CHARACTERIZATION OF ORGANIC CONSTITUENTS IN WATERS AND WASTEWATERS OF THE ATHABASCA OIL SANDS MINING AREA

by

M.T. STROSHER and E. PEAKE

Environmental Sciences Centre (Kananaskis)
The University of Calgary
Calgary, Alberta

for

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TABLE OF CONTENTS

TABLE OF CONTENTS (CONCLUDED)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (CONCLUDED)

ABSTRACT

The organic constituents of wastewaters discharged from the Great Canadian Oil Sands Ltd. (GCOS) plant and the Syncrude Canada Ltd. lease No. 17 were characterized and compared to those occurring naturally in the Athabasca River. Of the 16 chemical groups investigated in samples of upgrading plant effluent, coke storage area runoff, and Syncrude Canada Ltd. mine depressurization waters, the hydrocarbons, organic sulphur compounds, organic nitrogen compounds, and oxygenated organic compounds were found to be the most abundant constituents.

Upgrading plant effluents contained an average of 36 mg/ℓ of organic carbon, of which 17 mg/ℓ was extractable with organic solvents. Organic sulphur compounds comprised 24% of the extractable organic carbon, oxygenated compounds 17%, hydrocarbon 16%, asphaltenes 10%, and nitrogen compounds 7%.

Coke storage runoff revealed a total organic carbon content of 25 mg/ℓ, 15 mg/ℓ of which was extractable carbon. The extractable portion contained 18% asphaltenes, 13% oxygenated compounds, 11% sulphur compounds, 2% nitrogen compounds, and 1% hydrocarbons.

Mine depressurization waters averaged 30 mg/ℓ total organic carbon, 62% of which was extractable. Oxygen-containing compounds were the major contributors to the extractable fraction at 24%, with lesser contributions from sulphur compounds at 15%, asphaltenes 14%, nitrogen compounds 2%, and hydrocarbons 1%.

Waters of the Athabasca River upstream from the GCOS plant contained only 13 mg/ℓ total organic carbon, of which 4 mg/ℓ was extractable. The major component of the extractable carbon, 29%, occurred as polar compounds. The hydrocarbon content was low, 0.8% of the extractable carbon, comparable to amounts found in the mine depressurization waters, but far less than the 16% found in upgrading plant effluents. Under ice conditions on the Athabasca River, the chemical composition of the hydrocarbons 10 km downstream was directly comparable to those found in the upgrading plant effluent, diluted 70-fold.

Initial investigations of bottom sediments from the river revealed differences in samples taken upstream and downstream from the oil sands plant. Upstream sediments contained an average of 480 mg/kg of organic carbon and increased 40%, in the downstream sediments to 668 mg/kg. Asphaltenes were the major contributors, increasing from 30 to 35% of the carbon content from upstream to downstream samples. Increases also occurred in hydrocarbon content from 7 to 10%; however, polar compounds were relatively uniform in the two locations and averaged 5% of the organic carbon.

It was concluded from this and a previous investigation that the main source of light hydrocarbons in the section of the Athabasca River adjacent to GCOS is the upgrading plant, whereas the oxygenated compounds may be derived from the tailings pond dike filter drainage or natural sources, of which mine depressurization waters may be representative. Preliminary evidence indicated that organic materials released by the plant are fractionated in the river system with the sediments acting as a sink, particularly for heavier hydrocarbon components.

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1. INTRODUCTION

Concern over the possible environmental effects of organic matter released by oil sands mining, extraction, and processing led to this and a preceding study of organic constituents in effluents from the Great Canadian Oil Sands Ltd. (GCOS) plant near Fort McMurray, Alberta (Strosher and Peake 1976) in the Alberta Oil Sands Environmental Research Program (AOSERP) study area (Figure 1). Whereas the previous study dealt with the presence of several classes of organic compounds in tailings pond dike filter drainage and upgrading plant effluents, the present study considers not only industrial effluents but also the natural organic constituents of the Athabasca River.

The first study showed the presence of organic acids, phenolic compounds, sulphur compounds, nitrogen compounds, hydrocarbons, and several other classes of organic compounds in amounts totalling as much as 84 ppm in a single industrial mining effluent. A number of these compounds are believed to be toxic to aquatic organisms, and GCOS has since taken steps to control flow of the tailings pond dike filter drainage to the Athabasca River.

The present study is a partial response to recommendations (Strosher and Peake 1976) that an integrated investigation be conducted into the identity, physical state and toxicity of organic materials contained in effluents flowing into the Athabasca River and, further, that the identity and quantity of natural organic compounds in the river be determined. These investigations would provide an assessment of the effects of industrial effluents upon water quality and place their possible impact upon the biota of the Athabasca River into perspective. Additionally, year-round sampling and analysis of effluents is required to determine fluctuations in the amount and composition of organic components and to provide a basis to evaluate the likelihood of long term environmental effects.

Terms of reference of the present study are contained in Appendix 6.2 and include the following:

1. An assessment of the organic load in the GCOS upgrading plant effluent (based upon quarterly sampling);

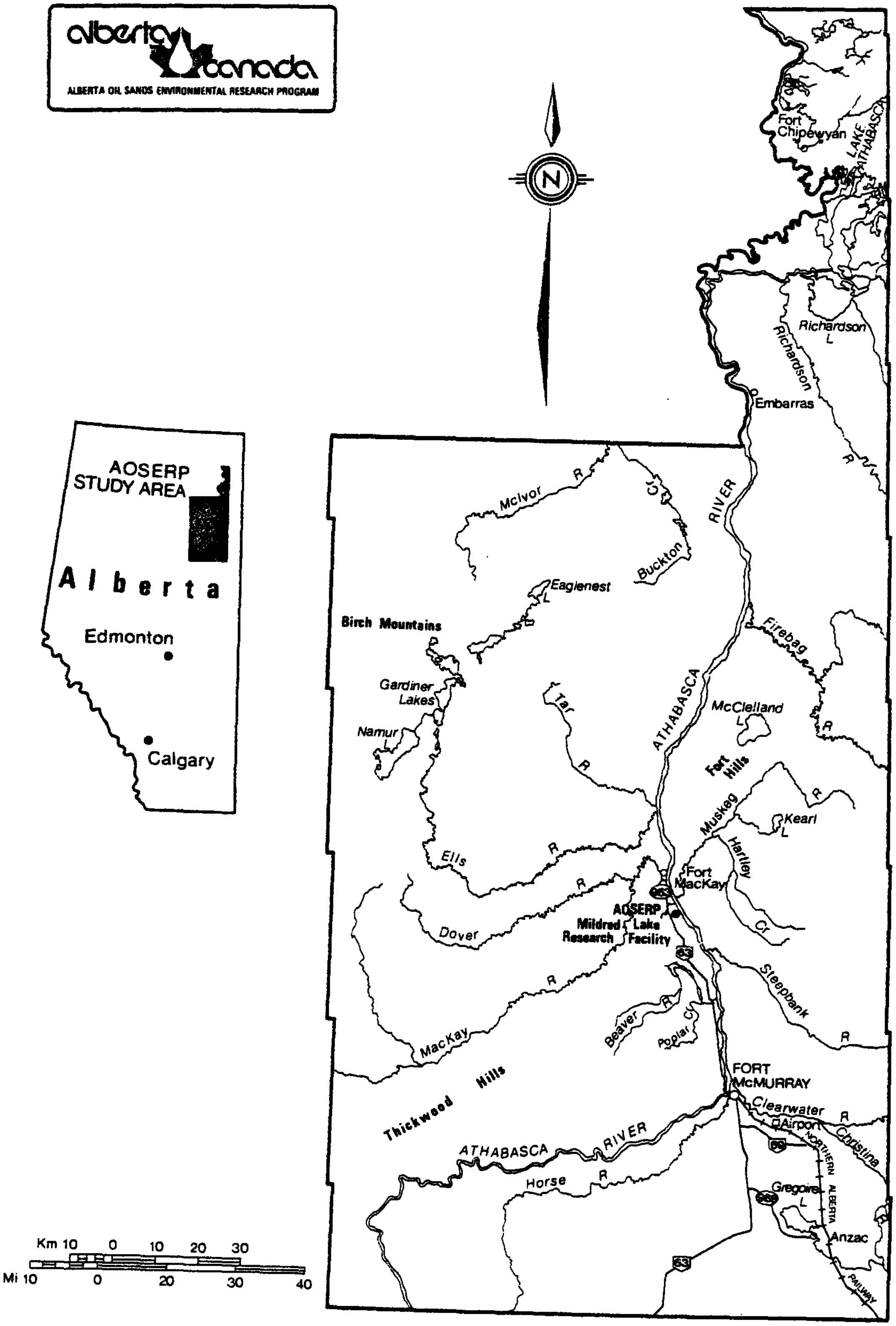


Figure 1. AOSERP study area.

2. Analyses of the amounts and types of organic constituents in runoff from coke storage areas;
3. An investigation of mine depressurization waters from the Syncrude mine development program; and
4. An assessment of the organic constituents of Athabasca River water and sediment, both upstream and downstream from the GCOS extraction plant (based upon quarterly sampling).

The short time frame of the present investigation, seven months, precluded those aspects which required year-round sampling and analysis. Time restraints limited the study to one sample of the GCOS coke storage pile runoff waters, two representative samples of Syncrude mine depressurization waters, three samples of GCOS upgrading plant effluent, and samples of Athabasca River water and sediments taken from each of three locations upstream from the GCOS extraction plant and three locations downstream from the plant.

The number of individual organic compounds which exist naturally or which may occur in wastewaters from oil sands processing is large. Rather than identify individual compounds, emphasis in this study was placed upon the identity and amount of classes or groups of compounds. Sixteen organic parameters were investigated in each of the samples and major groups of compounds were classified and quantified.

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

2. ANALYTICAL METHODS

No single, overall, analytical method or group of methods exists for the characterization and/or identification of the wide variety of compounds which occur in river waters and industrial effluents. Existing methods, including those used in this study (Appendix 6.3), determine groups of compounds on the basis of chemical properties, principally their acid-base characteristics and polarity, or are keyed to the detection of specific elements such as sulphur, nitrogen, phosphorous, chlorine, or carbon. In some cases a single compound may be measured by two methods of analysis, but more commonly, compounds such as the polar constituents may not be detected by any of the methods used and these results may be low. Despite these handicaps the available methods do indicate the amount of organic compounds occurring naturally in the Athabasca River and the influence of man's activities upon this system.

2.1 SAMPLE DESCRIPTION AND HANDLING

The current study began on 8 September 1976, and the first series of samples consisting of three wastewaters, two river waters and two river sediment samples, were taken on 14 and 15 September 1976. The first series of wastewater samples consisted of:

1. A sample of runoff waters from the coke storage area of the GCOS plant. This sample was a composite of water from two streams flowing east into the river from the base of a sand dike which separates the coke storage area from the river. These intermittent streams were near the northeast corner of the coke storage area which lies basically north-south along the river bank.
2. A sample of the final effluent of the GCOS upgrading plant taken immediately after filtration through straw and before its disposal to the river.

3. A sample taken at the Syncrude mine development field consisting of a composite of waters from five mine depressurization wells as selected by personnel of the former Aquatic Fauna sector of the Alberta Oil Sands Environmental Research Program (AOSERP) in co-operation with Syncrude. General sampling locations are shown in Figure 2 and sample descriptions, dates and detailed locations are given in Table 1.

The first series of river water and sediment samples was collected at two locations on 15 September 1976 (Figure 3, Table 1). Included were:

1. A river water sample collected within the top 10 cm of the water from the main channel of the river approximately 0.4 km upstream from the south end of the GCOS tailings pond;
2. A sediment grab sample also taken 0.4 km upstream from the GCOS tailings pond but in an area of deposition within 10 m of the east bank of the river;
3. A river water sample taken from the surface in the main channel of the river 10 km downstream from GCOS; and
4. A sediment grab sample also taken 10 km downstream of GCOS at the upstream tip of Morton Island within 10 m of west bank of the river.

All sites except the coke storage runoff were sampled on a number of occasions. The Syncrude mine waters were resampled on 30 November 1976. One of the five wells (No. 5) initially used in making up the composite water sample went dry. An adjacent well, No. 5a, was substituted. The locations of all six wells are given in Figure 3 and listed in Table 1. The GCOS upgrading plant effluent was sampled two more times: 15 December 1976 and 17 February 1977. Further sampling of the river system was carried out under ice. On 15 December the upstream and downstream water samples were obtained by drilling holes in the ice in the main channel. As the river was frozen solid at the original nearshore sediment

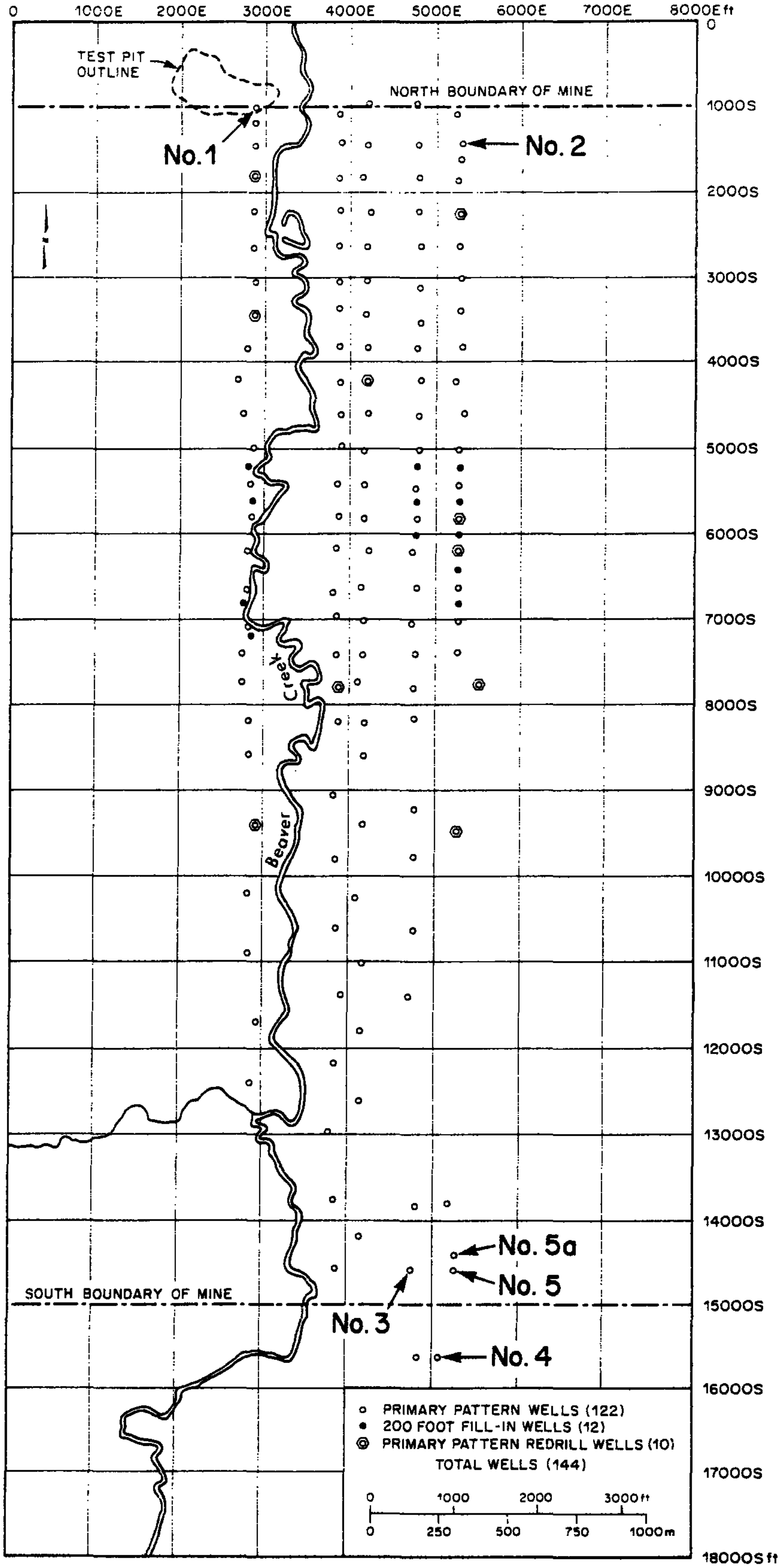


Figure 2. Syncrude Canada Ltd. mine development field with noted sampling points.

Table 1. Sample description.

