the gas chromatograph.

Calculated mean values of organic phosphorous in water samples ranged from 0.0003 to 0.0005 mg/ℓ with a precision of 0 to ±20%. Sediment values were slightly higher at 0.01 to 0.02 mg/kg with a precision range of 10 to 19%.

6.2.13 Organic Nitrogen Compounds

Organic nitrogen compounds were detected by the Hall electrolytic conductivity detector in the nitrogen mode. The method of detection for these compounds works on the principle of converting the nitrogen of organic compounds to ammonia by reacting with hydrogen in the presence of a nickel catalyst under high temperatures. The resulting ammonia, thus alters the conductivity of an electrolytic solution and is detected by an electrolytic conductivity cell. Interferences by other compounds are excluded from the analysis by use of specific scrubbers. Operating conditions for these analyses are as follows. A Tracor Model 700 Hall electrolytic conductivity detector fitted to a Varian 2100 gas chromatograph was used to specifically detect the nitorgen compounds. The chromatographic column used as a 1.8 m by 2 mm inside diameter glass column packed with 3% SE 30 Ultraphase coated on 60-80 mesh Chromasorb W. Oven temperature was programmed from 60^{o} to 265^{o}C at 10^{o}C/min, injection port temperature was 200^{o}C and delivery tube temperature was 225^{o}C.

The pyrolsis furnace was 850°C. Helium carrier flow was set at 60 cm^3/min and hydrogen reaction gas at 50 cm^3/min. A 1:1 (V/V) of n-propanol and water was used as the electrolytic solution, flowing at 1 cm^3/min. Quantiation was based on the response of this analytical method to atrazine.

Detected levels of the nitrogen containing compounds varied slightly throughout the water and sediment samples with mean values of 0.0006 to 0.0010 mg/ℓ or mg/kg. The coefficient of variance values were also uniform ranging from ±5 to 11%. Based on the trace quantities found in these samples, the precision is considered excellent.

6.2.14 Chlorinated Hydrocarbons

Chlorinated hydrocarbons were investigated by two different methods. Initially, gross extracts were examined by an electrolytic conductivity detector fitted to a gas chromatograph. The principle of detection was to convert chlorine from the chlorinated compounds to hydrochloric acid which also altered the conductivity of the electroyltic solution as in 6.2.13 above. Detector responses were calibrated to the standard compound aldrin.

In addition to the Hall detector, the refined fractions of extracts were examined on a Tracor Model 560 gas chromatograph fitted with a Ni 63 source in an electron capture detector. A 1.8 m by 6 mm inside diameter glass column was used, packed with 3% OV 17 on Chromosorb W. An isothermal column temperature of 200°C was used with an injector temperature of 230°C, and a detector temperature of 355°C. To reduce the numerous interferences that are encountered by the highly sensitive electron capture detector, samples were fractionated by liquid column chromatography on alumnia. Chlorinated hydrocarbons were eluted with hexane to try to eliminate the interferring polar compounds containing sulphur, phosphorous, and oxygen.

Levels detected in water samples averaged 0.009 to 0.012 mg/ℓ with a precision of ±13 to 22%. Sediments contained values of 0.14 and 0.16 mg/kg of these chlorinated hydrocarbons with variations of ±11 and 13% respectively.

6.2.15 Chlorins

Chlorophyll and its degradation product, pheophytin, were measured by spectrofluorescence directly on the benzene extracts of water and sediments. No special provision was made for the preservation of samples specifically for chlorophyll analysis. Excitation at a wavelength of 415 nm produced an emission response at 667 nm. This spectrofluorometric method has a detection limit of 10^{-11}g of chlorophyll per litre of water, far lower than can be obtained by more conventional spectrophotometric analytical methods. In order to calibrate the fluorescence analytical method, the chlorophyll content of acetone extracts of the algae *Scenedesmus obliques* was determined according to the absorption coefficients of Machinney (1941). These solutions were then diluted 100 to 1,000 times to bring them into the range of the fluorescence method.

The mean values for the triplicate analyses on each of the upstream, midstream and downstream water samples ranged from 0.0009 to 0.0011 mg/ℓ with a coefficient of variance of ±5 to 11%.

6.2.16 Amides

Amides were analyzed by a spectrophotometric method. The principle of detection relied on the conversion of the amides to the corresponding hydroxamate. The hydroxamate was then developed for colorimetric analysis with ferric chloride (Pesez and Bartos 1974). Results were based on a standard response curve obtained with a standard acetanilide.

Triplicate analysis were carried out on water samples where average values ranged from 0.39 to 0.56 mg/ℓ with a variation range of ±5 to 10%.

6.2.17 Tannins and Lignins

Tannins and lignins were also investigated by a colorimetric method, the principle of which relies upon the ability of these compounds to reduce tungstophosphoric and molybdophosphoric acids to produce a blue color which absorbs light in region of 700 nm (APHA-513). Quantitation is based on a standard tannic acid solution.

Mean values obtained in triplicate analysis of water samples ranged from 0.40 to 0.47 mg/ℓ with a precision of ±5 to 7%.

6.2.18 Water Soluble Organic Compounds

Many organic compounds found in industrial wastewaters are extractable using the previously described ASTM procedure, for example hydrocarbons, phenols and organic acids. Organic materials naturally occurring in river waters are not often extractable by these methods but may be concentrated using hydrophobic ion exchange resins such as Amberlite XAD-2, XAD-4 or XAD-7.

