SURVEY OF BASELINE LEVELS OF CONTAMINANTS IN AQUATIC BIOTA OF THE AOSERP STUDY AREA

by

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for

ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM
AQUATIC FAUNA SECTOR

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ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM
RESEARCH REPORTS

These research reports describe the results of investigations funded under the Alberta Oil Sands Environmental Research Program, which was established by agreement between the Governments of Alberta and Canada in February 1975.

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

Enquiries pertaining to the Alberta-Canada Agreement or other reports in the series should be directed to:

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Survey of Baseline Levels of Contaminants
in Aquatic Biota of the AOSERP Study Area

Project AF 2.1.1

AOSERP Report 17

LETTER OF TRANSMITTAL

The Hon. D. J. Russell
Minister of the Environment
222 Legislative Building
Edmonton, Alberta

and

The Hon. R. LeBlanc
Minister of Fisheries and the Environment
Parliament Buildings
Ottawa, Ontario.

Sirs:

Enclosed herein is the report on, "A Survey of Baseline Levels of Contaminants in Aquatic Biota of the AOSERP Study Area".

This report was prepared for the Alberta Oil Sands Environmental Research Program, through its Aquatic Fauna Sector, under the Alberta-Canada Agreement of 28 February 1975.

Respectfully,

W. Solodzuk, P.Eng.
Chairman, Steering Committee, AOSERP
Deputy Minister, Alberta Environment

J. S. Tener, Ph.D.
Member, Steering Committee, AOSERP
Assistant Deputy Minister
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Survey of Baseline Levels of Contaminants in Aquatic Biota Of The AOSERP Study Area

DESCRIPTIVE SUMMARY

ABSTRACT

Analyses are given for up to 12 metals and 4 pesticides with PCBs, of aquatic environment samples from 15 study sites along or near the Athabasca River from Fort McMurray north to the confluence of the Peace and Slave Rivers. There were 560 fish (8 species), 15 water, 14 sediment and a few phyto-plankton and invertebrate samples. Methods of analysis (by AAS and GLC) are outlined, and standard deviations and detection limits given. In a few cases, where suspected, elevated concentrations of metals and pesticides are discussed.

In fish, most As, Cr, Ni, V, Pb and Cd concentrations were close to detection limits (0.01, 0.1, 0.1, 0.04, 0.05, 0.01 μg/g, respectively). Cu, Hg, Se and Zn were not unusually high (means of 0.94, 0.15, 0.37, and 16.9 μg/g respectively); metal concentrations did not correlate well with body weight. Pesticides were mostly below detection limits, although yellow walleye and longnose sucker showed a few μg/g of methoxychlor, chlordane and dieldrin.

In water, As, Cr and Cd were mostly <1, <6 and <0.1 μg/ℓ respectively, below previously reported values for the Athabasca River at Fort McMurray. Cu (excepting 3 stations with 12 to 97 μg/ℓ) averaged 2 μg/ℓ. Fe, mostly particulate, and averaging 2500 μg/ℓ was higher than reported for many US waters, but in line with previous analyses for the area. Mn was also relatively high at 43 μg/ℓ, mean; it was particulate and also related to iron content. Ni (except for 2 stations) averaged 3.4 μg/ℓ, and V (one station excepted) was 3.1 μg/ℓ, mean. Vanadium was below the mean of 6 μg/ℓ found for many samples of drinking water in the US. Zn in 12 stations averaged 23 μg/ℓ, in line with earlier analyses from the area. Some high values may have been due to contamination. At the time samples were analyzed, phenol was below the detection limit but could have decomposed on storage.

Sediments were quite high in Fe content (5750 to 22400 μg/g) and in Mn (110 to over 300 μg/g). There were positive correlations

between iron content and in descending order, V, Zn, Mn, Se, As, Cu, Cr, with a weaker one for Cd. No metal concentrations seemed in any way unusual. Mercury contents were low. Ni and V content were positively correlated.

BACKGROUND AND PERSPECTIVE

This study was proposed in anticipation of potential adverse effects of industrial developments on aquatic ecosystems in the Athabasca oil sands region of northeastern Alberta. Through the mining, extraction and refining of the oil sands resource, the natural environment will be altered and it will be important to resource and environmental managers to be able to follow changes in the biophysio-chemical state of the environment and relate these to the development activities. With respect to the aquatic fauna, it is anticipated that certain components (metals, organics) will increase in concentration in the affected areas and, as a result, may increase in the flesh of the fauna. It is therefore important in defining the effects of oil sands development to be able to establish pre-development levels of contaminants in the aquatic ecosystem.

This study was initiated in August of 1975 to determine background levels of contaminants in aquatic fauna, water and sediments of the AOSERP study area. Four objectives were set forth at that time:

1. determine background levels of contaminants in fish, water, sediments, and invertebrates,
2. define the relationship between level of contaminant and size of fish,
3. identify natural sources of contamination,
4. provide baseline biological information on a number of potential sites for further experimental work.

ASSESSMENT

The report has been reviewed by the Aquatic Fauna Technical Research Committee and the Oil Sands Environmental Study Group (OSESG). The OSESG notes that background data contained in the report will be very useful as oil sands development proceeds.

The content of this report does not necessarily reflect the views of Alberta Environment, Fisheries and Environment Canada or the Oil Sands Environmental Study Group. The mention of trade names for commercial products does not constitute an endorsement or recommendation for use.

The Aquatic Fauna Technical Research Committee under the Chairmanship of Mr. J.S. Loch, Fisheries and Marine Service, Fisheries and Environment Canada, Winnipeg has recommended this report for publication. The Alberta Oil Sands Environmental Research Program on behalf of the Aquatic Fauna Technical Research Committee accepts the report, "Survey of Baseline Levels of Contaminants in Aquatic Biota of the AOSERP Study Area" as an important and valid background document and thanks the researchers for their contributions.

S. B. SMITH, Program Director
Alberta Oil Sands Environmental
Research Program

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Analyses are given for up to 12 metals and 4 pesticides with PCBs, of aquatic environmental samples from 15 study sites along or near the Athabasca River from Fort McMurray north to the confluence of the Peace and Slave Rivers. There were 560 fish (8 species), 15 water, 14 sediments and a few phytoplankton and invertebrate samples. Methods of analysis (by AAS and GLC) are outlined, and standard deviations and detection limits given. In a few cases, where suspected, elevated concentrations of metals and pesticides are discussed.

In fish, most As, Cr, Ni, V, Pb and Cd concentrations were close to detection limits (0.01, 0.1, 0.1, 0.04, 0.05, 0.01 μg/g respectively). Cu, Hg, Se and Zn were not unusually high (means of 0.94, 0.15, 0.37, and 16.9 μg/g respectively); metal concentrations did not correlate well with body weight. Pesticides were mostly below detection limits, although yellow walleye and longnose sucker showed a few ng/g of methoxychlor, chlordane and dieldrin.