Sample	Sample Number	General Location	Military Grid Reference	Sampling Date
Coke Storage Runoff	1	GCOS recovery plant, NE corner of coke storage area	12VVU708189	14 Sept 1976
Upgrading Plant Effluent	1	GCOS recovery plant, final effluent of the upgrading plant, after straw filtration	12VVU719176	14 Sept 1976
	2		719176	15 Dec 1976
	3		719176	17 Feb 1977
Mine Depressurization Waters	1	SYNCRUDE mine development field, 5 wells located by Syncrude coordinates of:	1)E2900, S1000; 2)E5300, S1400; 3)E4800, S14,600; 4)E5100, S15,700; 5)E5300, S14,600; 5a)E5300, S14,400	14 Sept 1976
	2			30 Nov 1976
Athabasca River Upstream	1	Approximately 0.4 km upstream of south end of GCOS tailings pond in main channel--100 m from west bank	12VVU724136	15 Sept 1976
	2		724136	15 Dec 1976
	3		724136	17 Feb 1977
Athabasca Sediment Upstream	1	10 m from east bank 0.4 km upstream of south end of GCOS tailings pond	12VVU726136	15 Sept 1976
	2	30 m from west bank	723136	15 Dec 1976
	3	100 m from west bank	724136	17 Feb 1977
Athabasca River Downstream	1	Approximately 10 km downstream of GCOS plant in main channel--300 m from west bank	12VVU672257	15 Sept 1976
	2		672257	15 Dec 1976
	3		672257	17 Feb 1977
Athabasca Sediment Downstream	1	10 m from Morton Isle 10 km downstream of GCOS plant	12VVU670257	15 Sept 1976
	2	30 m from Morton Isle	671257	15 Dec 1976
	3	300 m from west bank	672257	17 Feb 1977

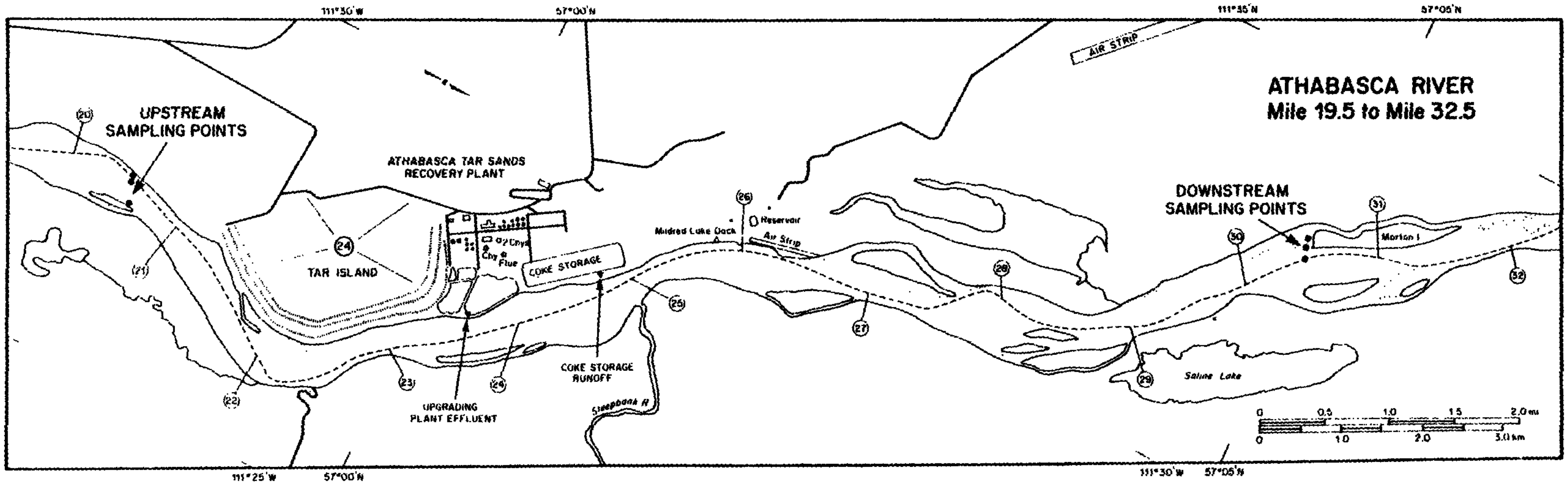


Figure 3. Navigational map of Athabasca River with noted sampling points.

sampling locations, sediment samples were collected 100 m from shore. On 17 February 1977, the last sampling occasion for the Athabasca River, both water and sediment samples were taken from the main channel (Figure 3). Sampling locations and dates are listed in Table 1.

Sample size for the major organic analyses varied from 60 to 80 ℓ of water with an additional 10 ℓ of each water sample being collected for individual tests which did not require pre-extraction of the organic matter. All samples were collected in glass containers that had previously been cleaned with nanograde benzene and treated with chromic acid to minimize contamination.

Organic matter was extracted from the 60 to 80 ℓ samples by a two-step process. Initially, the samples were acidified to pH 2 with hydrochloric acid (HCl) and extracted four times with benzene to remove acidic and neutral organic compounds. The pH was then adjusted to between 8 and 9 by the addition of sodium hydroxide (NaOH), and basic compounds, such as many nitrogen containing compounds, were extracted with benzene. Benzene, which has a solvent strength of 0.32 (Snyder 1968), is far more effective in extracting aliphatic and aromatic hydrocarbons than is hexane, which has a solvent strength of 0.01. Solvents with strengths of 0.6 or greater would be effective in extracting highly polar compounds. Unfortunately, these solvents also tend to be soluble in water and are not suitable for extraction of liquid samples.

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; second, organic compounds, collectively known as bitumens, were extracted from the sediments over a 24 hour period with a 9:1 V/V mixture of benzene/methanol which has a combined solvent strength of 0.89 (Murphy 1969; Evans et al. 1971).

2.2 FRACTIONATION OF ORGANIC CONSTITUENTS

The scheme used to fractionate the bitumens into groups of organic compounds was basically that developed in the previous investigation (Strosher and Peake 1976); its approach is derived from classical methods of organic geochemistry. The separation and analytical procedures for water samples are presented in the flow diagram, Figure 4, and for the sediments in Figure 5. Italicized letters and numbers in the following description of the analytical scheme refer to these figures.

In the case of water samples, analyses were conducted directly on the samples as received (*A*), upon the organic material extracted with benzene at pH 2 (*B*), and upon the organic material extracted with benzene at pH 9 (*C*). Analyses were conducted upon sediment dispersed in double distilled water (*1*) and upon the combined organic material extracted with acetone and with benzene/methanol (*2*). Tests were conducted upon the unextracted water for total organic carbon using a commercial carbon analyzer and upon both the unextracted water (*A*) and the dispersed sediment (*1*) for amides, aldehydes, ketones, phenols, and quinones using a variety of spectrophotometric and spectrofluorometric techniques.

The benzene-soluble material (*B*) from the water samples and the benzene/methanol-soluble material (*1*) from the sediment samples were each divided into four portions. Organic nitrogen compounds, organic sulphur compounds, organic phosphorous compounds, and chlorinated hydrocarbons were each determined directly on (*D*) and (*3*) by a variety of gas chromatographic techniques. In addition, organic nitrogen compounds were investigated in the solvent extract of the pH 9 water (*C*) and the weight of extractable organic carbon was determined using one portion of the sediment extract (*4*).

A portion of the extractable organic material from the water (*G*) and from the sediments (*6*) was analyzed for organic esters. This required saponification with potassium hydroxide (KOH) to convert the esters to free organic acids. The ester component was quantified by the difference in gas chromatography results before and after saponification.

Asphaltenes were measured on weighed portions of the extractable organic material (*E* and *4*) by precipitation from

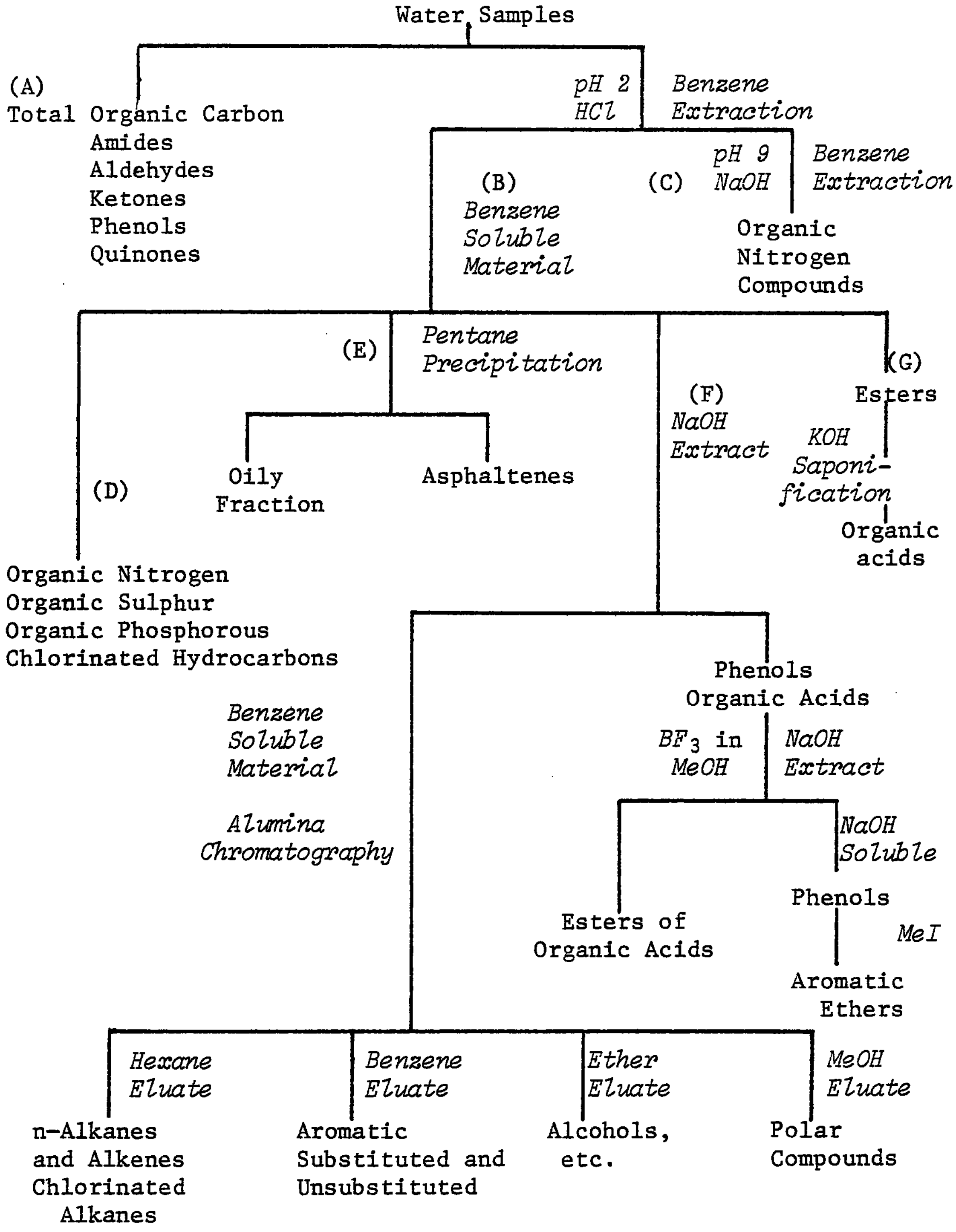


Figure 4. Flow diagram of separation and analytical procedures for water samples.

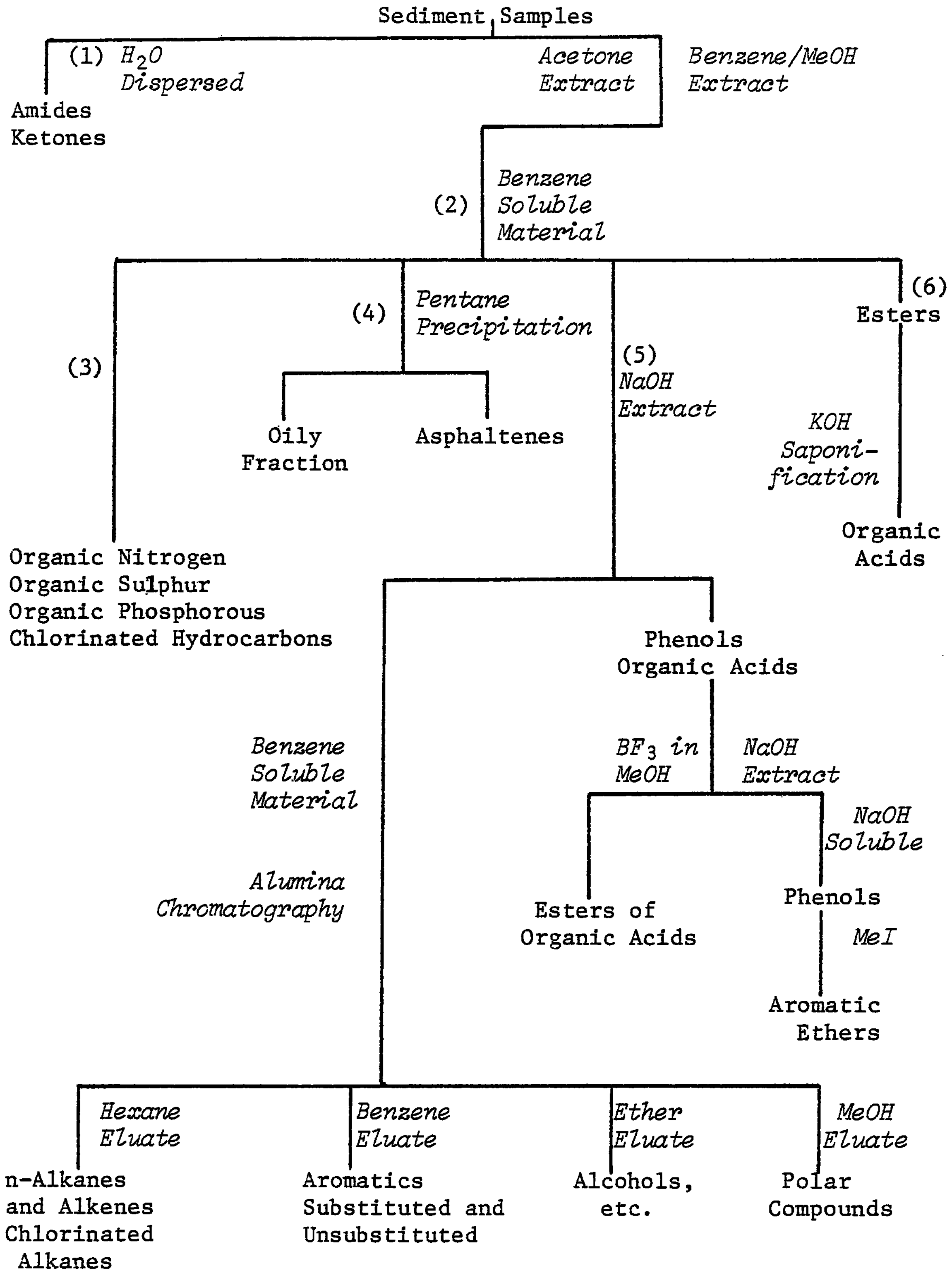


Figure 5. Flow diagram of separation and analytical procedures for sediment samples.

pentane. The resulting asphaltene precipitate was removed, dried and weighed.

The remaining portions of the extractable organic material (*F* and *5*) was used in the analyses of organic acids, phenols, aliphatic and aromatic hydrocarbons and polar compounds. First, the benzene fractions were extracted with aqueous sodium hydroxide (NaOH) to remove the phenols and acids from the oily fractions. The organic acids were then separated from phenols by derivatization 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. The phenols were then converted to aromatic ethers by heating with methyl iodide (MeI). The resulting organic acid esters and aromatic ethers were then quantified by gas chromatographic techniques. The remaining oily fraction was chromatographed on a liquid-solid alumina column where four different solvents were used to elute the various fractions: alkanes and alkenes were eluted with hexane, aromatic hydrocarbons with benzene, alcohols with ether, and the more polar compounds with methanol. These various fractions were quantified by gas chromatographic methods. A more complete description of the analytical methods is contained in Appendix 6.3.

3. RESULTS AND DISCUSSION

This study has produced a large amount of analytical data on samples which are diverse in their origin and composition. In the following sections these data are presented according to the individual type of analysis performed, and the results are evaluated and discussed. The summary section will integrate the data and provide a more comprehensive outlook of the possible effect of industrial mining wastewaters upon the Athabasca River system.

3.1 TOTAL ORGANIC CARBON

3.1.1 Waters

Wastewater samples exhibited a range of total organic carbon values from 24 to 41 mg/ℓ with the upgrading plant effluent containing the largest amounts (Table 2). The upgrading plant effluent varied from 31 mg/ℓ in September to 41 mg/ℓ in December. Mine depressurization waters contained total organic carbon levels of 35 mg/ℓ in September and 24 mg/ℓ at the end of November; the decreased value in organic carbon may be influenced by the substitution of one well in the second composite sample. The one coke storage runoff sample contained 25 mg/ℓ of total organic carbon. Residual, or non-extractable, organic carbon fractions of the wastewaters varied from 8 to 24 mg/ℓ. Upgrading plant effluents contained the higher non-extractable organic carbon values of 16 to 24 mg/ℓ, mine waters had 8 to 14 mg/ℓ, and the coke storage sample contained 10 mg/ℓ. These residual, or non-extractable, carbon values reveal that an average of 60% of the organic carbon was extractable from the coke storage runoff sample, 62% from the mine water samples, and 46% from upgrading plant effluent samples.

Total organic carbon values in the Athabasca River water samples were lower than in the wastewaters. Upstream samples contained 9 to 15 mg/ℓ of total organic carbon while residual values measured 6 to 12 mg/ℓ. In downstream water samples,

Table 2. Organic carbon content of waters and sediments.

Sample	Sample Number	Total Organic Carbon	Residual Organic Carbon	Extractable Organic Carbon	Percentage of Carbon Extracted
Waters (in mg/ℓ)					
Coke Storage Runoff		25	10	15	60
Syncrude Mine Waters	1	35	14	21	60
	2	24	8	16	64
GCOS Upgrading Plant Effluent	1	31	19	12	39
	2	41	22	19	46
	3	35	16	19	54
Athabasca River Upstream	1	15	12	3	20
	2	15	12	3	20
	3	9	6	3	33
Athabasca River Downstream	1	17	13	4	24
	2	18	14	4	22
	3	11	8	3	27
Sediments (in mg/kg of dry sediment)					
Athabasca Sediment Upstream	1			688	
	2			429	
	3			322	
Athabasca Sediment Downstream	1			944	
	2			571	
	3			488	

total organic carbon levels were 11 to 18 mg/ℓ and residual values were 8 to 14 mg/ℓ. These results show that only 20 to 33% of the organic carbon in the upstream river water and 22 to 27% in the downstream river water was extractable.