Two litres of river water, previously extracted with benzene at pH<2, pH>11 and pH 7, were boiled to remove dissolved benzene, the pH was adjusted to less than 2 with hydrochloric acid and the solution was passed slowly through a column of XAD-2 resin. The column had previously been freed of traces of water soluble organic material and prepared by the method of Junk et al. (1974). A total organic carbon analysis was conducted on the column eluate as a measure of the material not retained by the column. Organic material retained by the ion exchange resin, including humic and fulvic acids, was eluted with 2N sodium hydroxide. The visible absorbance spectrum of this basic eluate was measured and the total organic carbon content was determined.

Each analysis was conducted in triplicate with mean values ranging from 4.9 to 5.0 mg/ℓ with a precision of ±5 to 7%.

6.3 TERMS OF REFERENCE

6.3.1 General Objective

To obtain background data on the natural organic loading of the Athabasca River above the mining area and to assess the fate of organic matter, from natural or influenced sources, under winter conditions.

6.3.2 Specific Objectives

1. To determine, in terms of organic compounds, the influence of the oil sands deposit upon water quality of the Athabasca River, during winter, upstream of the existing oil sands plant.

2. To investigate the sediments of the Athabasca River, in the undisturbed area upstream of the existing oil sands plant and Fort McMurray, as a sink for organic compounds.

3. To examine the natural chemical and biological processes whereby the river may assimilate additional organic matter contributed to the river by oil sands development.

4. To improve the existing analytical techniques as they apply to the analysis of organic compounds in surface waters, ground waters and plant effluents in the Athabasca oil sands, with emphasis to be placed on analyses which may be conducted routinely and which may be diagnostic in predicting the effects of oil sands mining upon the Athabasca River system.

6.3.3 Outline of Work

1. Water samples will be collected at three locations on the Athabasca River (1) upstream of the oil sands deposit about 100 km from Fort McMurray, (2) within the oil sands deposit about 40 km upstream of Fort McMurray, (3) about 2 km upstream of Fort McMurray.

2. Sediment samples will be taken at each of the above locations.

3. Sediments will be taken at 5 sites across the river at each location. The 5 sediment samples from a given location will be combined to give a representative composite sample.

4. Extractions and analytical techniques will include those employed in previous complex organic chemistry studies for AOSERP and will be expanded to more clearly define organic water quality upstream of the oil sands deposit. Analysis will include:

a. aliphatic hydrocarbons
b. aromatic hydrocarbons
c. polar compounds
d. sulfur compounds
e. nitrogen compounds
f. chlorinated hydrocarbons
g. organic acids
h. phenolics
i. amides
j. phosphorous compounds
k. esters
l. asphaltenes (sediment samples)

5. All analyses will be conducted in replicate.

6. Coordinates of sampling sites will be indicated on suitable topographic maps.

7. AOSERP RESEARCH REPORTS

1.		AOSERP First Annual Report, 1975
2.	AF 4.1.1	Walleye and Goldeye Fisheries Investigations in the Peace-Athabasca Delta--1975
3.	HE 1.1.1	Structure of a Traditional Baseline Data System
4.	VE 2.2	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.		Housing for the North--The Stackwall System
7.	AF 3.1.1	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
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.		AOSERP Second Annual Report, 1976-77
22.	HE 2.3	Maximization of Technical Training and Involvement of Area Manpower
23.	AF 1.1.2	Acute Lethality of Mine Depressurization Water on Trout Perch and Rainbow Trout
24.	ME 4.2.1	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 the AOSERP Study Area, March 1976
28.	VE 2.1	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 I
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
40.	VE 7.1	Interim Report on Reclamation for Afforestation by Suitable Native and Introduced Tree and Shrub Species
41.	AF 3.5.1	Acute and Chronic Toxicity of Vanadium to Fish
42.	TF 1.1.4	Analysis of Fish Production Records for Registered Traplines in the AOSERP Study Area, 1970-75
43.	TF 6.1	A Socioeconomic Evaluation of the Recreational Fish and Wildlife Resources in Alberta, with Particular Reference to the AOSERP Study Area. Volume I: Summary and Conclusions
44.	VE 3.1	Interim Report on Symptomology and Threshold Levels of Air Pollutant Injury to Vegetation, 1975 to 1978
45.	VE 3.3	Interim Report on Physiology and Mechanisms of Air-Borne Pollutant Injury to Vegetation, 1975 to 1978

46.	VE 3.4	Interim Report on Ecological Benchmarking and Biomonitoring for Detection of Air-Borne Pollutant
47.	TF 1.1.1	A Visibility Bias Model for Aerial Surveys of Moose on the AOSERP Study Area
48.	HG 1.1	Interim Report on a Hydrogeological Investigation of 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 Data in the AOSERP Study Area
52.	ME 2.3.2	Plume Dispersion Measurements from an Oil Sands Extraction Plant, June 1977
53.	HY 3.1.2	Baseline States of Organic Constituents in the Athabasca River System Upstream of Fort McMurray
54.	WS 2.3	A Preliminary Study of Chemical and Microbial Characteristics of the Athabasca River in the Athabasca Oil Sands Area of Northeastern Alberta.
55.	HY 2.6	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

These reports are not available upon request. For further information about availability and location of depositories, please contact:

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