In water, As, Cr and Cd were mostly <1, <6 and <0.1 μg/ℓ respectively, below previously reported values for the Athabasca River at Fort McMurray. Cu (excepting 3 stations with 12 to 97 μg/ℓ) averaged 2 μg/ℓ. Fe, mostly particulate, and averaging 2500 μg/ℓ was higher than reported for many US waters, but in line with previous analyses for the area. Mn was also relatively high at 43 μg/ℓ, mean; it was particulate and also related to iron content. Ni, (except for 2 stations) averaged 3.4 μg/ℓ, and V (one station excepted) was 3.1 μg/ℓ, mean. Vanadium was below the mean of 6 μg/ℓ found for many samples of drinking water in the US. Zn in 12 stations averaged 23 μg/ℓ, in line with earlier analyses from the area. Some high values may have been due to contamination. At the time samples were analyzed, phenol was below the detection limit but could have decomposed on storage.

Sediments were quite high in Fe content (5750 to 22400 μg/g) and in Mn (110 to over 300 μg/g). There were positive

correlations between iron content and in descending order, V, Zn, Mn, Se, As, Cu, Cr, with a weaker one for Cd. No metal concentrations seemed in any way unusual. Mercury contents were low. Ni and V content were positively correlated.

1. INTRODUCTION

This study was proposed in August of 1975 to determine background levels of contaminants in aquatic fauna, water, and sediments in the AOSERP study area. Four main objectives were set forth at that time:

a) to determine background levels of contaminants in fish, water, sediments and invertebrates;
b) to define the relationship between level of contaminant and size of fish;
c) to identify natural sources of contamination;
d) to provide baseline biological information on a number of potential sites for further experimental work.

The study sites chosen were to represent the major water pathway in the area; above the industrial site starting at Fort McMurray to the south, at the industrial site, and downstream of the industrial site at Lake Athabasca to the north. Samples for this survey were obtained by Renewable Resources Consulting Service Ltd., Edmonton, Alberta (Appendix 8.1). Fifteen areas along the Athabasca River were chosen as collecting sites; subdivided into northern section, stations 1-5 and southern section, stations 7-16 (Fig. 1).

Four species of fish were to be collected; lake white fish (*Coregonus clupeaformis*), northern pike (*Esox lucius*), white sucker (*Catostomus commersoni*), and Arctic grayling (*Thymallus arcticus*). Some difficulty was experienced in obtaining the required number of fish from each station, consequently other species were included in the sampling; yellow walleye (*Stizostedion vitreum vitreum*), longnose sucker (*Catostomus catostomus*), burbot (*Lota lota*), and goldeye (*Hiodon alosoides*). The actual number and type of fish samples collected are given in Table 1.

Two water samples from each sampling site, one filtered through 0.45 μ Millipore filter and acidified; the other unfiltered and acidified were received in polyethylene containers in a frozen state. They were kept frozen until analyzed.

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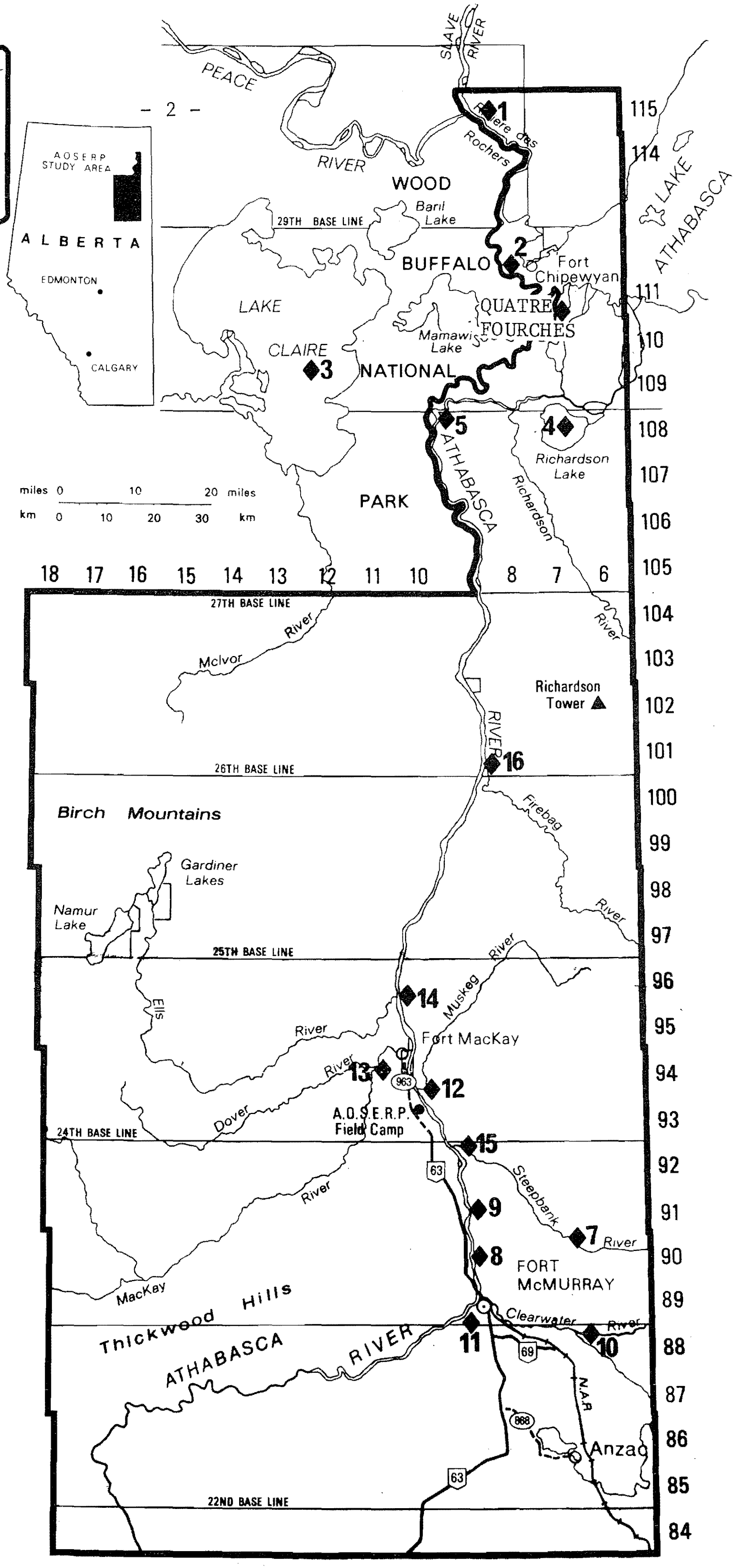

Produced by Surveys Branch, Alberta Transportation

WEST OF THE FOURTH MERIDIAN

FIGURE 1. Location of the AOSERP study area and sample sites.

Sediments from each site were received in a frozen state, kept frozen until analyzed.

There was a minimum of benthos and invertebrates which came to the laboratory in a frozen state. There was insufficient sample to do any chemical analysis on the benthic material, however, some plankton and invertebrates were analyzed.

2. METHODOLOGY

2.1 COLLECTION METHODOLOGY - See Appendix 8.1

2.2 ANALYTICAL METHODOLOGY - FISH

2.2.1 Sample Preparation. Whole individual fish were ground in a Hobart food grinder (using a medium cutter) by repeated passes through the grinder. Usually three passes through the grinder were sufficient to ensure a homogeneous sample. Fish were placed in individual labelled containers, refrozen and placed in -60°C refrigerator until used. Where there was sufficient fish from the same area and of the same weight they were blended together to form a pooled specimen for analysis. In a few areas small fish from the same area and species were also pooled.