Comparisons of the organic carbon in the Athabasca River and the wastewaters indicate that:

1. The GCOS upgrading plant effluent contains 9 to 16 mg/ℓ more extractable organic carbon and 7 to 10 mg/ℓ more residual carbon than the Athabasca River waters;
2. The Syncrude mine depressurization waters contain 13 to 18 mg/ℓ more extractable organic carbon than the Athabasca River waters but only 2 mg/ℓ more residual carbon; and
3. Coke storage runoff contains 12 mg/ℓ more extractable organic carbon than the river water but 2 mg/ℓ less residual carbon.

Thus, the concentration of extractable organic carbon in the wastewaters, 15 to 19 mg/ℓ, is approximately five times greater than the natural concentrations in the river, 3 to 4 mg/ℓ. The concentration of unextractable carbon in the mine waters and coke runoff is similar to that of the river waters, while the upgrading plant effluent is 1.5 to 2 times higher than the river waters.

It is speculated that the unextractable carbon consists of either:

1. Organic compounds adsorbed on the surface of inorganic particles or included within particles,
2. Organic carbon existing as discrete carbon particles, or
3. Polar compounds which are dissolved in water but which cannot be extracted with benzene.

If the unextractable carbon is in fact bound to clay particles or is otherwise unavilable to microorganisms, it likely will have little effect upon the biota of the river system; therefore, emphasis is placed upon the more abundant extractable organic material found in the effluents.

3.1.2 Sediments

The amount of extractable organic material from river bottom sediments was measured by weight. Organic compounds, which comprise the extractable fraction, contain approximately 80% carbon and are similar in carbon content to Athabasca bitumen, 83.3% (Berkowitz and Speight 1975).

The first set of sediments taken in mid-September was collected within 10 m of shore; both upstream and downstream samples consisted mainly of fine silt and clay particles. These sediments contained the highest amounts of extractable carbon calculated to be 688 mg/kg in the upstream sediment and 944 mg/kg in the downstream sediment on the basis of 80% of the organic material being carbon. The mid-December sampling was carried out approximately 30 m from shore at the same location; the sediments sampled had a slightly coarser texture due to the increased sand content. These sediments showed a lower extractable organic carbon content; the upstream and downstream samples contained 429 mg/kg and 571 mg/kg, respectively. The February sampling was carried out in the main channel where the sediments were found to contain basically the coarser sand particles. Extractable organic carbon contents were lowest in these sediments; however, the values still increased from 322 mg/kg in the upstream sample to 488 mg/kg in the downstream sediment. The increases in downstream values were consistent through the three respective samplings; downstream to upstream extractable carbon ratios were found to be 1.4:1, 1.3:1, and 1.5:1.

Although care should be exercised in reaching conclusions on the basis of so few samples from such a variable system, it appears that the river sediments downstream from the GCOS plant are acting as a sink for organic material released to the Athabasca River.

Having gained an overview of the amounts and distribution of organic carbon in the wastewaters, river waters, and river sediments, investigations were carried out to determine what types of organic compounds were contained within the extractable carbon fraction.

3.2 ASPHALTENES

Oil or bitumen may be divided into two fractions on the basis of solubility in normal pentane. The oily fraction (or maltenes) is soluble in pentane, whereas the asphaltenes precipitate from a pentane solution.

Chemically, asphaltenes are organic materials with molecular weights in the order of 1000 to 5000 and although the most powerful modern techniques have been applied in the investigations of asphaltenes, the structure of these compounds is still largely undefined. They appear to consist of a core of five stacked sheets, with each sheet composed of an average of 16 condensed aromatic rings (Speers and Whitehead 1969). Contained within, or attached to this core, are aliphatic hydrocarbon chains, oxygen, sulphur, and nitrogen atoms, and trace metals such as nickel and vanadium.

Asphaltenes were quantified in wastewater and sediment samples but not in river water samples which contained only small amounts of extractable organic material in the asphaltene analyzed fraction. Occurrences of asphaltenes in wastewaters ranged from 2.7 mg/ℓ in the coke storage runoff sample, to 1.8 to 3.4 mg/ℓ in the mine waters, and 1.3 to 2.0 mg/ℓ in the upgrading plant effluents. These respective values represent 18% of the extractable organic carbon in the coke storage sample, 12 to 16% in the mine waters, and 10% in the upgrading plant effluents (Table 3). These results compare with 17 to 25% asphaltenes measured in the crude bitumen (Strosher and Peake 1976; Berkowitz and Speight 1975).

The Athabasca sediment samples contained comparatively higher amounts of asphaltenes. Upstream sediments revealed asphaltene values of 77 to 301 mg/kg of dry sediment, while the downstream sediments contained 171 to 437 mg/kg. These asphaltene values, in terms of organic carbon, represent 30 to 40% of the

Table 3. Organic constituents extracted from waters and sediments.

Sample	Number	Asphal-tenes	Aliphatic Hydrocarbons	Aromatic Hydrocarbons	Polar Compounds
Waters (in mg/ℓ)					
Coke Storage Runoff		2.7	0.03	0.05	0.08
Syncrude Mine Waters	1	3.4	0.11	0.06	0.03
	2	1.8	0.01	0.02	0.02
GCOS Upgrading Plant Effluent	1	1.3	0.33	0.19	0.10
	2	1.9	3.00	1.27	0.74
	3	2.0	1.62	0.97	0.13
Athabasca River Upstream	1	-	0.004	0.009	0.030
	2	-	0.001	0.002	0.010
	3	-	0.001	0.001	0.002
Athabasca River Downstream	1	-	0.006	0.006	0.030
	2	-	0.001	0.001	0.010
	3	-	0.024	0.016	0.003
Sediments (mg/kg of dry sediment)					
Athabasca Sediment Upstream	1	301	33.5	11.9	9.0
	2	204	24.1	9.7	4.1
	3	77	19.5	6.6	2.3
Athabasca Sediment Downstream	1	437	54.5	38.3	11.9
	2	236	50.9	36.2	2.2
	3	171	24.6	21.6	2.2

extracted organic carbon in the upstream sediments and 30 to 39% in the downstream sediments.

The high percentage of asphaltenes in the river sediments as compared to the oil sands bitumen or the organic material contained in the process effluent is in keeping with natural weathering processes. Chemical and microbial oxidation processes degrade aliphatic hydrocarbons (Davis 1967; Bailey et al. 1973) and the degradation products may be leached from the sediments by river water (Duffy et al. 1975; Dietz 1972).

3.3 ALIPHATIC HYDROCARBONS

Aliphatic hydrocarbons, separated by liquid column chromatography from the remainder of the organic matter, were measured by gas chromatography. Wide variations occurred in the amount of aliphatics detected. Upgrading plant wastewaters contained 0.03 to 3.0 mg/ℓ, mine waters 0.01 and 0.11 mg/ℓ and the coke storage runoff 0.03 mg/ℓ. The Athabasca River waters revealed considerably lower concentrations: 0.001 to 0.004 mg/ℓ in upstream samples and 0.001 to 0.024 mg/ℓ in downstream samples. The upstream river sediments had 19.5 to 35.5 mg/kg and the downstream sediments 24.6 to 54.4 mg/kg (Table 3).

The mine waters, upgrading plant effluents, and some river water and sediment samples contained normal straight chain alkanes in the nC_8 to nC_{30} range, as evidenced by the peaks which rise above the "hump" on the gas chromatogram of an upgrading plant effluent fraction in Figure 6. The hump in the gas chromatogram is created by a mixture of unresolved, extremely complex, branched and cyclic saturated compounds which constitute the major portion of the aliphatic hydrocarbon fractions (Gearing et al. 1976).

The hydrocarbons displayed in Figure 6, extracted from the mid-February sample of the upgrading plant effluent, closely resemble the hydrocarbons found in the downstream river water sample collected on the same day (Figure 7) and are in sharp

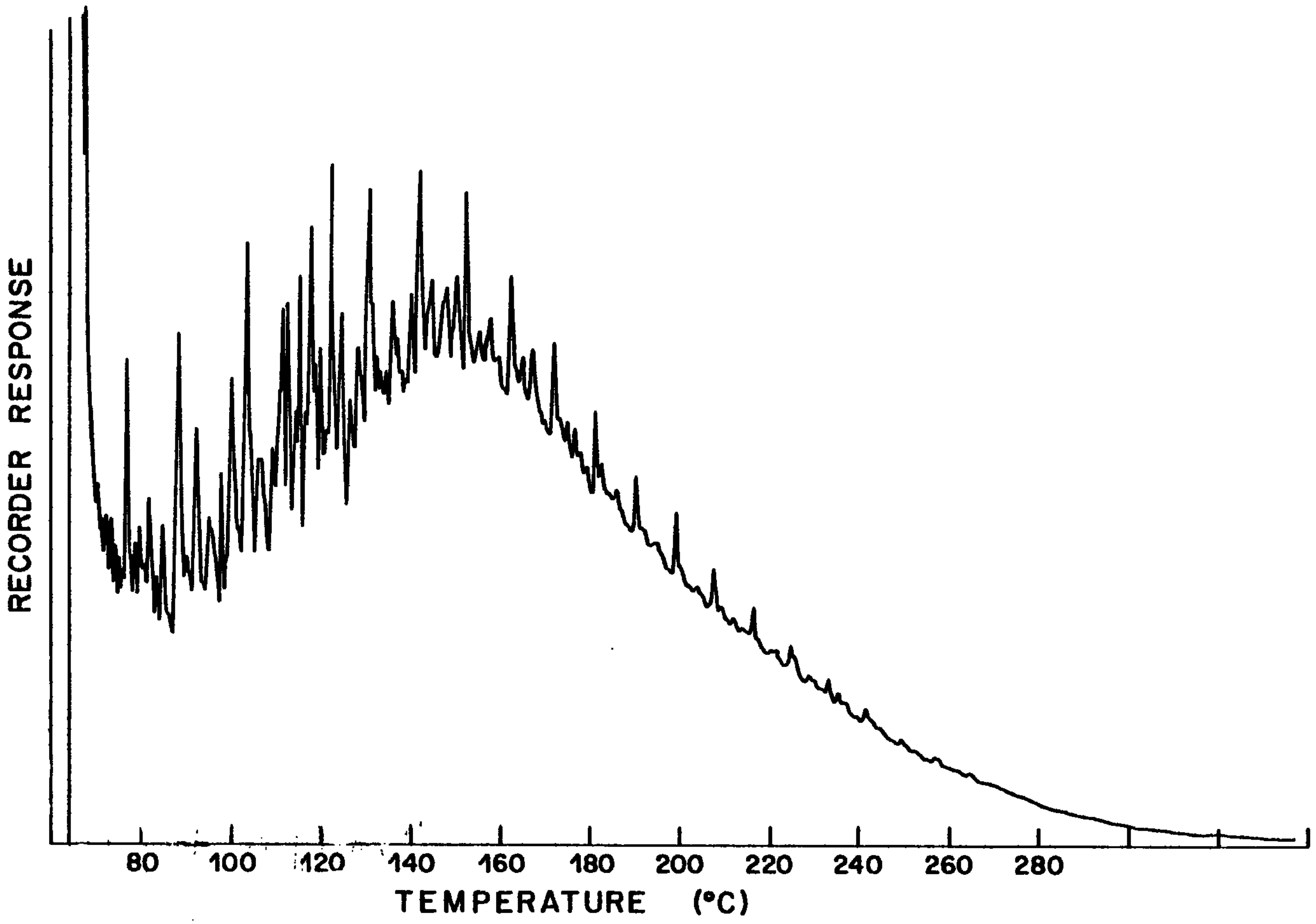


Figure 6. Gas chromatogram of aliphatic hydrocarbons extracted from upgrading plant effluent, February 1977.

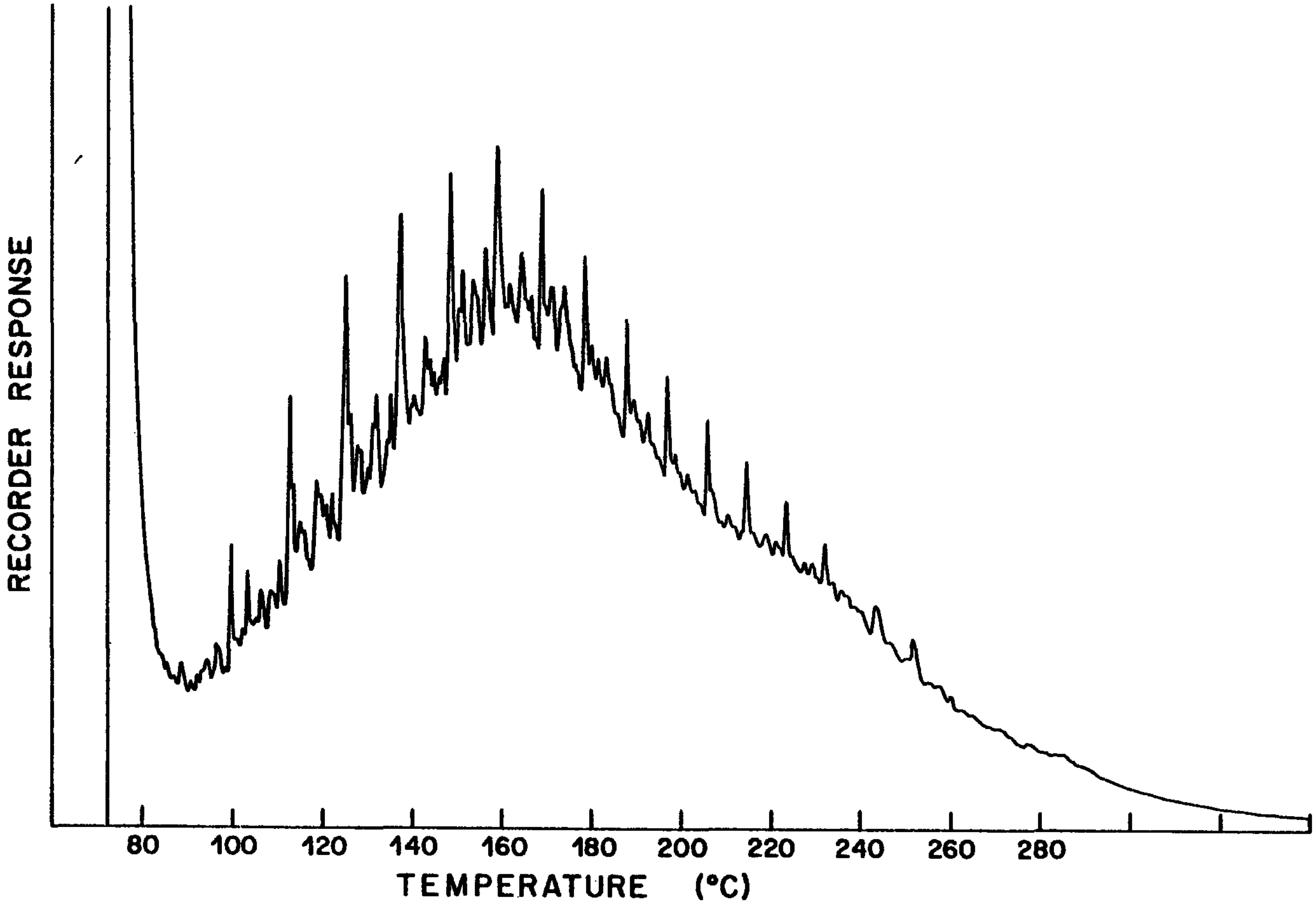


Figure 7. Gas chromatogram of aliphatic hydrocarbons extracted from downstream Athabasca River, February 1977.

contrast with the upstream water sample (Figure 8). Comparison of the quantities of hydrocarbons in this wastewater with quantities in river water taken about 10 km downstream from the plant, indicate an approximate 70-fold dilution of the hydrocarbons in the river (under heavy ice cover and low water flow conditions) from 1.62 to 0.024 mg/ℓ.

Results of the aliphatic hydrocarbon investigations revealed considerably greater amounts of these hydrocarbons in downstream sediments as compared to the upstream sediments. The sediments collected in September, within 10 m of shore, were 60% higher in concentration in the downstream sediment, while the December sediments, collected approximately 30 m from shore, contained 100% more aliphatic hydrocarbons in the downstream samples and the February sediments, collected in the main channel, showed 25% more hydrocarbons in the downstream sediment.

3.4 AROMATICS

Aromatic hydrocarbons, eluted from the alumina column with benzene, were analyzed by gas chromatography. The types of compounds found in these samples ranged from substituted naphthalenes to the multiringed compounds. Many compounds were unresolved because of the numerous substituted as well as unsubstituted aromatics present. Gas chromatographic analyses revealed that upstream river water contained the lowest levels of aromatics at 0.001 to 0.009 mg/ℓ, while downstream water was slightly higher at 0.001 to 0.016 mg/ℓ (Table 3). Wastewater samples contained larger amounts of aromatics with 0.05 mg/ℓ found in the coke storage effluent, 0.02 to 0.06 mg/ℓ in the mine water sample, and 0.19 to 1.27 mg/ℓ in the upgrading plant wastewaters. Sediment extracts revealed 6.6 to 11.9 mg/kg in upstream sediments, and higher levels of 21.6 to 38.3 m/kg in the downstream sediments.

Comparison of the gas chromatogram of aromatics extracted from the mid-February sample of the upgrading plant effluent (Figure 9) with that of aromatics from the downstream river water

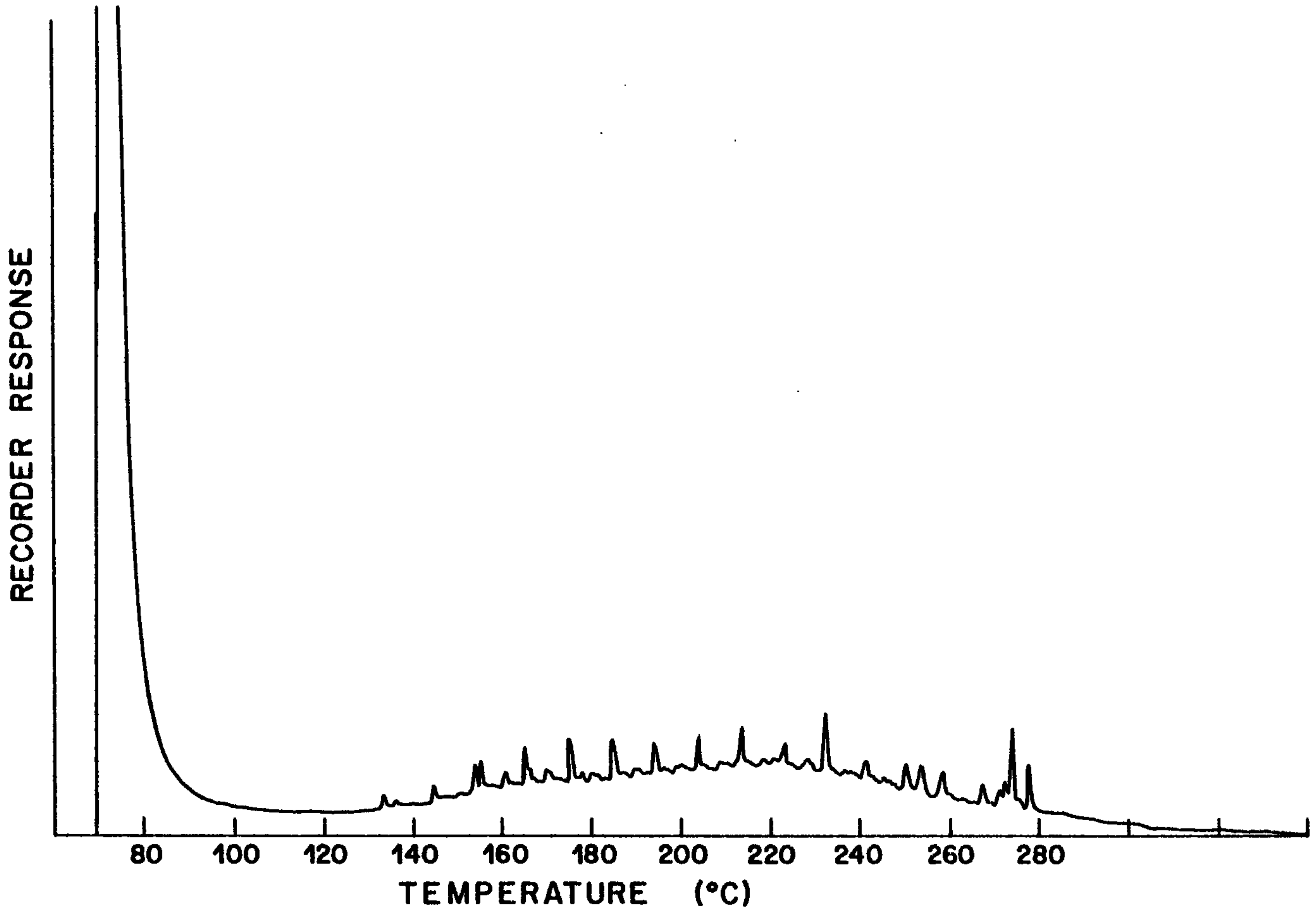


Figure 8. Gas chromatogram of aliphatic hydrocarbons extracted from upstream Athabasca River, February 1977.

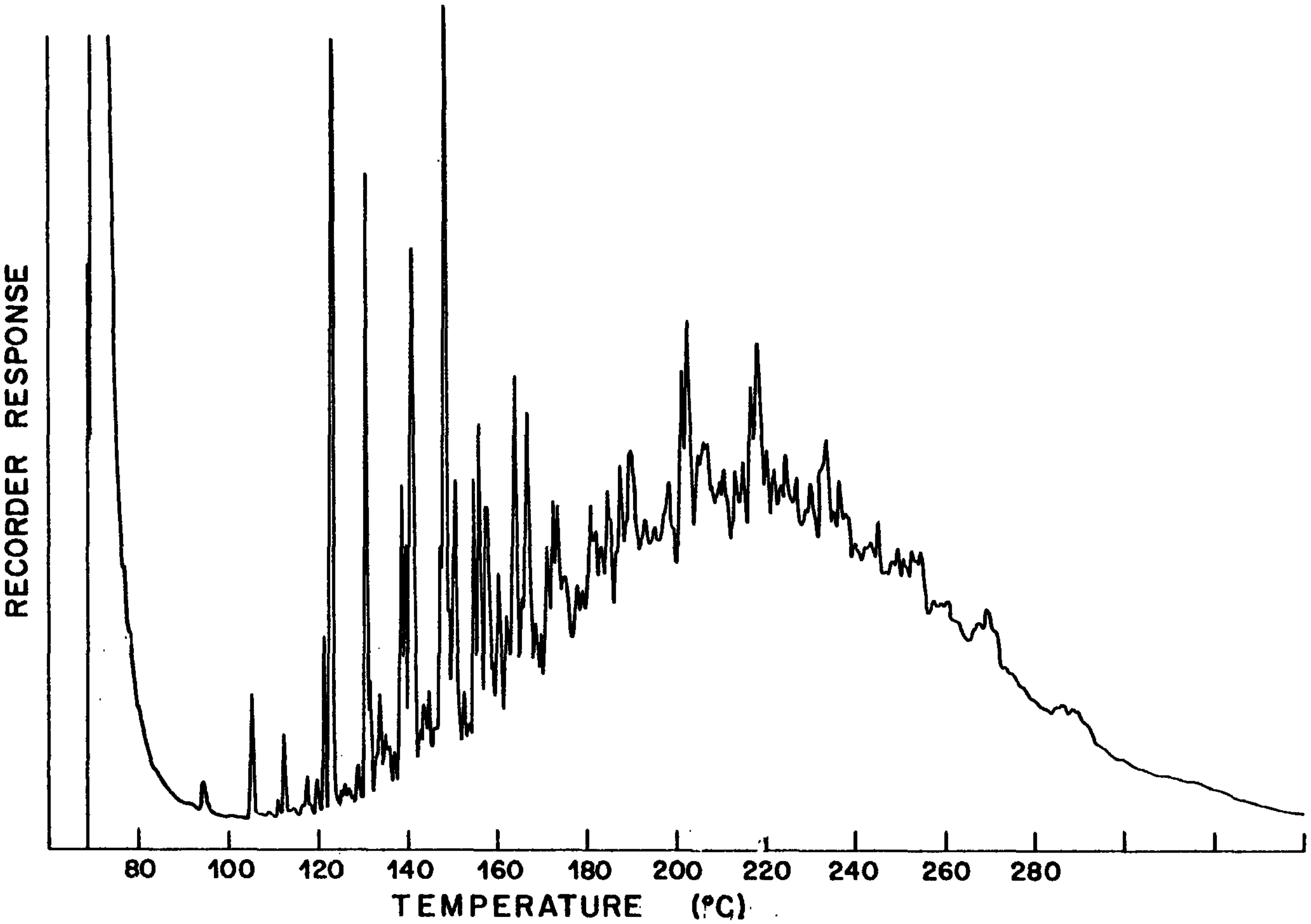


Figure 9. Gas chromatogram of aromatic hydrocarbons extracted from upgrading plant effluent, February 1977.

collected on the same day (Figure 10) shows the two to be almost identical. In contrast, upstream waters showed little aromatic material. This aromatic material was also of a different composition (Figure 11). The upgrading plant effluent contained 0.97 mg/ℓ aromatic hydrocarbons and the downstream river water 0.016 mg/ℓ, a dilution of 65 times that is comparable to 70-fold dilution of the aliphatic hydrocarbons.

The upstream sediment samples showed an average of 9.4 mg of aromatic hydrocarbons per kilogram of dry sediment and the downstream sediments 32 mg/kg. These aromatics represent 2.0% of the organic carbon extractable from the upstream sediments whereas they represent 4.9% of the extractable carbon from the downstream sediments. Thus, there appears to be an enrichment of the aromatic fraction of the organic material in the downstream sediments.

The hydrocarbon results indicate an input of aliphatic and aromatic material into the river from the GCOS plant. The lighter hydrocarbons may be dissolved or dispersed in the effluent and river waters from which, in the summer, they may be lost to the atmosphere. In the winter these hydrocarbons are retained in the water under the ice cover and are carried downstream. Heavier hydrocarbons dispersed in effluent waters or bound to mineral particles may become incorporated into the river sediments.

3.5 POLAR ORGANIC COMPOUNDS

Polar organic compounds were extracted from water samples with benzene and from sediment samples with acetone/benzene/methanol. They were eluted from a column of alumina with diethyl ether/methanol and measured by gas chromatography. Only the least polar compounds could be measured by this technique with the majority of the polar material being retained on the alumina column or not eluted from the gas chromatographic column. The analysis does, however, provide a useful basis for comparing samples.

Concentrations of polar compounds extracted from the 18 different samples are given in Table 3. Extracts of the coke

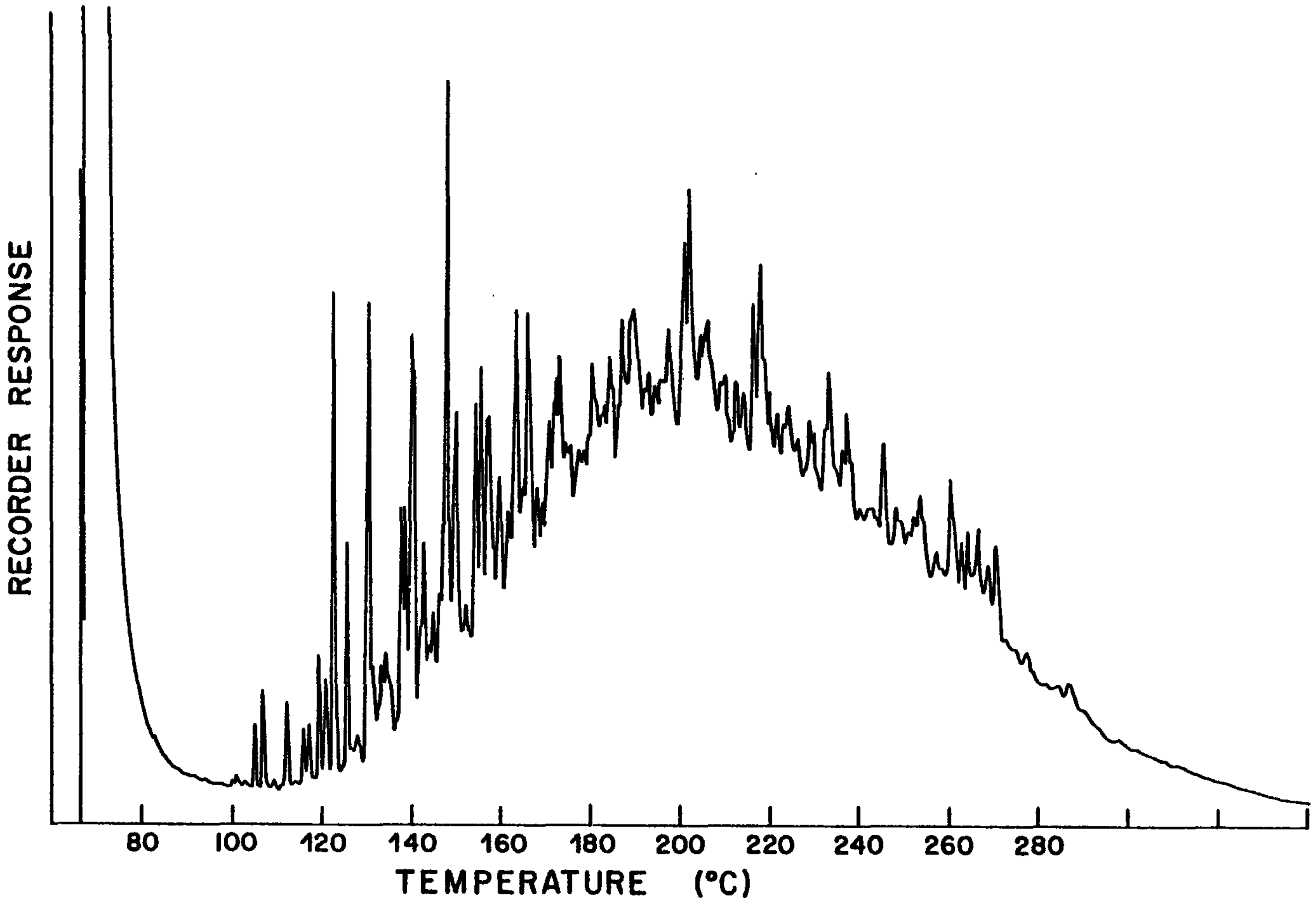


Figure 10. Gas chromatogram of aromatic hydrocarbons extracted from downstream Athabasca River, February 1977.

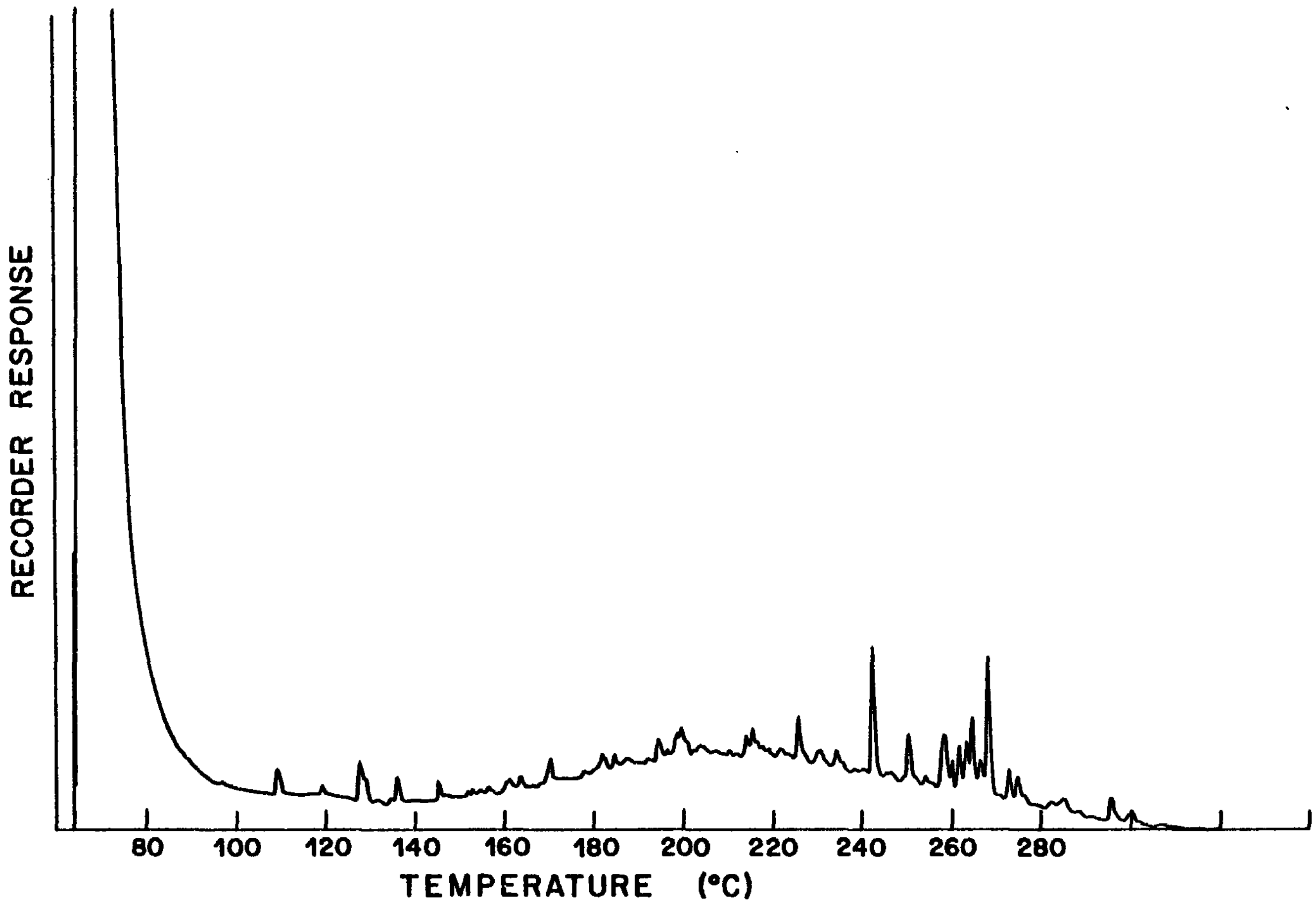


Figure 11. Gas chromatogram of aromatic hydrocarbons extracted from upstream Athabasca River, February 1977.

storage runoff sample contained 0.08 mg/ℓ polar compounds, mine depressurization water 0.02 to 0.03 mg/ℓ, and upgrading plant effluents 0.10 to 0.74 mg/ℓ. Extracts of the river waters and sediments gave values of 0.002 to 0.03 mg/ℓ for upstream water, 0.003 to 0.03 mg/ℓ for downstream water, 2.3 to 9.0 mg/kg for upstream sediments and 2.2 to 11.9 mg/kg for downstream sediments.