For organochlorine pesticide analysis a composite sample from each sample site representing the four main species (sucker, yellow walleye, northern pike and lake whitefish) was made. It was not possible to obtain all the four species from every area, consequently only 44 analytical samples were obtained instead of the required 60.

2.2.2 Metal Analysis

2.2.2.1 Arsenic. One gram samples of fish homogenates were digested in 13 x 150 mm Pyrex tubes by addition of 5 ml of a mixture of nitric, sulfuric, and perchloric acids (10:4:1) in an aluminum block to SO_3 fumes. The clear digests were made to 25 ml volume with distilled water and an aliquot transferred to a sample cup for the estimation of arsenic by a modification of the semi-automated borohydride reduction method of Vijan and Wood (1974). The modification consisted of a heated quartz cell constructed with a quartz window and the inlet tube at the same end. Standards, blanks, and N.B.S. orchard leaves reference material[1] were carried through the entire procedure. An electrodeless discharge hollow cathode arsenic lamp was used with a Perkin Elmer 403 Atomic Absorption Spectrophotometer at 193.7 nm.

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[1] National Bureau of Standards, Office of Standard Reference Materials. Washington, D. C. 20234

2.2.2.2 Cadmium, Chromium, Copper, Lead, Nickel, Vanadium, and Zinc. Twenty-five gram samples were taken to dryness on a hot plate with 20 ml concentrated nitric acid and then ashed in a muffle furnace for 10-12 hours at 450°C. The ash was dissolved in 2 ml concentrated nitric acid and made to volume with distilled water (Chemical Procedures, National Shellfish Sanitation Program, 1975). Standards, blanks, and N.B.S. bovine liver reference material[1] were taken through the entire procedure.

Cadmium, Chromium, Copper, Nickel, and Zinc - were analyzed directly by flame atomic absorption spectroscopy using their respective resonance line and a nearby non-absorbing line to correct for background interference (Van Loon, 1973). Quantitation was against suitable standards.

Lead - an aliquot of the fish ash digest was extracted with a 1% (w/v) solution of diethyl ammonium diethyldithiocarbamate in spectrograde n-butyl acetate and analyzed by flame atomic absorption using the 217 nm line.

Vanadium - the pH of a sample aliquot was adjusted to 2.8 - 3.2 followed by addition of 5 ml 2% (w/v) ascorbic acid, 5 ml acetate buffer pH 3.2, and 3 ml of 0.3% (w/v) 5,7-dichloro-oxine in n-butyl acetate (Chau & Lum-Shue-Chan, 1970). The sample was shaken for twenty-five minutes, layers allowed to separate, and the organic layer aspirated into a nitrous oxide-acetylene flame.

2.2.2.3 Mercury. All fish samples were analyzed by the method of Hendzel and Jamieson (1976).

2.2.2.4 Selenium. All fish samples were analyzed by the method of Beal (1975).

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[1] National Bureau of Standards, Office of Standard Reference Materials. Washington, D.C. 20234

2.2.3 Organochlorine Pesticide Residues

Five gram samples were extracted with 25 ml of 3:1 (v/v) ethyl acetate - toluene mixture for one minute using a Polytron PT Homogenizer (Brinkman Instruments). Five ml of the filtered extract was placed on a Autoprep 1001 Gel Permeation Chromatograph (Analytical Biochemical Laboratories Inc., Columbus, Missouri) for automated clean-up according to the method of Johnson et al. (1976).

The cleaned-up eluent was brought to volume and injected into a Hewlett Packard 5750 gas chromatograph equipped with a Ni^{63} electron capture detector. The column was 4'x4 mm I.D. 2% OV-1, 4% OV-210 on Chromosorb W HMDS (acid-washed).

2.3 ANALYTICAL METHODOLOGY - WATER

2.3.1 Metal Analysis

2.3.1.1 Arsenic. Twenty milliliters of water were acidified with sulfuric acid and analyzed by the modified borohydride reduction method of Vijan and Wood (1974) (see 2.2.2.1).

2.3.1.2 Cadmium, Copper, Chromium, Iron, Manganese, Lead, Nickel, Vanadium, and Zinc. A 750 ml portion of water was gently evaporated on a hot plate in silica beaker to near dryness and then made to 25 ml volume with quartz distilled water.

Iron, Manganese, and Zinc - were analyzed using an air acetylene flame on the Varian AA5 Atomic Absorption Spectrophotometer with a BC-6 simultaneous background corrector to compensate for any non-specific absorption.

Copper, Chromium, Cadmium, Lead, Nickel, and Vanadium - the concentrates were analyzed by carbon rod atomization using the model 63 Carbon Rod Atomizer on a Varian AA5 Atomic Absorption Spectrophotometer with a BC-6 simultaneous background corrector.

2.3.2 Phenol by Gas Liquid Chromatography

Samples were analyzed for phenol using 100 ml of water and extracted with 20 ml chloroform (Murray, 1975).

2.4 ANALYTICAL METHODOLOGY - SEDIMENT

2.4.1 Sample Preparation

Sediments were air dried, ground in a Fisher Mortar Grinder and passed through a 1 mm mesh stainless steel screen.

2.4.2 Metal Analysis

2.4.2.1 Mercury. One gram dry sediment was digested with 10 ml aqua regia, hydrochloric:nitric acids (3:1), and made to 25 ml volume. Standards and blanks were carried through the procedure. An aliquot of this digest was analyzed for mercury by the semi-automated method of Armstrong and Uthe (1971).

2.4.2.2 Chromium, Copper, Iron, Manganese, Nickel, Zinc, and Vanadium. One-half gram dry sediment was weighed into a platinum crucible; wetted with a few drops of 20% (v/v) sulfuric acid, 1 ml of hydrofluoric acid was added and heated on a hot plate to dryness. The hydrofluoric acid treatment was repeated twice more. To the cooled crucible one-half gram of potassium persulfate was added and the sample was fused over a Meker burner. The fused sample was dissolved in hot hydrochloric acid (1:1) and made up to 25 ml volume. Standards and blanks were similarly treated. Aliquots (or diluted aliquots) of these digests were analyzed for the above metals (except vanadium) using an air-acetylene flame on a Varian AA5 Atomic Absorption Spectrophotometer equipped with a Model BC-6 simultaneous background corrector. Vanadium was analyzed using a nitrous oxide-acetylene flame on a Perkin Elmer 403 Atomic Absorption Spectrophotometer. No background absorption was evident on checking these samples.

2.4.2.3 Cadmium and Lead. Portions of the mercury digests were diluted and aliquots injected into the carbon rod of a Model 63 Varian Carbon Rod Atomizer and subjected to the appropriate drying, ashing, and atomization cycles. Standards and blanks were similarly treated. The BC-6 simultaneous background corrector was used to correct for any non-specific absorption.

2.4.2.4 Arsenic and Selenium. Two grams of dried sediment were digested in aqua regia and carefully heated at low heat to dryness, then taken up in 7.5 ml hydrochloric acid and made to 25 ml volume. Aliquots were analyzed for arsenic by the modified borohydride reduction method of Vijan and Wood (1974) (see 2.2.2.1).

The digest being 30% with respect to hydrochloric acid enabled selenium to be done on the same solution (Vijan and Wood, 1976). A selenium electrodeless discharge lamp was used with the Perkin Elmer 403 Atomic Absorption Spectrophotometer set at 196.0 nm. The manifold and instrument parameters were the same as for the determination of arsenic. Blanks and standards were carried through the whole procedure.