Comparison of amounts and relative composition of the oily fraction in terms of aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds reveals some fundamental similarities and differences in the samples. The polar compounds comprised 50% of the measurable organic compounds in the coke storage sample extract, 27% in the mine water extract, and only 12% in the upgrading plant wastewater extract. The aromatic portion of the measurable organic compounds was relatively constant with 31% in the coke storage water extract, 35% in the mine water extract, and 30% in the upgrading effluent extract. Considerable variation occurred in the aliphatic hydrocarbon portion with 19% in coke storage water extract, 38% in mine water extract, and 58% in the upgrading effluent extract. In comparison, river water extracts contained 20% aliphatics, 20% aromatics, and 60% polar compounds whereas extracts of the upstream sediments contained an average of 64% aliphatics, 23% aromatics, and 13% polar compounds and of the downstream sediments 54% aliphatics, 39% aromatics, and 7% polar compounds. It is apparent that the oily constituents of the sediment are different in composition from those of the river water, indicating a fractionation process occurring between the water and the sediments in the river system. The more polar organic compounds show a greater affinity for the water than do the aliphatic hydrocarbons and as a consequence are more readily transported away from the sediments by the river waters.

The composition of the hydrocarbons extracted from sediment samples taken upstream of the GCOS plant is different from the composition of hydrocarbons found in extracts of downstream sediments. The primary difference lies in the proportion of aromatic hydrocarbons, which comprise 23% of the hydrocarbon fraction upstream and 39% downstream. Such differences could be caused by effluent from the GCOS plant if such effluent contained a greater average proportion of aromatic hydrocarbons than is normally found in bottom sediments of the Athabasca River or by material from additional inputs such as the Steepbank River.

3.6 ORGANIC SULPHUR COMPOUNDS

Organic sulphur compounds were detected in solvent extracts of all samples with the use of a flame photometric detector coupled to a gas chromatograph. Values ranged from 0.01 to 0.06 mg/ℓ and 0.02 to 0.07 mg/ℓ in upstream and downstream waters, respectively, to 6.2 to 26.3 mg/kg and 12.9 to 33.8 mg/kg in upstream and downstream sediment samples, respectively (Table 4). The coke storage runoff contained 1.6 mg/ℓ of the organic sulphur compounds. Amounts of these compounds in mine depressurization waters varied from 2.7 to 3.3 mg/ℓ, and in upgrading plant wastewaters from 2.6 to 6.3 mg/ℓ.

The organic sulphur compounds detected in most samples are a complex mixture of mainly aromatic structures as previously determined (Strosher and Peake 1976), the majority of which cannot be resolved by gas chromatography. Figure 12 shows the gas chromatographic detection of such a complex mixture taken from the mine depressurization water sample and can be directly related to previous findings from crude bitumen. Upon processing of the crude bitumen, these complex mixtures of sulphur compounds are altered to form the more identifiable structures such as mercaptans, sulphides, and thiophenes, which in turn are found in processing waters such as the upgrading plant wastewater (Figure 13).

In addition to the organic sulphur compounds, elemental sulphur was also quantitatively measured in all samples. The coke storage sample, mine water samples, and river water samples all registered very low levels of elemental sulphur. Upgrading plant effluents contained from 0.15 to 1.38 mg/ℓ of elemental sulphur, while upstream sediments had 0.17 to 1.44 mg/kg and downstream

Table 4. Organic sulphur and phosphorous compounds and elemental sulphur in waters and sediments.

Sample	Sample Number	Sulphur Compounds	Elemental Sulphur	Phosphorous Compounds
Waters (in mg/ℓ)				
Coke Storage Runoff		1.6	<0.001	0.00023
Syncrude Mine Waters	1	2.7	<0.001	<0.00001
	2	3.3	<0.001	<0.00001
GCOS Upgrading Plant Effluent	1	2.6	0.15	<0.00001
	2	3.1	0.42	<0.00001
	3	6.3	1.38	<0.00001
Athabasca River Upstream	1	0.06	0.003	0.00001
	2	0.04	0.001	0.00002
	3	0.01	<0.001	0.00006
Athabasca River Downstream	1	0.07	0.003	0.00006
	2	0.06	0.002	0.00001
	3	0.02	0.001	0.00002
Sediments (mg/kg of dry sediment)				
Athabasca Sediment Upstream	1	26.3	0.17	0.0128
	2	20.2	1.44	0.0091
	3	6.2	0.99	0.0146
Athabasca Sediment Downstream	1	33.8	5.09	0.0053
	2	32.4	4.19	0.0050
	3	12.9	2.63	0.0272

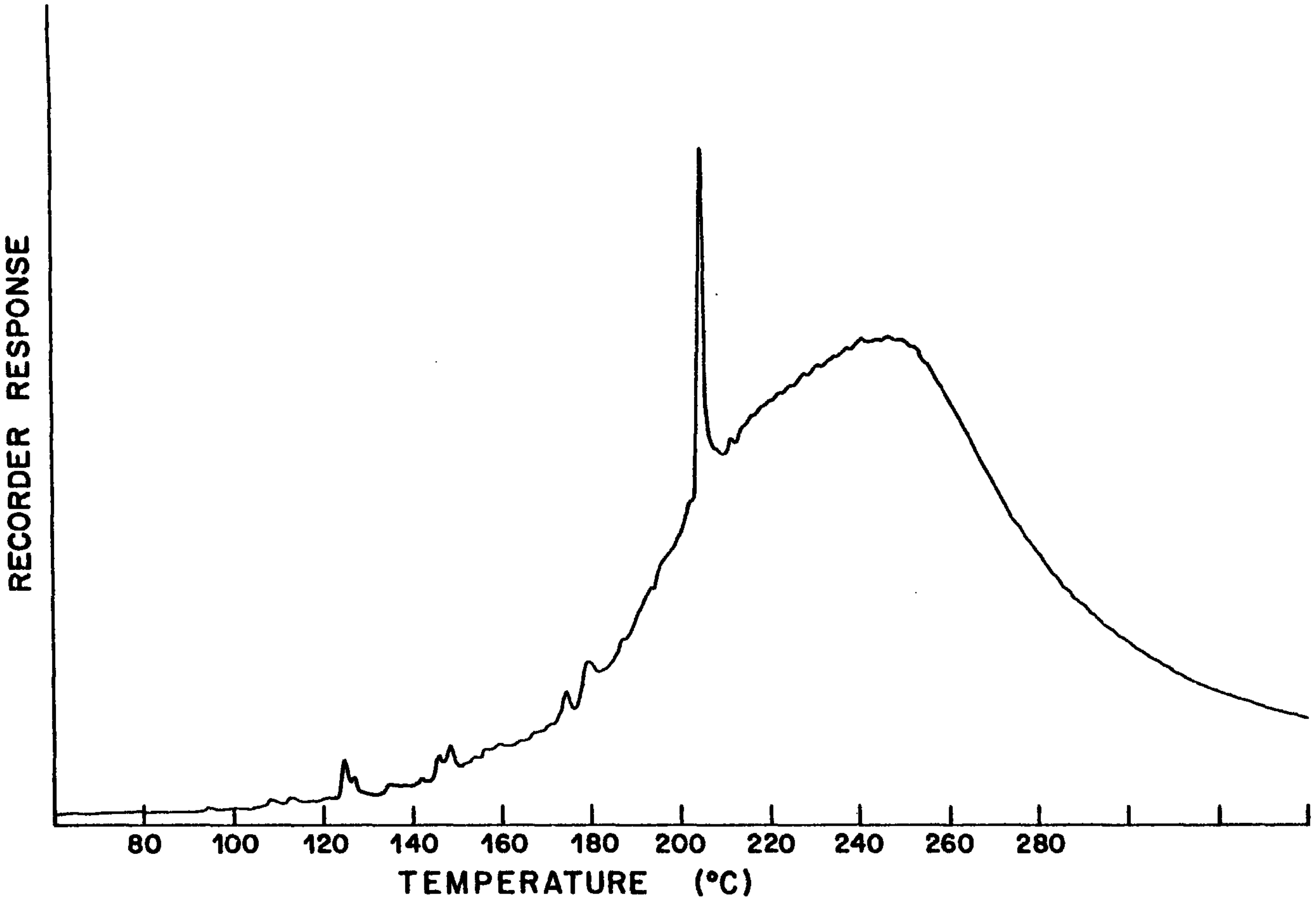


Figure 12. Gas chromatogram of organic sulphur compounds extracted from Syncrude mine water composite.

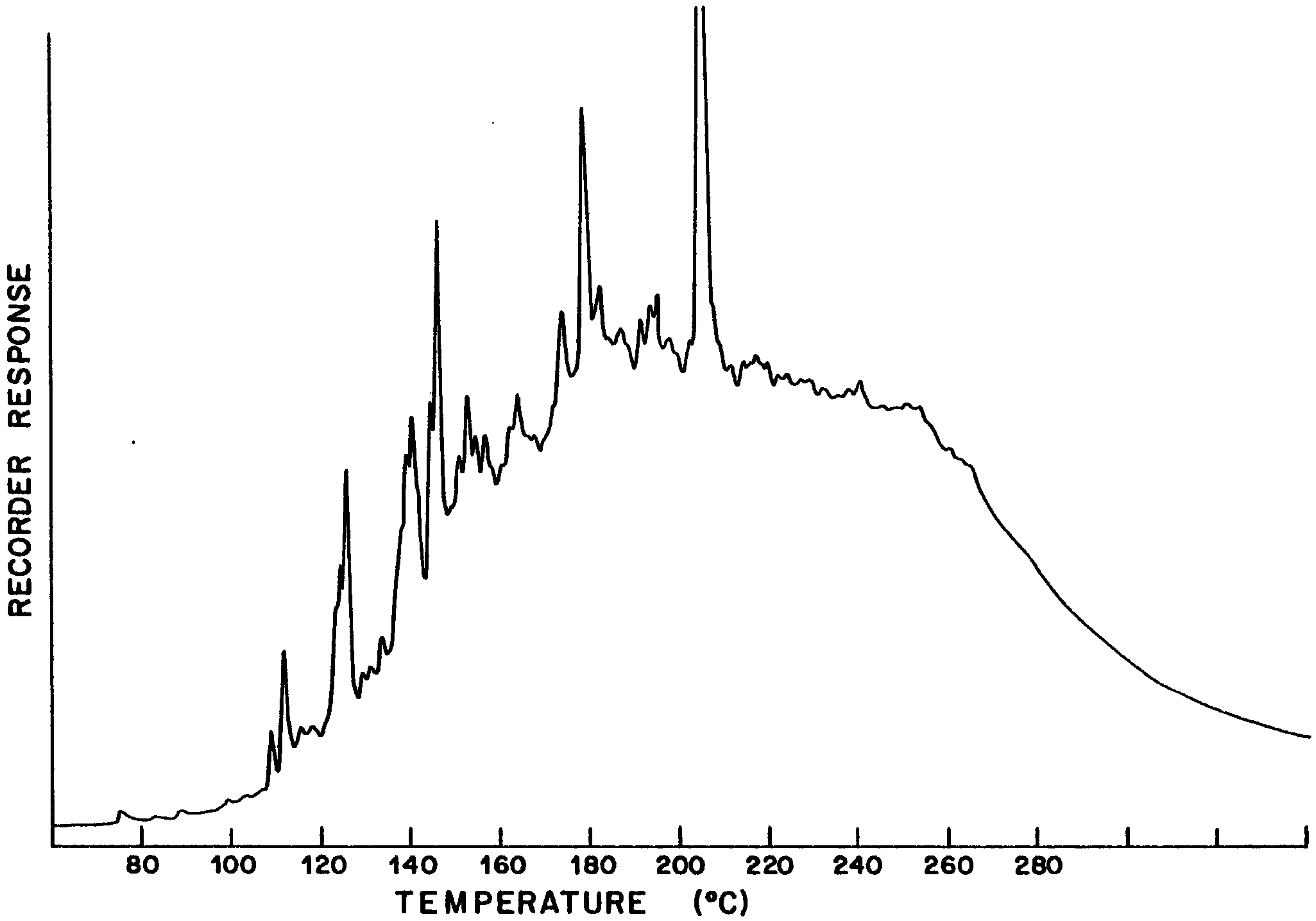


Figure 13. Gas chromatogram of organic sulphur compounds extracted from upgrading plant effluent.

sediments from 2.63 to 5.09 mg/kg. Although the larger amounts of elemental sulphur in the downstream sediments may be due to plant effluents, there is presently insufficient evidence to support such a postulation.

3.7 ORGANIC PHOSPHOROUS COMPOUNDS

Organic phosphorous compounds were measured by gas chromatography using a flame photometric detector. The method is similar to that used in the detection of sulphur compounds except that a filter designed to pass light emitted by phosphorous is used. Because of the inability of filters to transmit monochromatic light, there tend to be interfences from flame responses of other compounds, particularly sulphur. Sulphur compounds in these samples were in much greater quantities than were the phosphorous compounds and did cause interferences. However, mercury treatment reduced these interferences to a point at which the lower phosphorous responses could be measured.

Organic phosphorous compounds were detected mainly in the river system where 0.00001 to 0.00006 mg/ℓ were found in both upstream and downstream water samples (Table 4). The sediments contained considerably higher levels with 0.0009 to 0.00146 mg/kg in upstream sediments and 0.00050 to 0.00272 mg/kg in downstream sediments. The coke storage runoff sample was the only wastewater to contain any appreciable amount of the phosphorous compounds at 0.00023 mg/ℓ.

Gas chromatography revealed the presence of two distinct phosphorous compounds in river water and sediment samples. Figure 14 presents these compounds as detected in the downstream water collected in February 1977; the relative amounts of compound A to compound B were 2.5:1. Examination of these compounds in the previous two samplings of the downstream water showed a dramatic difference in these ratios; the compound A to B ratios had been 1:1.5 in December and 1:8 in September. Though the identity of the compounds is unknown, their occurrence in waters and sediments

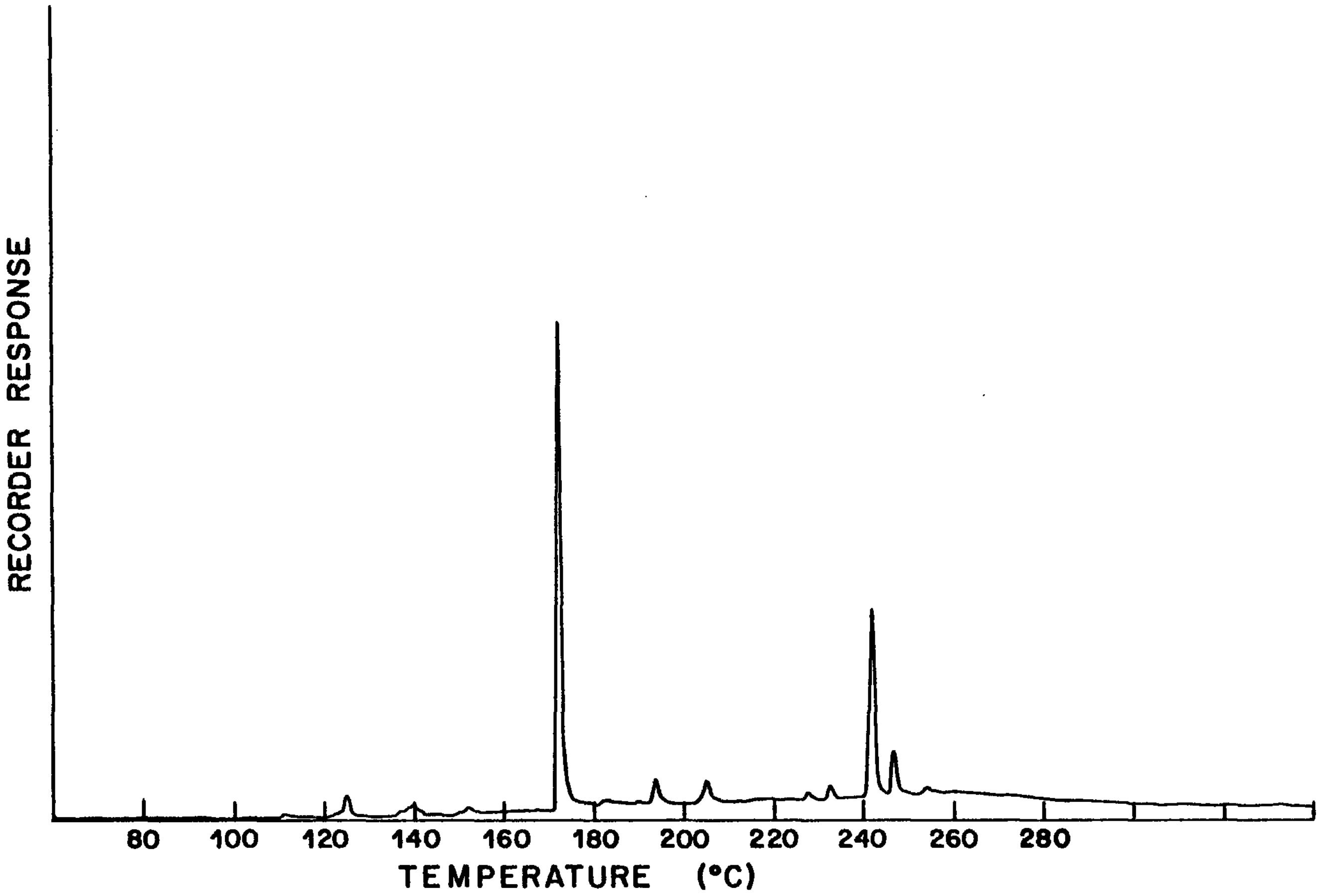


Figure 14. Gas chromatogram of organic phosphorous compounds extracted from downstream Athabasca River.

both upstream and downstream would indicate that they are natural constituents of the river system, possibly being synthesized by aquatic organisms such as algae or bacteria. The changing ratios may reflect a physiochemical response to changing water temperatures in the river or simply variations in the stability of the two compounds at different temperatures.