2.4.2.5 Loss on Ignition. Five gram sediment samples were weighed into porcelain crucibles and placed in a muffle furnace. The temperature was raised to 600°C and the furnace was kept at that temperature for four hours. The samples were cooled, dessicated, and weighed to a constant weight. The loss in weight represented organic matter.

2.5 ANALYTICAL METHODOLOGY - INVERTEBRATES & PLANKTON

2.5.1 Sample Preparation

Samples were thawed and dried at 105°C overnight. Invertebrate samples were ground in a Wiley mill. Plankton samples were dried in tared acid washed glass dishes and transferred into digestion tubes by addition of nitric acid to solubilize the residue.

2.5.2 Metal Analysis

Portions of invertebrate samples were weighed into digestion tubes and heated after addition of 5 ml nitric acid to near charring. The samples were removed from the hot block and 50% hydrogen peroxide added until clear. The samples were made up to 25 ml volume and atomic absorption analysis was performed on the following metals: Cd, Cr, Cu, Fe, Mn, V, and Zn as previously described.

3. RESULTS & DISCUSSION

3.1 FISH

3.1.1 Metals

For all species, the majority of chromium, nickel, vanadium, lead, and cadmium values were close to or below the detection limits for these metals, that is 0.1, 0.1, 0.04, 0.05, and 0.01 µg/g respectively. This is normally the case for freshwater fish taken from unpolluted areas.[2] Regression analyses (on log-log transformed data) to determine relationships between contaminant level and weight of fish were not done for these elements; however, correlation coefficients and t statistics were calculated for arsenic, copper, mercury, selenium, and zinc where the number of samples was ≥ 3. The majority of t statistics, calculated at the 95% level of confidence, indicated weak relationships between level of contaminant and weight of the fish. Station 4 showed the greatest number of correlations; the most frequent and strongest being for mercury for whitefish, northern pike, and longnose sucker. It was expected that if weight-ppm relationships were found it would be for those samples taken from closed systems (lakes) as opposed to those sampled along the Athabasca River where the fish are highly mobile. Any significant r values that were found were not consistent for a particular metal for any one species or area.

Means and standard deviations were calculated for each of the metals for each species. This data is presented in Tables 2 to 9 together with mean weight and range. None of the metal levels found were unusually high and they agreed well with previously reported data (Hatfield et al., 1972 and Uthe and Bligh, 1971). There were no apparent trends regarding interstation differences but due to sampling inadequacies, this was understandable. There were large variations in the number of samples and mean weights, thereby making comparisons difficult. From the available data no

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[2] Unpublished data, Department of Fisheries and Environment, Industry Services Branch, Winnipeg.

one area appeared to be contaminated.

Overall mean metal levels were calculated for each of the metals for each species. These data are presented in Table 10. No one species has consistently higher metal levels than the others. Burbot showed the highest arsenic levels with a mean of 0.23 μg/g. Means for the other species analyzed ranged from <0.01 to 0.10 μg/g. High copper levels were found in longnose sucker at 1.28 μg/g and white sucker at 1.44 μg/g. Means of the other species analyzed ranged from 0.67 to 0.94 μg/g. Yellow walleye had the highest mercury concentration at 0.32 μg/g with means for the other species analyzed ranging from 0.09 to 0.19 μg/g. The highest selenium concentration was found in goldeye at 0.58 μg/g. Means of the other species analyzed ranged from 0.24 to 0.43 μg/g. Northern pike had the highest zinc concentration (36.1 μg/g), nearly double that for the next highest species, goldeye at 18.2 μg/g. Means for the other species analyzed ranged from 10.7 to 16.4 μg/g.

3.1.2 Organochlorine Pesticide Residues and Polychlorinated Biphenyls

The results of the gas chromatographic analysis is given in Table 11. The only species with measurable quantities of contaminants were yellow walleye and longnose sucker. The remainder were all less than the level of detection. This data agrees well with that previously reported (Hatfield et al., 1972).

3.2 WATER

Trace metal levels for As, Cd, Cr, Cu, Fe, Mn, Ni, V, and Zn are detailed in Table 12 for unfiltered water samples and Table 13 for filtered water samples. Analysis for mercury was not undertaken as the samples were not preserved properly for this metal (Feldman, 1974). Fish mercury levels and sediment mercury levels indicate that this metal would be in extremely low concentrations in the water and would not be considered a contaminant.

3.2.1 Metals

Results from all stations for arsenic, cadmium, and chromium are well below those reported in the Water Quality Data for Alberta for the station on the Athabasca River at Fort McMurray (Inland Waters Directorate, 1975). As only two of fifteen stations had arsenic values for unfiltered waters greater that 1 μg/ℓ, analysis for arsenic on the filtered samples was not attempted. The two stations having the higher arsenic values are Lake Claire (station 3) at 3.6 μg/ℓ and Richardson Lake (station 4) at 2.1 μg/ℓ. Ten of fifteen stations had higher cadmium levels in the filtered compared to unfiltered samples indicating contamination from the filtration apparatus (Robertson, 1968; Dulka and Risky, 1976). Cadmium values are low with a mean concentration level of 0.07 μg/ℓ. Chromium values are all less than the average value reported (10 μg/ℓ) in the Athabasca River at Fort McMurray in the Water Quality Data for Alberta (Inland Waters Directorate, 1975).

Results for copper from station 5, 8, and 11 are 12, 24, and 97 μg/ℓ respectively and may indicate possible contamination in spite of the precautions taken. The remainder of the stations have a mean of 2.0 μg/ℓ which compares with the values obtained for the Athabasca River at Fort McMurray by the Inland Waters Directorate (1975) whose average is 3 μg/ℓ. At these low copper concentration levels the problem of contamination appears to be evident on the filtered samples as well.

Iron values range from a low of 449 μg/ℓ at station 7 to a high of 8040 μg/ℓ at station 3. These values are much higher than those obtained from 1500 samples from waters within the United States (Kopp & Kroner, 1969) but they would appear within the range of data from this area as reported by the Inland Waters Directorate for Alberta (1975); Athabasca River at Fort McMurray 1400 μg/ℓ; Clearwater River at Fort McMurray 1500 μg/ℓ; and Athabasca River at Athabasca - high 13400 μg/ℓ, average 2600 μg/ℓ. Mean of these fifteen stations is 2520 μg/ℓ. The major portion of the iron is present in the particulate form as evidenced by the low filtered values.

The mean for manganese of all stations except 3 and 4 is 43 ± 11 μg/ℓ. Stations 3 and 4 have values of 226 and 164 respectively. The mean for the Athabasca River at Fort McMurray is 50 μg/ℓ, however, the Athabasca River at Athabasca has a high of 650 μg/ℓ. As can be expected the manganese follows the trend of iron and is present in the water mainly as particulate with much lower values in the filtered samples.

Two stations, 3 and 11 had 12 and 17 μg/ℓ nickel respectively while the remainder had a mean of 3.4 μg/ℓ. These values are similar to the results from the Athabasca River at Fort McMurray - average 4 μg/ℓ. The high values are not quite as high as that reported for the Athabasca River at Athabasca (19 μg/ℓ).

Station 3 had the highest value for vanadium - 13.0 μg/ℓ, the remaining stations had a mean of 3.1 μg/ℓ. These low values are within the mean concentration of 6 μg/ℓ found in United States drinking water (Standard Methods, 1971).

The mean value for zinc from station 1-12 was 23 μg/ℓ. These values are within the levels recorded for the Athabasca River at Athabasca by the Inland Waters Directorate (1975). The ubiquitous nature of zinc does not preclude the possible contamination of samples from the other four sites. Contamination from the filtering apparatus is a possibility in the filtered samples (Robertson, 1968).

3.2.2 Organics

Phenol. At a detection limit of 0.1 μg/ℓ, no phenol was detected. A standard phenol solution at a concentration of 1.0 μg/ℓ showed a 30% loss in three days at room temperature, so if phenol was present in small amounts, it would probably have decomposed before analysis. Head space analysis showed some peaks in freshly thawed water samples which disappeared rapidly on storage.

3.3 SEDIMENTS

Heavy metal data are presented in Table 14. Two digestion procedures were attempted. It was discovered that the aqua regia digestion was inadequate for the release of all these metals into solution. The greatest discrepancy occurred in the concentrations of chromium, nickel, and vanadium. Copper, cadmium, iron, manganese, lead, and zinc values did not change appreciably.

3.3.1 Metals

Arsenic concentrations were low with a mean of 3.2 μg/g, ranging from 0.46 to 6.9 μg/g. Station 1 had a concentration of 0.60 μg/g cadmium while the remaining thirteen all had less than 0.2 μg/g. Chromium concentrations varied from 34 to 116 μg/g with a mean of 77.8 μg/g. Copper concentrations ranged from 2.4 to 59.5 μg/g, with a mean of 21.4 μg/g.

The high iron concentrations in the sediments (5750-22,400 μg/g) were reflected in the relatively high concentrations present in the water (756-8040 μg/ℓ), invertebrates (212-3230 μg/g dry wt.) and plankton (8040-38600 μg/g dry wt.). Iron had a significant positive correlation with the following metals in the order V>Zn>Mn>Se>As>Cu>Pb>Cr>Cd, with their respective r values of 0.95; 0.94; 0.90; 0.87; 0.85; 0.70; 0.69; 0.66; 0.60.

The mean value for manganese was 230 μg/g, ranging from 101 to 327 μg/g.

Station 1 (Slave River) had a concentration of 30.4 μg/g and station 4 (Richardson Lake) 13.8 μg/g; the remainder all are less than 10 μg/g lead. The mean value for lead is 7.4 μg/g.

Nickel concentrations ranged from 9.0 to 87.8 μg/g with a mean of 33.2 μg/g. The presence of bitumen suggests that there be a correlation between nickel and vanadium (Barry et al, 1975). There is a slight positive nickel:vanadium correlation of 0.66 in the sediments although no such correlation exists in the water.

Selenium concentrations were low with a mean of 0.23 μg/g, ranging from 0.02 to 0.65 μg/g.

Vanadium values ranged from 12 to 102 μg/g with a mean of 53.9 μg/g.

Zinc values ranged from 10.5 to 75.8 with a mean of 41.7 μg/g.

Mercury levels were low, with a few at or below the detection limit. The highest concentration was 0.05 μg/g.

3.4 INVERTEBRATES

3.4.1 Metals

The invertebrates submitted were Hemiptera and results of metal analysis are presented in Table 15. Not all stations were sampled and due to sample size not all metal analyses were completed. Cadmium, iron, manganese, and nickel had mean values of 1.6, 1460, 121, and 17.3 μg/g (dry wt.) respectively, and had a wide range as evidenced by their respective standard deviations of 1.8, 1180, 127, and 13.5. Chromium, copper, lead, and zinc had means of 2.7, 25.6, 31.8, and 160 μg/g (dry wt.) respectively with a much narrower range and standard deviations of 0.89, 4.5, 6.4, and 22.8 respectively. Mercury levels were low (mean 0.12 μg/g dry wt.) and represented background levels.

3.5 PLANKTON

3.5.1 Metals

Heavy metal data are presented in Table 16. The stations represented were the three lakes; Athabasca (station 2), Claire (station 3), Richardson (station 4), and a sample from the Lower Birch River. Sample size restricted completion of all the metal analysis. There was no species identification of the plankton.

The mean cadmium concentration was 3.4 μg/g with three stations having identical values of 2.3 μg/g. Lake Richardson value was 6.7 μg/g cadmium. A mean of 12.4 μg/g was obtained for chromium and 255 μg/g for copper. Iron varied from 8040 to 15200 μg/g on samples taken from the lakes with a high of 38600 μg/g from the Lower Birch River. Manganese concentrations varied from 330 μg/g to 720 μg/g with a mean of 540 μg/g. Lead concentrations were constant from the lake samples (mean 198 μg/g) with a slightly lower concentration of 135 μg/g from the Lower Birch River. Vanadium results were variable from less than 10 to 200 μg/g with a mean of 110 μg/g. Nickel concentrations were variable as well, with a mean of 89 μg/g (range 51-110 μg/g). Zinc concentrations were more consistent with a mean of 327 μg/g, ranging from 246 to 470 µg/g.

Marine plankton concentrate metals 100-100,000 fold compared to their aqueous environment (Goldberg, 1965). The results in this report indicate that trace metals are similarly concentrated by freshwater organisms.

4. CONCLUSIONS

Mean metal concentrations of all substrates analyzed are presented in Table 17.

4.1 FISH

Variability in the sampling (species, size, location) restricted the statistical evaluation of the data. Any significant relationships between level of contaminant and weight of fish that were found did not correlate for species, data, or station. No natural sources of contamination were evident. Despite limitations caused by sampling, the data agrees well with that previously reported and is felt to be a true reflection of baseline levels in the area.

4.2 WATER

All metal concentrations in filtered water were well within the accepted values for human use as set by the Water Quality Criteria, 1972, Except for manganese and iron all other metals in the unfiltered waters fall into this category as well. However, iron and manganese are not considered toxic at these levels and are objectionable for aesthetic reasons only.

In this study the field crew had problems with the filter apparatus (Appendix 8.1), consequently, a number of anomalies exist where the filtered sample concentration is greater than the unfiltered. At these low levels, contamination is a real probability. With these irregularities in mind the values in this report appear to be consistant with data previously reported in unpolluted waters and are felt to be indicative of baseline levels.

4.3 SEDIMENTS

No data was available from the same geological location or unpolluted source for comparison. The reported values reflect the baseline levels of trace metals in the sediments in this area.

4.4 INVERTEBRATES

While the invertebrate metal levels are much greater than the detection limits, there does not appear to be any accumulation in the food chain (namely fish) as evidenced by the number of metals at or below the detection limits.

4.5 PLANKTON

For the metals studied there appears to be an accumulation of the metals by freshwater plankton.

5. RECOMMENDATIONS

Future studies of this nature should provide uniform sampling from site to site for a valid statistical evaluation. For fish, efforts should be concentrated on collecting only 4 or 5 species evenly distributed over an appropriate size range. With respect to water samples, fewer stations could be sampled but replicate samples should be taken to provide some degree of assurance against contamination.

Table 1. Fish Samples Received for Analysis from Renewable Resources Consulting Services Ltd.