3.8 CHLORINATED HYDROCARBONS

Chlorinated hydrocarbons determined by electrolytic conductivity were found in concentrations of 0.006 mg/ℓ in the coke storage sample, 0.006 to 0.010 mg/ℓ in mine waters, and 0.002 to 0.020 mg/ℓ in upgrading plant effluents (Table 5). River waters contained lesser concentrations of chlorinated compounds, reaching a maximum of 0.001 mg/ℓ in both December samples. Sediment samples gave values ranging from 0.059 to 0.215 mg/kg in upstream sediments and 0.081 to 0.199 mg/kg in the downstream sediments.

A typical response for the chlorinated hydrocarbons by the electrolytic conductivity method is shown in Figure 15. This is a chromatogram of chlorinated compounds extracted from the upstream river water, and it contains two distinct indications of chlorine-containing compounds. Further examination by electron capture gas chromatography has failed to identify them as commonly used pesticides.

3.9 ORGANIC NITROGEN COMPOUNDS

The analysis of nitrogen-containing compounds was carried out on extracted organic material by an electrolytic conductivity/ gas chromatography method similar to the chlorinated hydrocarbon investigations. Only compounds amenable to extraction from water with benzene or from sediments with benzene/methanol and eluted from the gas chromatographic column were measured. Amounts detected were 0.001 mg/ℓ in river water samples, 0.008 mg/ℓ in the coke storage water, 0.014 to 0.029 mg/ℓ in mine waters, and 0.044 to 0.78 mg/ℓ in upgrading plant wastewaters (Table 5). Extracts of

Table 5. Chlorinated hydrocarbons and organic nitrogen compounds in waters and sediments.

Sample	Sample Number	Chlorinated Hydrocarbons	Organic Nitrogen Compounds
Waters (in mg/ℓ)			
Coke Storage Runoff		0.006	0.008
Syncrude Mine	1	0.010	0.014
Waters	2	0.006	0.029
GCOS Upgrading	1	0.002	0.078
Plant	2	0.019	0.044
Effluent	3	0.020	0.076
Athabasca	1	<0.001	0.001
River	2	0.001	0.001
Upstream	3	<0.001	0.001
Athabasca	1	<0.001	0.001
River	2	0.001	0.001
Downstream	3	<0.001	0.001
Sediments (mg/kg of dry sediment)			
Athabasca	1	0.07	0.20
Sediment	2	0.22	0.49
Upstream	3	0.06	0.24
Athabasca	1	0.08	0.24
Sediment	2	0.17	0.69
Downstream	3	0.20	0.42

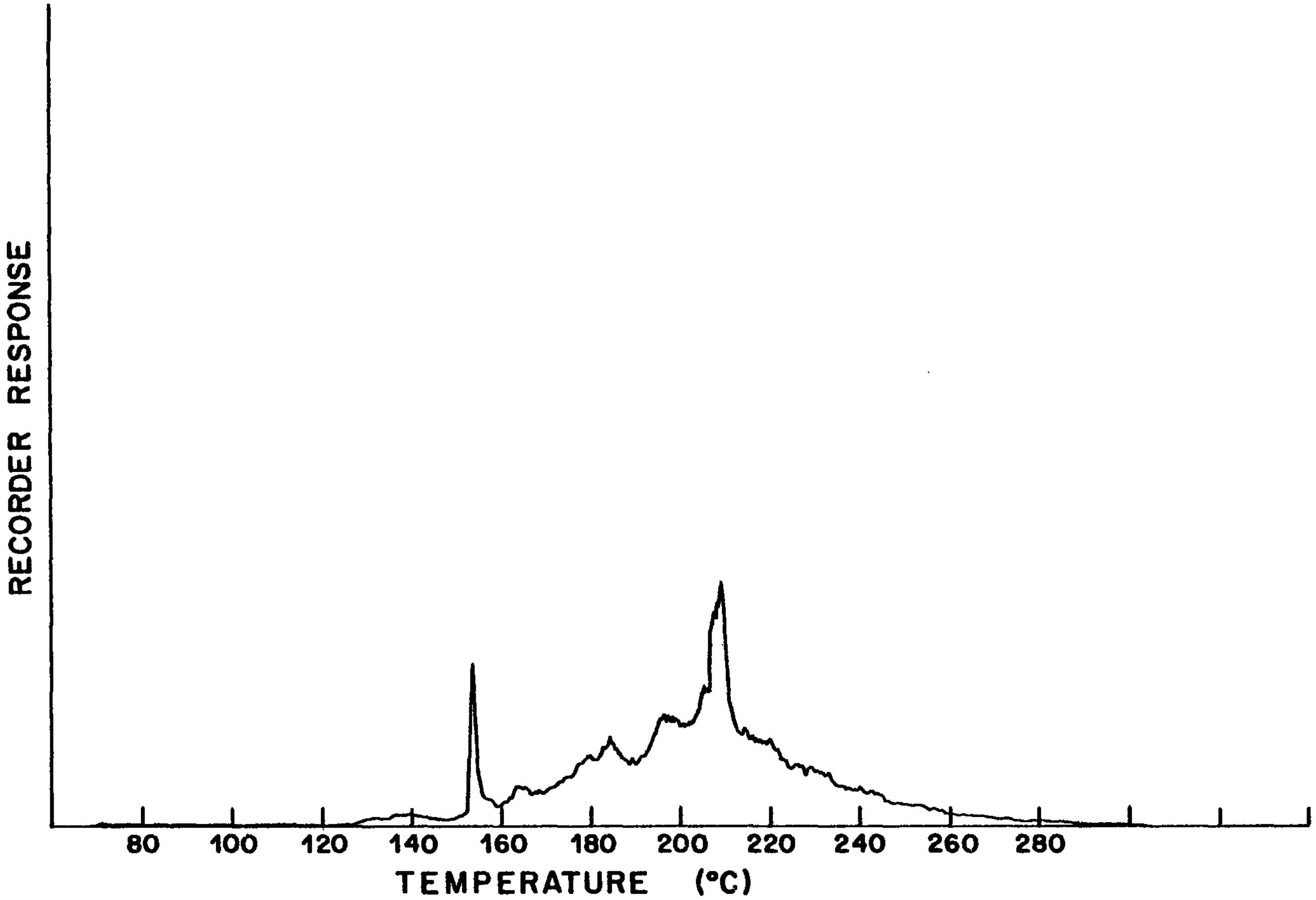


Figure 15. Gas chromatogram of chlorinated hydrocarbons extracted from upstream Athabasca River.

upstream river sediments gave values of 0.20 to 0.49 mg/kg and downstream sediments 0.24 to 0.69 mg/kg.

These results were confirmed using gas chromatography with an electrolytic detector specific to nitrogen. Figure 16 is a typical gas chromatogram of the nitrogen compounds extracted from upgrading plant wastewater. It shows a number of partially resolved compounds that were detected above the mixture of unresolved compounds contained within the "hump" of the chromatogram.

3.10 ALDEHYDES

Aldehydes were detected in all water samples by a standard colorimetric method. River waters exhibited the lowest levels and varied from 0.19 to 0.48 mg/ℓ in upstream waters and from 0.17 to 0.53 mg/ℓ in downstream samples (Table 6). The wastewaters averaged slightly higher levels with 0.30 mg/ℓ in coke storage water, 0.48 to 0.54 mg/ℓ in mine waters and 0.49 to 0.53 mg/ℓ in upgrading plant effluents.

3.11 KETONES

The fluorometric analyses for ketones detected 0.60 mg/ℓ in the coke storage runoff sample and 0.33 to 0.35 mg/ℓ in upgrading plant wastewaters (Table 6). River water samples and mine waters were considerably lower in ketone content; all contained <0.01 mg/ℓ. Upstream sediments dispersed in water showed 0.03 to 0.05 mg/kg of ketones while downstream sediments exhibited 0.07 to 0.12 mg/kg.

3.12 QUINONES

Quinones were determined spectrophotometrically in concentrations ranging from 0.15 to 0.17 mg/ℓ in upgrading plant effluents to 0.45 to 0.55 mg/ℓ in mine waters and 0.65 mg/ℓ in the coke storage runoff waters (Table 6). Athabasca River waters contained 0.10 to 0.12 mg/ℓ in upstream samples and 0.38 to 0.45 mg/ℓ in downstream samples.

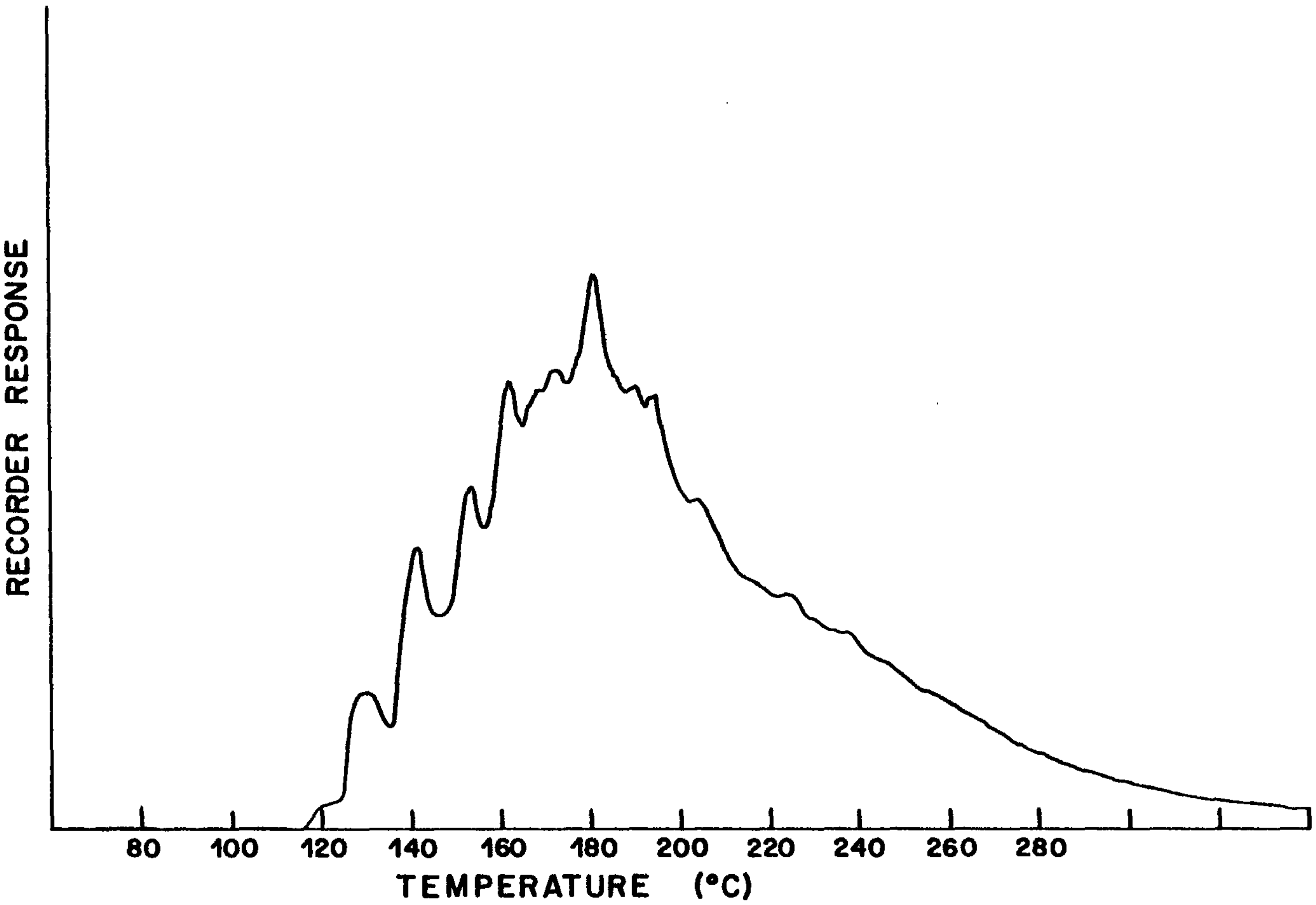


Figure 16. Gas chromatogram of organic nitrogen compounds extracted from upgrading plant effluent.

Table 6. Organic compounds detected by colorimetric tests in waters and sediments.

Sample	Sample Number	Aldehydes	Amides	Ketones	Quinones
Waters (in mg/ℓ)					
Coke Storage Runoff		0.30	0.30	0.60	0.65
Syncrude Mine	1	0.48	0.36	<0.01	0.45
Waters	2	0.54	0.27	<0.01	0.55
GCOS Upgrading	1	0.53	1.1	0.33	0.15
Plant	2	0.49	1.2	0.35	0.17
Effluent	3	0.53	1.2	0.35	0.15
Athabasca	1	0.19	0.50	<0.01	0.10
River	2	0.26	0.42	<0.01	0.12
Upstream	3	0.48	0.22	<0.01	0.10
Athabasca	1	0.17	0.41	<0.01	0.45
River	2	0.53	0.24	<0.01	0.40
Downstream	3	0.24	0.10	<0.01	0.38
Sediments (mg/kg of dry sediment)					
Athabasca	1	-	2.1	0.03	-
Sediment	2	-	1.3	0.05	-
Upstream	3	-	0.5	0.05	-
Athabasca	1	-	2.6	0.10	-
Sediment	2	-	1.8	0.07	-
Downstream	3	-	0.6	0.12	-

3.13 AMIDES

Amides were detected in all samples by a colorimetric method. Most water samples contained similar levels of amides: 0.30 mg/ℓ in coke storage water, 0.27 to 0.36 mg/ℓ in mine waters, and 0.22 to 0.50 mg/ℓ in upstream river waters as compared to 0.10 to 0.41 mg/ℓ in downstream river waters (Table 6). The upgrading plant effluents were consistently higher, with 1.11 to 1.23 mg/ℓ. Upstream sediments dispersed in water gave values of 0.48 to 2.05 mg/kg while downstream sediments varied from 0.57 to 2.62 mg/kg.

Two of the four colorimetric tests failed to produce acceptable results in the analyses of sediments. Interferences by fine particulate matter in the analysis for aldehydes and quinones made quantification impossible.

Three of the four preceding colorimetric tests--the aldehyde, ketone, and amide tests--consistently showed greater amounts of the respective compounds in wastewaters than in river waters. The exception was the quinone test which showed 3 to 4 times more in the downstream river waters than in the upstream waters or the plant wastewaters. Values for quinones in the downstream waters were similar to those for Syncrude mine water (which is basically groundwater from the bitumen deposit), indicating a natural source for the quinones in the downstream water samples.

3.14 ORGANIC ESTERS

Esters of organic acids were determined by the gas chromatographic techniques described in Appendix 6.3.14. The coke storage runoff water extracts contained 0.13 mg/ℓ of the esters, the mine water extracts revealed levels of 1.15 to 1.34 mg/ℓ, and the upgrading plant wastewater extracts had 0.71 to 0.94 mg/ℓ (Table 7). Extracts of river waters contained considerably lower levels with 0.001 to 0.029 mg/ℓ in upstream samples and 0.001 to 0.013 mg/ℓ in downstream samples. Upstream sediment extracts contained 7.3 to 10.0 mg/kg and downstream sediment extracts 10.8 to 17.2 mg/kg.

Table 7. Esters, phenols, and organic acids in waters and sediments.

Sample	Sample Number	Esters	Phenols Colorimetric	Phenols by GC	Organic Acids
Waters (in mg/ℓ)					
Coke Storage Runoff		0.13	<0.001	0.07	0.08
Syncrude Mine Waters	1	1.2	0.003	0.19	1.1
	2	1.3	<0.001	0.19	2.6
GCOS Upgrading Plant Effluent	1	0.71	0.135	0.12	0.29
	2	0.78	0.133	0.11	0.92
	3	0.94	0.204	0.19	0.92
Athabasca River Upstream	1	0.001	<0.001	0.01	0.01
	2	0.029	<0.001	0.01	0.01
	3	0.027	0.001	0.01	0.01
Athabasca River Downstream	1	0.001	<0.001	0.01	0.01
	2	0.013	<0.001	0.01	0.01
	3	0.010	<0.001	0.01	0.03
Sediments (mg/kg of dry sediment)					
Athabasca Sediment Upstream	1	7.3	-	2.8	1.8
	2	10.0	-	1.4	3.4
	3	7.8	-	1.7	2.7
Athabasca Sediment Downstream	1	14.0	-	2.1	2.7
	2	17.2	-	3.1	4.7
	3	10.8	-	2.4	1.4

3.15 PHENOLS

Phenols were analyzed by two different methods, the standard colorimetric method and the gas chromatographic method developed in the previous investigation (Strosher and Peake 1976). Colorimetric investigations were carried out for comparative purposes only as they do not represent the total phenolic content of the samples. Results from this test indicate simple phenol concentrations of <0.001 mg/ℓ in coke runoff, <0.001 to 0.003 mg/ℓ in mine waters, 0.133 to 0.204 mg/ℓ in upgrading plant effluents, and <0.001 to 0.001 mg/ℓ in the river waters (Table 7). Sediment samples were not analyzed by this method.