	Species								
Sample Area	YW	NP	AG	GE	LW	WS	LS	BT	Total
Station 1 - Slave River	-	2	-	1	-	-	3	5	11
Station 2 - Lake Athabasca	-	28	-	-	2	-	-	-	30
Station 3 - Lake Claire	-	36	-	-	3	-	-	-	39
Quatre Fourches	1	-	-	-	13	2	-	-	16
Station 4 - Richardson Lake	4	32	-	-	72	-	6	-	114
Station 5 - Athabasca River (near Embarass)	15	24	-	-	22	9	-	-	70
Station 7 - Steepbank River	-	-	-	-	-	-	-	-	0
Station 8 - Athabasca River (at Clarke River)	15	1	4	4	17	1	11	-	53
Station 9 - Athabasca River (at McLean Creek)	17	1	6	7	16	-	2	-	49
Station 10 - Clearwater River	1	3	-	-	-	2	24	-	30
Station 11 - Athabasca River	7	1	2	-	28	-	15	-	53
Station 12 - Muskeg River	4	10	9	-	4	19	6	-	52
Station 13 - MacKay River	2	4	-	-	7	-	13	-	26
Station 14 - Ells River	-	-	-	-	-	-	-	-	0
Station 15 - Steepbank River	-	1	10	-	3	3	-	-	17
Station 16 - Firebag River	-	-	-	-	-	-	-	-	0
GRAND TOTAL	66	143	31	12	187	36	80	5	560

YW - Yellow Walleye
NP - Northern Pike
AG - Arctic Grayling
GE - Goldeye
LW - Lake Whitefish
WS - White Sucker
LS - Longnose Sucker
BT - Burbot

Table 2. Mean Metal Levels of Longnose Sucker.

Station	Number of Samples	Mean Weight and range (g)	Metal Level (µg/g wet weight)				
			As	Cu	Hg	Se	Zn
1	3	780(670-910)	0.06±0.04	1.3±0.10	0.21±0.09	0.54±0.08	13.8±2.2
4	6	1080(720-1960)	0.16±0.06	1.2±0.17	0.03±0.02	0.34±0.04	11.4±1.4
8	9	640(120-1340)	0.11±0.07	1.2±0.34	0.06±0.03	0.33±0.16	15.1±3.7
9	1	804	0.08	1.0	0.07	0.37	18.5
10	24	400(150-810)	0.04±0.03(17)	1.3±0.49	0.05±0.04	0.22±0.06	19.0±2.2
11	12	640(290-1570)	0.06±0.07	0.98±0.14	0.17±0.10(10)	0.42±0.10	14.0±2.7
12	6	1020(240-1730)	0.18±0.10	1.08±0.18	0.11±0.04	0.36±0.05	13.5±2.8
13	13	1210(660-1810)	0.19±0.09	1.7±0.84	0.08±0.06	0.43±0.17	11.0±1.4

Where (n) = number of samples analyzed if different from that specified for each station.

Table 3. Mean Metal Levels of Lake Whitefish.

Station	Number of Samples	Mean Weight and Range (g)	Metal Level (μg/g wet weight)				
			As	Cu	Hg	Se	Zn
2	1	418	0.12	0.60	0.10	0.29	18.8
3	3	470(120-790)	0.05±0.04	0.76±0.21	0.10±0.03	0.35±0.02	14.4±1.4
Quatre Fourches	8	400(220-730)	0.03±0.01	1.06±0.20	1.10±0.02	0.37±0.03	16.8±1.9
4	39	620(30-1520)	0.06±0.03	0.74±0.25	0.07±0.04	0.40±0.05	16.2±2.2
5	18	690(320-970)	0.04±0.02	0.64±0.16	0.08±0.03	0.38±0.06	15.4±2.2
8	15	1040(510-1890)	0.03±0.02	0.64±0.11	0.11±0.04	0.38±0.09	18.2±1.8
9	13	840(440-1170)	0.03±0.02	0.60±0.14(12)	0.09±0.04	0.38±0.04	17.2±2.9
11	22	900(400-1550)	0.05±0.09	0.68±0.24	0.11±0.04	0.41±0.09	16.7±1.7
12	4	920(670-1360)	0.06±0.02	0.75±0.13	0.07±0.03	0.38±0.07	16.9±1.6
13	7	670(460-910)	0.03±0.01	0.94±0.29	0.11±0.05	0.35±0.02	14.4±2.6
15	3	650(580-760)	0.05±0.03	1.2±0.34	0.10±0.01	0.43±0.08	16.1±1.9

Where (n) = number of samples analyzed if different from that specified for each station.

Table 4. Mean Metal Levels of Yellow Walleye.

Station	Number of Samples	Mean Weight and Range (g)	Metal Level (μg/g wet weight)				
			As	Cu	Hg	Se	Zn
Quatre Fourches	1	190	0.04	0.73	0.11	0.50	6.75
4	4	990(670-1250)	0.06±0.06	0.75±0.13	0.17±0.10	0.40±0.02	12.1±0.68
5	14	1140(600-2250)	0.02±0.00	0.80±0.24	0.38±0.12	0.46±0.06	10.8±1.4
8	11	620(190-1700)	<0.01-0.10	0.59±0.08	0.27±0.10	0.39±0.10	11.7±1.1
9	17	740(300-1280)	<0.01-0.04	0.61±0.12	0.29±0.12	0.40±0.04	11.9±2.2
11	6	990(410-2340)	0.02±0.00	0.62±0.15	0.43±0.20	0.42±0.05	11.5±1.2
12	4	1000(760-1370)	0.02±0.01	0.62±0.19	0.38±0.17	0.44±0.02	10.4±0.83
13	2	1260(1020-1500)	0.02±0.00	0.90±0.28	0.36±0.18	0.36±0.05	12.2±0.14

Table 5. Mean Metal Levels of Burbot.

Station	Number of Samples	Mean Weight and Range (g)	Metal Level (µg/g wet weight)				
			As	Cu	Hg	Se	Zn
1	5	2250(1530-3370)	0.23±0.15	0.91±0.06	0.14±0.02	0.43±0.04	10.7±0.80

Table 6. Mean Metal Levels of Goldeye.

Station	Number of Samples	Mean Weight and Range (g)	Metal Level (µg/g wet weight)				
			As	Cu	Hg	Se	Zn
1	1	180	0.01	0.87	0.14	0.44	9.31
8	4	180(130-290)	0.02±0.01	0.70±0.05	0.18±0.03	0.61±0.06	18.6±3.7
9	6	220(140-400)	<0.01-0.02	0.73±0.14	0.14±0.03	0.59±0.08	19.4±1.4

Table 7. Mean Metal Levels of Northern Pike.

Station	Number of Samples	Mean Weight and Range (g)	Metal Level (µg/g wet weight)				
			As	Cu	Hg	Se	Zn
1	2	1880(640-3120)	0.04±0.00	0.80±0.13	0.33±0.00	0.42±0.00	30.4±12.0
2	28	1070(80-2500)	0.04±0.02	0.69±0.34(27)	0.19±0.06	0.33±0.05	34.3±6.2
3	23	1000(250-3450)	0.04±0.01	0.84±0.20	0.22±0.06	0.35±0.07	39.8±4.9
4	32	1440(100-5220)	0.03±0.01(29)	0.83±0.46	0.15±0.08	0.29±0.05	34.5±5.7
5	24	1310(310-2800)	0.03±0.01	0.83±0.27(20)	0.26±0.09	0.32±0.05	38.2±6.2
8	1	550	0.02	0.66	0.05	0.15	44.5
9	1	1380	0.02	0.48	0.18	0.16	39.8
10	1	390	0.02	2.1	0.10	0.20	47.7
11	1	730	<0.01	0.82	0.07	0.27	41.9
12	9	550(140-1460)	<0.01-0.02(8)	0.76±0.15	0.08±0.02	0.15±0.04	32.8±6.3
13	4	340(50-610)	0.03±0.01	0.74±0.40(3)	0.16±0.05	0.38±0.13	34.4±14.8
15	1	200	–	0.62	0.09	0.24	27.5

Where (n) = number of samples analyzed if different from that specified for each station.

Table 8. Mean Metal Levels of Arctic Grayling.

Station	Number of Samples	Mean Weight and Range (g)	Metal Levels (μg/g wet weight)				
			As	Cu	Hg	Se	Zn
8	1	370	0.01	1.0	0.11	0.17	16.5
9	5	390(260-510)	<0.01-0.02	0.75±0.07	0.12±0.03(4)	0.27±0.02	15.8±1.9
11	2	340(250-440)	<0.01	0.92±0.02	0.18±0.01	0.33±0.04	15.0±1.4
12	9	470(320-700)	<0.01-0.02	0.84±0.11	0.10±0.03	0.19±0.03	15.7±2.6
15	7	200(60-300)	0.01(1)	1.20±0.28	0.10±0.03	0.25±0.02	15.7±1.8

Where (n) = number of samples analyzed if different from that given for each station.

Table 9. Mean Metal Levels of White Sucker.

Station	Number of Samples	Mean Weight and Range (g)	Metal Level (µg/g wet weight) As	Cu	Hg	Se	Zn
Quatre Forches	2	263(259-266)	0.02±0.00	1.13±0.50	0.06±0.00	0.44±0.08	10.0±2.8
5	8	2110(1210-2940)	0.07±0.03	1.2±0.26	0.16±0.06	0.38±0.04	11.0±1.0
8	1	600	0.02	1.2	0.07	0.19	11.5
10	2	600(490-710)	0.02±0.00	1.9±0.71	0.10±0.03	0.24±0.08	11.4±0.85
12	18	590(70-1620)	0.05±0.04	1.41±0.41	0.08±0.02(16)	0.23±0.10	12.1±1.1
15	3	650(350-890)	0.03±0.01(2)	2.2±0.71	0.17±0.09	0.24±0.07	9.44±0.86

Where (n) = number of samples analyzed if different from that specified for each station.

Table 10. Summary of Mean **Metal Levels in Fish.**

Species	Number of Samples	Mean Metal Level (µg/g wet weight)				
		As	Cu	Hg	Se	Zn
Northern Pike	131	*	0.80	0.19	0.31	36.1
Longnose Sucker	74	0.10	1.28	0.09	0.34	15.0
Lake Whitefish	133	0.05	0.73	0.09	0.39	16.4
Yellow Walleye	59	*	0.67	0.32	0.42	11.4
Burbot	5	0.23	0.91	0.14	0.43	10.7
Goldeye	11	*	0.73	0.15	0.58	18.2
Arctic Grayling	24	*	0.94	0.11	0.24	15.7
White Sucker	34	0.05	1.44	0.11	0.28	11.4

* Some values less than detection limit, no mean calculated.

Table 11. Organochlorine Pesticide Residue and Polychlorinated Biphenyl Levels of Composite Fish Samples.

		Contaminant (ng/g wet weight)				
Species	Number of Samples	PCB	Chlordane	Dieldrin	Methoxychlor	DDT and Metabolites*
Northern Pike	12	<20	≤4	≤1	<6	≤11
Yellow Walleye	8	<20	≤4	≤1	(see note 1)	≤11
Lake Whitefish	11	<20	≤4	≤1	<6	≤11
Longnose Sucker	8	<20	(see note 2)			
White Sucker	5	<20	≤4	≤1	<6	≤11

* namely op' and pp' DDT, op' and pp' DDE, and pp' DDD.

Note: 1. All samples <6 ppb except 2 from stations 4 and 8 at 19 and 27 ppb respectively.

2. All samples <4 ppb chlordane except 2 from stations 12 and 13 at 14 and 13 ppb respectively.
All samples ≤1 ppb dieldrin except 3 from stations 4, 12, and 13 at 4, 6, and 6 ppb respectively.
All samples <6 ppb methoxychlor except 4 from stations 4, 18, 12 and 13 at 46, 31, 35 and 39 ppb respectively.
For the 8 samples analyzed pp' DDE = 5.8±4.1 ppb.
Three samples from stations 11, 12 and 13 at 3, 7 and 5 ppb pp' DDT respectively.

Table 12. Metal Levels in Unfiltered Water (μg/l).

Station	As	Cd	Cr	Cu	Fe	Mn	Ni	V	Zn
1	0.4	0.04	4.2	3.0	1780	47	3.5	4.1	11
2	0.4	0.07	2.9	2.4	2360	63	4.6	2.6	13
3	3.6	0.11	5.6	4.8	8040	226	12	13	40
4	2.1	0.06	1.8	3.7	5180	164	4.6	1.9	18
5	0.4	0.05	1.9	12	1580	50	8.2	2.9	17
7	<0.4	0.03	0.8	1.3	449	28	0.4	3.7	3.7
8	<0.4	0.07	2.2	24	1450	47	2.6	1.6	49
9	0.4	0.03	1.3	1.4	897	41	2.9	2.7	7.7
10	<0.4	0.12	1.6	3.0	1860	54	3.5	2.2	10
11	<0.4	0.22	1.7	97	872	27	17	1.6	57
12	<0.4	0.04	1.2	0.1	756	44	1.7	5.7	30
13	0.7	0.14	1.6	1.4	6610	51	4.0	5.7	1010
14	0.7	0.04	1.8	1.4	3750	40	5.0	3.3	294
15	<0.4	0.04	-	1.1	1280	38	1.8	-	560
16	<0.4	0.03	0.7	0.9	1010	27	0.8	2.0	528

All lead values less than the detection limit.

Table 13. Metal Levels in Filtered Water (μg/l).

Station	Cd	Cr	Cu	Fe	Mn	Ni	V	Zn
1	0.07*	1.4	3.1	116	3.8	1.0	-	20*
2	0.13*	1.2	2.4	65	2.4	0.3	2.2	27*
3	0.08	1.4	3.6	98	2.1	2.8	3.5	49*
4	0.16*	1.8	7.5*	437	14	2.2	1.9	42*
5	0.06*	0.8	28*	307	7.6	1.8	2.7	38*
7	0.19*	0.9*	22*	322	16	0.6*	1.0	10*
8	0.09*	0.9	4.4	416	7.6	0.3	1.8	5.3
9	0.03	2.0*	2.5*	165	2.6	1.7	4.1*	4.0
10	0.21*	0.5	22*	337	14	4.8*	1.6	6.3
11	0.05	0.5	12	127	4.4	2.8	3.3	11
12	0.03	0.9	1.3	718	31	3.1	4.3	25
13	0.17*	1.7	4.3*	47	34	2.6	3.1	1170*
14	0.03	1.0	2.2*	486	18	2.6	1.8	2.1
15	0.08*	1.2	1.2*	897	23	1.2	-	21
16	0.08*	0.4	1.5*	859	13	0.8	2.7	16

All lead values less than 0.2 μg/l.
*Filtered values > unfiltered.