The gas chromatographic method, which provides a more complete measure of phenolic content, detected higher concentrations of phenol compounds in extracts of all water samples except those of the upgrading plant effluents where both methods resulted in similar values. Amounts measured by gas chromatography were 0.11 to 0.19 mg/ℓ as compared to the 0.133 to 0.204 mg/ℓ found by the colorimetric test, indicating that the simpler phenols comprise the majority of the total phenolic content of these wastewaters. Other gas chromatographic values include 0.07 mg/ℓ in the coke storage water, 0.19 mg/ℓ in mine waters, and 0.01 mg/ℓ in all river water samples. Extracts of sediment samples were also analyzed by gas chromatography and were found to contain much higher levels of the phenol compounds. Upstream sediments ranged from 1.4 to 2.8 mg/kg, while downstream sediments showed slightly higher values of 2.1 to 3.1 mg/kg.

3.16 ORGANIC ACIDS

Organic acids were analyzed as their respective methyl ester derivatives which were obtained from the separation process devised for the phenol and organic determinations. On the basis of the analyses of extracted organic material, coke storage water contained 0.08 mg/ℓ, upgrading plant wastewaters 0.29 to 0.92 mg/ℓ, mine waters 1.1 to 2.6 mg/ℓ and river waters about 0.01 mg/ℓ. Upstream sediments contained from 1.8 to 3.4 mg/kg and downstream sediments 1.4 to 4.7 mg/kg.

4. SUMMARY AND CONCLUSIONS

4.1 UPGRADING PLANT EFFLUENTS

Upgrading plant effluents contained an average of 36 mg/ℓ of organic carbon when sampled on three occasions between September 1976 and February 1977. This value is identical to that obtained in the previous study conducted during November and December of 1975. The extractable organic carbon content of these wastewaters averaged 17 mg/ℓ, or 46% of the total organic carbon, which is comparable to the extractable content of the 1975 wastewaters (42%). The extractable carbon likely exists as dissolved or dispersed liquid hydrocarbons and other compounds of low polarity which are readily extractable with benzene from water. The remaining total organic carbon may exist in one or more forms: as dissolved polar compounds (possibly including humic and fulvic acids), as compounds adsorbed on the surface of clay particles or occluded within particles, or as discrete carbon particles.

The source of the extractable carbon is mainly the upgrading plant whereas the source of the non-extractable carbon in the upgrading plant effluent is the river water. During the study period, Athabasca River waters upstream of the plant contained 9 to 15 mg/ℓ organic carbon, of which 3 mg/ℓ was extractable. The upgrading plant effluents contained 31 to 41 mg/ℓ organic carbon, of which 12 to 19 mg/ℓ was extractable. Thus, the upgrading plant contributed 16 to 26 mg/ℓ organic carbon to the water, of which the majority, 9 to 16 mg/ℓ, is extractable.

The physical state of organic compounds--e.g. dissolved, as a micellar dispersion, associated with inorganic particulate matter or as discrete organic particles--may have an important bearing upon their biological effect. For example, organic compounds tightly bound to mineral surfaces may not be available to aquatic life and would have little or no environmental impact. It is the biological effects of the extractable carbon together with those of the dissolved polar compounds which are of particular interest, as these compounds are in a form most readily available to aquatic organisms.

Organic sulphur compounds were one of the major contributors to the upgrading plant effluents, representing 24% of the extractable organic matter, or 4 mg/ℓ. These compounds, which are composed largely of substituted benzothiophenes (Figure 13), contain approximately 17% sulphur, thus making the sulphur content of the extractable organic matter roughly 4%. This value is in good agreement with the 4.2% sulphur content of the Athabasca bitumen (Berkowitz and Speight 1975). The toxicological effects of organic sulphur compounds on aquatic life have received little study and there is a lack of basic research (Delisle and Schmidt 1973). It is known that low molecular weight mercaptans, phenyl mercaptan and tolyl mercaptan are toxic to fish; metatolyl mercaptan is 4 times as toxic as phenol, and p-tolyl mercaptan is 8.5 times as toxic as phenol (Geradorff 1938).

The second major group of extractable organic compounds were the oxygen-containing compounds, including organic acids, organic acid esters, phenols, aldehydes, ketones, and quinones. These compounds account for 17% of the extractable organic matter and occur at concentrations averaging 3 mg/ℓ. When the amides (which contain both oxygen and nitrogen atoms) are included in the oxygenated values, they increase the percentage to 24% of the extractable material. The estimated content of oxygenated compounds in bitumen is 10%. It is therefore indicated that a large percentage of the oxygenated compounds found in upgrading plant effluents is likely formed during processing of the extracted bitumen.

Some low molecular weight oxygenated compounds such as phenols are toxic to fish (Leithe 1973a), and Zitko (1975) has predicted the toxicity of other low molecular weight oxygenated compounds on the basis of their chemical structure. Little is known of the toxicity to fish of higher molecular weight oxygenated compounds or of their effect upon other aquatic organisms.

Hydrocarbons and weakly polar compounds were the next most abundant group investigated. They comprise an average of 16%

of the extractable carbon, or 2.8 mg/ℓ. The main source of these compounds is the upgrading plant. Fifty-eight per cent were aliphatic hydrocarbons, 30% were aromatic hydrocarbons and 12% were polar compounds. The composition is more similar to that of synthetic crude oil, which is 79% aliphatics, than that of the raw bitumen which contains only 19% aliphatics. It is greatly different from that of the upstream river water which averaged only 4% aliphatics, confirming the upgrading plant as the source of these hydrocarbons.

The remaining constituents examined in the wastewaters were the asphaltenes, which account for 10% of the extractable organics, and the nitrogen-containing compounds, which account for 7%. As the synthetic crude produced by the upgrading plant is devoid of asphaltenes and the raw bitumen contains 17 to 19% asphaltenes (Strosher and Peake 1976; Berkowitz and Speight 1975), the asphaltenes in the upgrading plant effluents likely originated in the oil sands bitumen.

Several major groups of oxygen, nitrogen and sulphur-bearing compounds together with hydrocarbons were also detected and measured in tailings pond dike drainage waters and process effluents during the initial study conducted in 1975-76. A number of specific compounds were identified. However, many individual compounds remain to be identified, including some of the major class components. Considerable effort may be required to identify specific compounds which may be toxic. Organic acids, the most abundant group of compounds in the tailings pond dike drainage waters and mine depressurization waters, are chemically complex and their separation, determination of their structure, and their identification requires considerable effort. Similarly, other groups of organic compounds found in upgrading plant effluent and dike filter drainage, such as organic sulphur compounds, and require further investigation. Phenols, although not one of the major constituents, are nevertheless present in significant amounts and warrant further investigation, as do other less abundant groups of compounds. Polycyclic aromatic hydrocarbons occur in small quantities. This class of organic compounds includes a number of known carcinogens and bears further investigation to determine to what extent these compounds exist in effluents from oil sands extraction and processing. The organic constituents of oil sands wastewaters require further characterization and the major components of each group of compounds, the organic acids, organic sulphur compounds, phenols, and aromatic hydrocarbons need further identification. The identification of these compounds would facilitate studies of their toxicity to aquatic flora and fauna and may aid in the development of procedures for their removal.

4.2 MINE DEPRESSURIZATION WATERS

Mining operations in Syncrude lease 17 require the lowering of the water table by pumping groundwater from wells in the mine area. The mine waters contained an average 30 mg/ℓ of total organic carbon, of which 62%, or 19 mg/ℓ, was in the form of extractable organic carbon. This relatively high level of extractable carbon indicates that the organic compounds are likely either directly dissolved or dispersed in a micellar form within these waters.

Oxygen-containing compounds were the most abundant group of compounds in the mine water composites, averaging 24% of the extractable organics, or 4.6 mg/ℓ. The majority of these compounds were in the form of organic acids (39%) and organic acid esters (28%). Phenols, aldehydes, and quinones comprised the remaining 33% of the oxygenated compounds. Although bitumen contains an average 10% of oxygen-containing compounds, these compounds are preferentially dissolved from the bitumen by the slightly basic groundwaters, a natural process somewhat analogous to the more potent alkali extraction method used in commercial oil sands extraction.

The high percentage of oxygenated compounds in the mine depressurization waters is in keeping with previous findings in tailings pond waters where 89% of the extractable carbon was as oxygenated compounds, mainly organic acids.

Organic sulphur compounds represented 15% of the extractable organic matter, or 3 mg/ℓ. Asphaltenes were the next in abundance, comprising 14% of the extractables (2.6 mg/ℓ). Both nitrogen-containing compounds (2%) and hydrocarbons (1%) were very minor contributors to the extractable organic matter. Sulphur compounds and asphaltene contents of the waters are in close proportion to the respective 17% organic sulphur and 19% asphaltene content of the bitumen; however, the hydrocarbons and nitrogen compounds are not extracted by the basic groundwaters.

The above analyses represent only two samples taken during September and November of 1976. Further analyses are required to determine changes in the amount or types of organic compounds which occur as a result of extensive dewatering.

4.3 COKE STORAGE RUNOFF

Coking of the Athabasca bitumen, with its mainly cyclic chemical structures and O, N, and S content, is likely to produce a wide variety of organic compounds. It is indicated that some of these compounds are being leached from the coke piles by meteoric water. Meteoric water percolating through the coke storage pile and sand tailings, used to contain the coke, contained 25 mg/ℓ total organic carbon, of which 60%, or 15 mg/ℓ, was in the form of extractable organic carbon. The finding of a high percentage of extractable organic carbon in the coke runoff is not surprising as the coke contains traces of synthetic crude oil including aliphatic and aromatic hydrocarbons and weakly polar compounds. The source of the unextractable carbon is less clear; it may be coke particles or carbon associated with clay particles derived from sand tailings used to contain the coke pile.

Asphaltenes, at 18% or 2.7 mg/ℓ, were found to be the major component of the extractable organics in the coke storage waters. These compounds could be derived either from the sand tailings where some bituminous material still remains, or from the coke pile, which is basically the carbonaceous residue from the upgrading process.

Oxygen-containing compounds accounted for 13% of the extractable organic matter and organic sulphur compounds for 11%. Oxygenated compound values are in keeping with the 10% contained in bitumen; these compounds could therefore be derived from the sand tailings. However, processing of bitumen does produce oxygen-containing organics, some of which could be carried into the coke. In the delayed coking process used by GCOS, sulphur which occurs as both inorganic and organic sulphur compounds in the bitumen, is partially retained in the coke. On the basis of benzothiophene, a 4 to 5% sulphur content of the coke would result in 24% of the organic compounds bearing sulphur, readily accounting for the 11% sulphur-containing organic compounds found in the coke runoff.

The remaining groups of compounds measured in the extractable organic matter were the nitrogen-containing compounds at 2% and the hydrocarbons at 1%. These compounds may be derived from either the bitumen or the upgrading process.

The amount and composition of organic material contained in the coke storage runoff may be a function of the volume of water flow and the temperature of the coke pile. Regular flow measurements and analyses would be required to determine the contribution of organic material from the coke pile to the river and to groundwaters.

4.4 ATHABASCA RIVER SYSTEM

Rivers contain a variety of organic compounds, both dissolved in the water and attached to suspended sediments. Although the role of these organic compounds is little understood, they are believed to affect and regulate the flora and fauna, playing vital roles in such activities as the spawning of fish. River sediments act as a sink for organic compounds which may be either natural or introduced to the river by man.

Athabasca River samples consisted of water and bottom sediment samples immediately upstream and 10 km downstream from the GCOS extraction plant. Upstream waters contained an average 13 mg/ℓ total organic carbon, 24% of which was extractable. In comparison, downstream waters averaged 15 mg/ℓ of total organic carbon with extractable organic carbon content also being 24%. The high values of unextractable material are directly related to the humic and fulvic acid content of these waters, which average 10 mg/ℓ (water quality data supplied by B. Froleich, AOSERP, May 1977 and carried out by Water Quality Branch, Inland Waters Directorate).

Organic carbon values for sediments were determined from the extractable organic material. These values averaged 480 mg/kg of dry sediment in the upstream samples and 668 mg/kg of dry sediment in the downstream samples. All water samples were collected in the main channel of the river whereas sediments were collected in three different locations. The September 1976 sediments were both collected within 10 m of shore, the December 1976 samples approximately 100 m from shore, and February 1977 samples in the main channel. These locations are noted because of the variations in relative organic composition of the sediment samples.

Asphaltenes were the largest single component of the organics in the river system. Asphaltenes comprised 20 to 40% of the extracted organic matter in the upstream sediment samples and 30 to 39% in the downstream sediments. The comparative asphaltic content of oil sands bitumen (17 to 19%) implies that the organic matter contained in the sediments is not composed mainly of unaltered bitumen but that a partitioning of bitumen is taking place within the river system whereby oily materials are partially removed by the waters. The sediments, acting as a sink, are thus enriched in asphaltic content. Upgrading plant effluents, which also contain asphaltenes, may contribute to the sediments in the same way, thereby partially accounting for the increased asphaltene content of the downstream sediments. Asphaltic enrichment due to hydrocarbon depletion from bacteriological activity is considered minimal in light of hydrocarbon data which follow.

Hydrocarbons, including both aliphatic and aromatic compounds, were the second major group of compounds found in sediment samples and comprised an average of 7% of the organic matter in upstream sediments and 10% in the downstream sediments. By comparison, these hydrocarbon values in the respective water samples were relatively low--0.7% of the extractables were measured in the upstream samples and 0.9% were found in the downstream waters. These hydrocarbons, however low in value, play an extremely important role in determining the effect of natural and disturbed organic loading upon this river system.

The comparison of amounts and relative composition of the oily fractions of these samples in terms of aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds reveals a number of processes which take place in the river system. The upstream river waters contain 14% of these measurable compounds as aliphatic hydrocarbons, 20% as aromatics, and 66% as polar compounds. Downstream waters revealed slightly different values with 26% as aliphatic hydrocarbons, 20% as aromatics, and 54% as polar compounds. In comparison, the composition of these measurable organic compounds in the sediments was very different, with upstream sediments containing 64% aliphatics, 23% aromatics, and 13% polar compounds while downstream sediments contained 54% as aliphatics, 39% as aromatics, and 7% as polar compounds.

It is apparent that the composition of these oily constituents of the sediments are very different from those of the river waters indicating that a fractionation process occurs between the water and sediments in the river system. The more polar compounds show a greater affinity for the water than do the hydrocarbons; as a result, they are readily transported by the river waters away from the sediments, whose alphatic content is thus increased.

The difference in the composition of oily material found in the sediments above and below the GCOS plant on the Athabasca river lies primarily in the relative proportion of aromatic hydrocarbons. Such a difference could be caused by a contribution of these hydrocarbons to the sediment by the effluent from the GCOS plant if such effluent contained a greater proportion of aromatics than are normally found in the Athabasca bitumen (22 to 28%). Although the data are sparse, two of the three upgrading plant effluent samples collected in this study and two of four samples in the previous investigation did contain aromatic values greater than 28%. These aromatic values are also enhanced by evaporation processes of the lighter aliphatic hydrocarbons and the affinity of the river waters for the more polar compounds, thus accounting for the higher aromatic values in the downstream sediments.

Results of the February 1977 sampling show the downstream movement of pollutants released to the Athabasca river from the GCOS plant. Aliphatic and aromatic hydrocarbon fractions from the GCOS upgrading plant effluent were directly comparable in composition to the aliphatic and aromatic hydrocarbon fractions of the downstream river water sample, and both were in sharp contrast to those of the upstream waters. Based on the measured quantities in the effluent and the downstream water sample, aliphatic hydrocarbon dilution was found to be 70-fold and was substantiated by the aromatic dilution values of 65:1. River flows were low, 7,800 cfs (August 1977 communique from Water Survey of Canada, Inland Waters Directorate) and the river was ice-covered. Dilution rates were measured on the Athabasca river in February 1974 using neutral dyes (communique dated 29 September 1977 from S. Beltaos, Research Officer, Alberta Research Council). Dilution rates depend upon the flow of the river, the amount of effluent discharged, the distance downstream from the discharge, and the sampling location relative to the main channel of the river. Based upon information obtained in these studies, the estimated dilution value 10 km downstream from the GCOS outfall is 130 times.

In view of the large number of variables this value is in reasonable agreement with that determined by measurement of the aliphatic and aromatic hydrocarbons.

Seasonal effects are evident in the occurrence of low molecular weight dissolved hydrocarbons, which are present in the winter water samples but lacking in the samples taken during September 1976. In the summer, when river waters are exposed to the air, these hydrocarbons diffuse to the atmosphere. In the winter, ice cover prevents this natural aeration. Clearly, low molecular weight dissolved hydrocarbons, which make up the bulk of the hydrocarbons discharged with the process effluent to the river, are retained in the river water and are carried downstream under the ice.

Though quantities of these hydrocarbons in the river are small, even during winter months, minute amounts of dissolved aromatic hydrocarbons are known to be toxic to fish; for example, the critical concentration of naphthalene is 2.5 to 5 mg/ℓ (Leith 1973b).

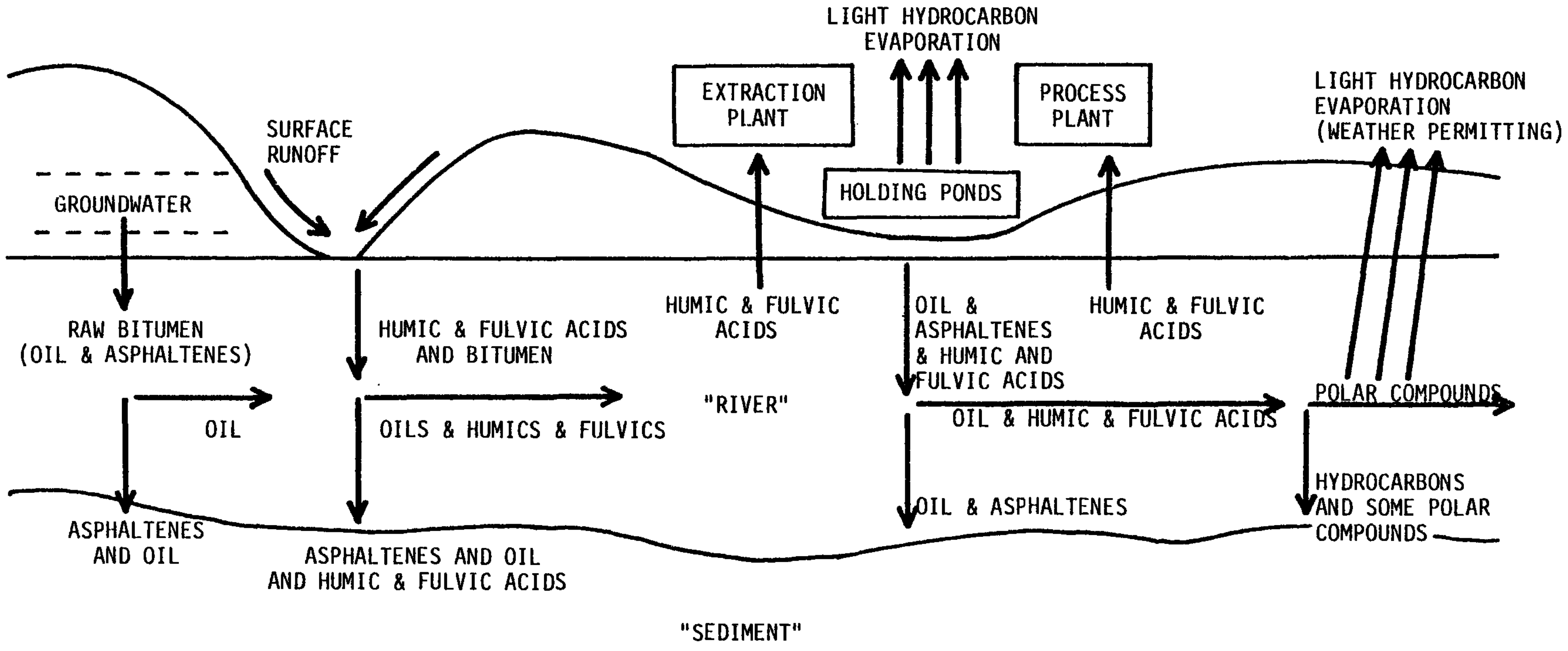
The remaining data obtained on the various samples from the river system substantiate some of the previous findings. Oxygen-, nitrogen-, and sulphur-containing compounds which comprise the polar compounds account for about 29% of the extractable organic matter in river water samples. In comparison, these compounds only account for approximately 5% of the organic matter in the river sediments.

No pronounced differences in the organic constituents of the river as a function of the volume of flow were found. The discharge of the Athabasca river below Fort McMurray was 46,300 cfs at the time of the first sampling 14 September 1976, as compared with the 1976 mean of 24,000 cfs. The flow rates on the other sampling dates were much lower, 7,000 cfs on 15 December and 7,300 cfs on 17 February 1977 (August 1977 communique from Water Survey of Canada, Inland Waters Directorate). Undoubtedly, seasonal differences do occur in the organic components of the river particularly during the spring runoff, but three samples over a 6-month period are insufficient to indicate any seasonal changes which may occur. Similarly, the amount and composition of the organic material in the plant effluents released to the river may vary over a period of a few days or even seasonally, but such differences would not be detected with the small number of samples taken during this study. Ideally, monthly analyses should be conducted on major effluent streams to determine the year-round organic load contributed by an oil sands extraction and upgrading plant to the Athabasca river. To evaluate the effect of present and future oil sands extraction and processing upon the organic constituents of the river system, samples of water and sediments should be taken at the following points:

1. Upstream from the Athabasca Oil Sands deposit;
2. Upstream and downstream from the existing oil sands plant;
3. At incremental distances downstream from the extraction plants; and
4. Near the Peace-Athabasca Delta.

The samples should be taken on a monthly basis.

Although care must be exercised in the interpretation of the present limited data, a model of the river system in terms of the organic constituents is emerging (Figure 17). This simplified model, albeit incomplete, without quantification or kinetics, does provide a vehicle to better understand the mechanics of the river system.



ALL SEDIMENTS EXCEPT MAIN CHANNEL
ENRICHED IN ASPHALTENES

Figure 17. Model of the Athabasca River in terms of organic constituents as measured in the oil sands mining area.

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6. APPENDICES

6.1 LIST OF ABBREVIATIONS AND SYMBOLS

ASTM	American Society for Testing and Materials
BF_3	boron trifluoride
°C	degrees Celsius (centigrade)
cm^3	cubic centimetres
cfs	cubic feet/sec (0.03 cubic metres/sec)
g	gram
GC	gas chromatograph
HCl	hydrochloric acid
kg	kilogram
KOH	potassium hydroxide
ℓ	litre
m	metre
m^3	cubic metre
MeI	methyl iodide
MeOH	methanol
mg	milligram (10^{-3} gram)
min	minutes
ml	millilitre (10^{-3} litre)
mm	millimetre (10^{-3} metre)
N	nitrogen
NaOH	sodium hydroxide
Ni	Nickel
O	Oxygen
pH	hydrogen-ion exponent
ppm	parts per million
S	sulphur
V/V	volume/volume

6.2 TERMS OF REFERENCE

6.2.1 General Objectives

To study the chemical nature of organic contaminants in effluents from oil sands mining, extraction, and processing plants and to measure the contribution of these organic constituents to the Athabasca River system to achieve an understanding of the environmental impact of such effluents.

6.2.2 Statement of Work

To conduct a study which includes but does not limit analyses in accordance with amended July 1976 proposal as follows:

1. Three samples of upgrading plant effluent;
2. One sample of coke storage runoff;
3. Two samples of Syncrude mine depressurization waters; and
4. Three samples of the Athabasca River water and sediment both upstream and downstream from GCOS.

6.2.2.1 Year round assessment of the organic load in effluents from the GCOS extraction plant. The limited duration of the initial study allowed sampling of only two effluent streams, the process waste waters and one portion of the tailings pond dike drainage, during November and December of 1975. Sampling over a short time frame during the winter months may not be representative of actual year-round conditions. Ideally monthly analysis should be conducted on major effluent streams to establish the year-round organic load contributed to the Athabasca River. In view of the complexity of the complete analysis for organic compounds it is proposed that: quarterly samples of the process effluent be taken by AOSERP and that these samples be analyzed by the Environmental Sciences Centre (Kananaskis) for TOC, TON, extractable organic carbon, organic acids, phenols, organic esters, sulphur compounds, nitrogen compounds, oxygenated compounds (aldehydes, ketones, etc.) and hydrocarbons.

So data may be obtained for a full year it is proposed that sampling begin one month after the awarding of the contract and continue for a full year. It is therefore estimated that sampling will begin 1 September 1976; however, fiscal constraint of the contract limits the study to 31 March 1977.

6.2.2.2 Organic contaminants of coke storage area runoff. The previous study was confined to a dike drainage effluent and process wastewater. It is proposed that an additional effluent be analyzed, namely drainage from the coke storage area.

Coking of the Athabasca bitumen with its mainly cyclic chemical structures and O, N, and S content is likely to produce a wide variety of organic compounds. It is to be expected that some of these compounds will be leached from the coke piles by meteoric water. It is recommended that one sample be taken during the summer of 1976 and three additional samples during the spring and fall of 1977 from coke storage runoff and that these waters be analyzed for the complete range of organic compounds as per section 6.2.2.1.

6.2.2.3 Organic constituents of Syncrude mine depressurization water. Mining operations in Syncrude lease 17 require the lowering of the water table by pumping groundwater from wells in the mine area. It is proposed to examine the organic constituents of these waters as per previous studies of effluents from the GCOS plants. Samples will be taken on a summer sampling basis over a three-year period (two samples in the 1976 fiscal year) and analyzed for a complete range of organic compounds to determine:

1. What compounds are present and in what concentration; and
2. If changes in the amount and types of organic compounds occur as a result of extensive dewatering.

6.2.2.4 Organic compounds in the Athabasca River system. Rivers contain a variety of organic compounds both dissolved in the water and attached to suspended sediments. Although the role of these organic compounds is little understood, they are believed to affect and regulate the flora and fauna and to play vital roles in such activities as the spawning of fish. River sediments may act as a sink for organic compounds which may be natural or introduced to the river by man. Ideally, to determine the effect of present and future oil sands extraction and processing upon the organic constituents of the river system, samples of water and sediments should be taken at the following points:

1. Upstream from the Athabasca Oil Sands deposit;
2. Upstream and downstream from existing oil sands plant;
3. Upstream and downstream from the Syncrude plant; and
4. Near the Peace-Athabasca Delta, the samples to be taken on a monthly basis.

A study of this magnitude would require substantial resources; it is therefore proposed that limited studies be initiated on waters and sediments upstream and downstream from the existing plant and upstream from the Athabasca Oil Sands deposit as an indication of the effect of the present extraction plant. Samples will be taken and analyzed on a quarterly basis during 1976-77.

6.3 ANALYTICAL METHODS

Analytical methods employed in this investigation consist of standard test methods, methods previously designed and adapted for this study, and methods developed specifically for this study. They include standard colorimetric tests, gravimetric analyses, analyses by a commercial carbon analyzer, and gas chromatographic analyses on groups of compounds previously extracted and separated by techniques developed or modified for the study. Analyses were carried out in duplicate with procedural and analytical blanks used throughout the investigations. The following is a more detailed description of the specific analytical methods employed.

6.3.1 Total Organic Carbon

Total organic carbon analyses were carried out on all water samples both as received and after extraction of the soluble organic compounds with benzene. Water samples were vigorously shaken before analysis to ensure a representative measurement of the total organic carbon content of these samples.

A Beckman Model 915 total carbon analyzer was used to obtain the organic carbon analysis on each water sample as received. The principle of detection is the conversion of carbon compounds to carbon dioxide, which in turn is measured by infrared spectrophotometry. The limits of detection as given by the manufacturer are ±1 mg/ℓ with a precision of 5%. Organic carbon analyses are calculated from the difference in total carbon and inorganic carbon measurements, thus giving a cumulative error of ±2 mg/ℓ. After measurement of the total organic carbon contents, samples were then extracted with benzene pH 2 and pH 9, 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 carbon extracted by benzene could be determined by difference and used as a basis for a carbon balance of organic material upon completion of the investigation.

The amount of extractable organic compounds in the sediment was obtained by weighing a portion of the acetone and benzene/methanol extracts and relating this to the dry weights of sediments. Organic carbon analysis of this weighted fraction revealed that 80% of this organic material occurred as organic carbon; thus, the total organic carbon content of sediments was calculated on this basis.

6.3.2 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.

6.3.3 Aliphatic Hydrocarbons

Aliquots 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 fraction eluted from the alumina with n-hexane contained 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 individual GC responses to normal straight chain aliphatic hydrocarbons in the range of nC_8- nC_{30}.

6.3.4 Aromatic Hydrocarbons

The second group of organic compounds to be separated on the alumina column was the aromatic hydrocarbon fraction which was eluted from the column with benzene. Analyses were conducted by gas chromatography as described in 6.3.3. Gas chromatographic responses were calibrated to the detector response to anthracene (Strosher and Hodgson 1975).

6.3.5 Polar Organic Compounds

Organic compounds eluted from the alumina column with methanol were designated as O, N, and S polar compounds. It should be noted, however, that O, N, and S compounds may also appear in hexane and benzene eluates from liquid chromatography on alumina, and that strongly polar compounds may be irretrievably absorbed by the alumina or may be undetectable by gas chromatography. In order to further fractionate the polar compounds, two solvents were successively passed through the alumina liquid chromatography column. The first was diethyl ether; the second was the more polar methanol. Gas chromatography, as previously described in 6.3.3 was used to analyze the polar compounds with quantitation based on the detector response to anthracene. 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 to assess possible degradation processes that might be taking place.

6.3.6 Sulphur Compounds

Samples were analyzed for organic sulphur compounds and elemental sulphur by a gas chromatograph equipped with a flame photometric detector (Martin and Hodgson 1973). A Tracor Model 560 gas chromatograph equipped with a flame photometric detector and linearizer were 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 was 65 cm^3/min, and air was 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 samples with responses based on the gas chromatographic detection of parathion and elemental sulphur.

6.3.7 Organic Phosphorous Compounds

Examination of extracts for the possible occurrences of organic phosphorous compounds was 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.

6.3.8 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. A Tracor Model 700 Hall electrolytic conductivity detector fitted to a Varian 2100 gas chromatograph was used to specifically detect the chlorinated compounds. 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. Oven temperature was programmed from 60 to 265°C at 10°C/min, injection port temperature was 200°C and delivery tube temperature was 225°C. The pyrolysis 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. Detection 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 alumina. Chlorinated hydrocarbons were eluted with hexane to try to eliminate the interfering polar compounds containing sulphur, phosphorous, and oxygen.

6.3.9 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 the same as listed in 6.3.8 and quantitation was based on the response to atrazine.

6.3.10 Aldehydes

A colorimetric test was conducted for aldehydes in which a derivative of 2,4-dinitrophenylhydrazone was formed in a combined acetic-hydrochloric acid media. The intensity of the resulting yellow-orange color was read with a spectrophotometer. As ketones also form derivatives by this method, they interfere in the aldehyde determination. Tests revealed that the largest interferences of ketones was created by the response of this test to acetone. Acetone responses were determined as one-third the response obtained for benzaldehyde to give the same spectrophotometric response. The aldehyde results were calculated and corrected on this basis. Quantitation was based upon the response of the aromatic aldehyde benzaldehyde (Pesez and Bartos 1974).

6.3.11 Ketones

The specific test used for ketone detection was a fluorometric method which relied upon the quenching effect that ketones have on the fluorescent compound, β-naphthol (Hynie and Vercerek 1961). Standard curves were obtained by adding various quantities of acetone to β-naphthol and measuring the difference in fluorescent intensities. Ketone concentrations in samples were accordingly measured by comparison with the acetone response. To ensure that the data represented ketones rather than interferences, analyses were carried out on the aldehyde, benzaldehyde, and the standard quinone, 1,4-benzoquinone. Results indicated that interferences by these compounds were low, requiring at least 50 times as much of the aldehyde or quinone to produce the same response as acetone. It was therefore concluded that results of this test represented a measurement of ketones and no corrections for interferences were necessary.

6.3.12 Quinones

Quinones were examined by a spectrophotometric method that measured their dinitrophenylhydrazone derivatives (Pesez and Bartos 1974). Unlike the aldehyde method which produced the yellow-orange derivative in an acid media that absorbed light in the region of 412 nm, the quinone derivative was developed with ammonium hydroxide which produced a brown-red to green complex which absorved light in the region of 550 nm. Possible interferences of similar oxygen-bonded compounds such as aliphatic acids, ketones, and aldehydes, were investigated and found to be negligible. Quantitation was based on the standard compound, 1,4-benzoquinone.

6.3.13 Amides

Another group of compounds analyzed by spectrophotometric methods was the amides. The principle of detection relied on the conversion of the amides to the corresponding hydroxomate. The hydroxomate was then developed for colorimetric analysis with ferric chloride (Pesez and Barton 1974). Results were based on a standard response curve obtained with a standard acetanilide.

6.3.14 Organic Esters

Esters were determined by differences in gas chromatographic response before and after saponification of the extractable material from individual samples. Gross quantitation of organic material was first obtained by gas chromatography. The organic material that saponified with potassium hydroxide to convert the esters of acids into free acids which are not detected by GC. The de-esterified product was re-examined by gas chromatography and the difference in the two chromatograms was attributed to the ester component. These GC results were calculated on the basis of the detector response to anthracene.

6.3.15 Phenolic Compounds

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 benzene. 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 unrelated 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 6.3.3 with detector response calibrated to anthracene.

6.3.16 Organic Acids

Organic acids were separated, derivatized and measured by gas chromatography as was described in the previous phenol analysis section.

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
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22.	HE 2.3	Maximization of Technical Training and Involvement of Area Manpower
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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
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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 from Fort McMurray: Volume I

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Alberta Oil Sands Environmental Research Program
15th Floor, Oxbridge Place
9820 - 106 Street
Edmonton, Alberta
T5K 2J6