Table 14. Metal Levels in Sediments (μg/g dry weight).

Station	As	Cd	Cr	Cu	Fe	Mn	Pb	Ni	Se	V	Zn	Hg	Loss on Ignition (%)
1	6.9	0.60	100	59.5	22,000	306	30.4	28.0	0.45	92	75.8	0.05	5.2
2	4.3	0.19	116	17.4	16,200	307	8.6	46.6	0.25	66	52.6	0.04	5.2
4	3.6	0.17	103	58.0	18,300	330	13.8	87.8	0.44	102	71.8	0.05	9.7
5	4.1	0.15	116	33.6	15,900	275	10.0	48.3	0.25	56	46.3	0.05	5.4
7	0.46	0.02	52	2.4	5,750	111	1.7	19.3	0.02	12	10.5	<0.01	0.44
8	3.5	0.08	75	12.0	12,400	232	3.8	33.9	0.17	39	32.1	0.02	2.8
9	3.5	0.06	91	15.5	14,600	262	4.5	38.3	0.18	53	44.4	0.02	4.5
10	3.0	0.07	100	11.1	17,000	314	4.5	28.4	0.16	58	41.8	0.02	4.7
11	4.0	0.09	92	18.4	16,900	249	4.0	33.7	0.22	65	49.3	0.03	5.7
12	3.5	0.10	59	26.2	22,400	327	9.9	20.5	0.65	86	57.2	0.04	6.4
13	3.4	0.06	71	19.4	16,400	205	5.6	37.4	0.20	62	46.8	0.04	2.5
14	2.6	0.04	40	8.2	10,700	101	2.9	23.5	0.13	33	24.2	0.02	2.4
15	1.4	0.04	34	5.1	6,600	104	1.6	9.0	0.07	16	15.2	<0.01	1.4
16	0.95	0.01	41	12.3	6,680	102	2.4	9.4	0.05	15	16.2	0.02	1.6

Table 15. Metal Levels in Invertebrates (μg/g dry weight).

Station	Cd	Cr	Cu	Fe	Mn	Pb	Ni	Zn	Hg
1	5.7	2.6	27.0	1260	76	37	14	193	-
8	1.1	2.2	28.2	485	35	22	5.7	129	0.09
9	1.4	4.5	22.5	212	19	-	-	183	0.15
10	0.8	2.6	26.7	2440	220	32	43	143	-
12	0.7	1.6	23.6	3230	360	28	17	148	-
13	0.4	2.8	18.7	400	20	32	7.4	153	0.13
15	1.4	2.7	32.6	2190	120	40	17	168	-

Vanadium - all values less than 10 μg/g.

Table 16. Metal Levels in Plankton (μg/g dry weight).

Station	Cd	Cr	Cu	Fe	Mn	Pb	V	Ni	Zn
2	2.3	12.1	320	9200	490	197	30	110	319
3	2.3	13.6	220	15200	720	193	100	92	246
4	6.7	15.4	290	8040	330	204	<10	51	470
Lower Birch River	2.3	8.3	190	38600	610	135	200	104	273

Table 17. Metal Levels in Water, Fish, Sediment, Invertebrates, and Plankton (Mean concentrations).

		As	Cd	Cr	Cu	Fe	Mn	Pb	Ni	Se	V	Zn	Hg
Unfiltered Water µg/l	x̄	1.08	0.07	2.1	2.0	2520	63	*	4.8	**	3.8	23.3	**
	SD	1.17	0.05	1.3	1.35	2320	56		4.5		3.0	18	
	n	8	15	14	12	15	15		15		14	11	
Fish µg/g (wet wt.)	x̄	0.11	*	*	0.94	**	**	*	*	0.37	*	16.9	0.15
	SD	0.08			0.28					0.11		8.2	0.08
	n	4			8					8		8	8
Sediments µg/g (dry wt.)	x̄	3.2	0.12	77.8	21.4	14400	230	7.4	33.2	0.23	53.9	41.7	0.03
	SD	1.6	0.15	28.7	17.8	5350	90	7.5	19.8	0.17	28.4	20	0.01
	n	14	14	14	14	14	14	14	14	14	14	14	12
Invertebrates µg/g (dry wt.)	x̄	**	1.64	2.71	25.6	1460	121	31.8	17.3	**	*	160	0.12
	SD		1.83	0.89	4.5	1180	127	6.4	13.5			22.8	0.03
	n		7	7	7	7	7	6	6			7	3
Plankton µg/g (dry wt.)	x̄	**	3.4	12.4	255	17760	540	182	89	**	111	327	**
	SD		2.2	3.0	60	14240	167	32	26		84	100	
	n		4	4	4	4	4	4	4		3	4	

* below detection limit.

** analysis not done.

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8. APPENDICES

8.1 APPENDIX I - Collection Methodology

Synoptic Survey of Baseline Levels of Contaminants

in the

Aquatic Fauna of the AOSERP Region

Preliminary Review: Collection Phase

INTRODUCTION

The general purpose of the field program outlined by the Aquatic Fauna Committee was to collect fish, invertebrate, sediment and water samples in the Alberta Oil Sands Environmental Research Program (AOSERP) study area. Samples collected during the field studies were to be used to provide baseline information on levels of contaminants in the aquatic fauna of the region.

Initially ten (10) sample sites were proposed, five (5) of these in the Fort Chipewyan region and five (5) in the Fort McMurray area. An additional five sites in the Fort McMurray or southern sector were included subsequent to the completion of work on the initial sample areas.

To the extent possible and as outlined in the terms of reference Renewable Resources Consulting Services Ltd. was to:

1) Collect fish by whatever procedures were necessary to ensure a maximum possible size and age range; there were to be ten (10) arithmetic length intervals with a minimum of three (3) fish per interval. A minimum of 300 gms and preferably 900 grams of fish was to be collected per size interval. The species of fish to be collected were lake whitefish, northern pike, white sucker, and where possible, Arctic grayling. Yellow walleye was also acceptable as an alternate to Arctic grayling.

2) Collect invertebrates at each study site. The weight of each sample was to exceed thirty (30) grams.

3) Collect water samples at each study site; river water was to be collected midstream at the surface; two samples were required - one was to be filtered through a 0.045 mm Millipore filter and then acidified with concentrated nitric acid at a concentration of 5 mg/1; the other water sample was to be acidified but not filtered.

4) Collect sediment at each study site; sediment was to be sampled using a corer; in rivers, sampling was to occur at quarter points across the study site; sampling in lakes should occur at quarter points across the longitudinal axis of the lake at the site; and samples should be composited to 200 grams and frozen.

5) All samples were to be frozen in the field and shipped to the Freshwater Institute (Winnipeg, Manitoba).

6) Sampling was to occur between 15 September 1975 and 31 October 1975.

7) Additional or alternate sample locations could be selected following the notification of the Chairman of the Aquatic Fauna Technical Research Committee.

STUDY APPROACH

The fifteen (15) sample areas which were included in the study are listed in Table 1. One of the originally requested sample sites, the Athabasca River near the Algar River, could not be reached with the riverboat and as a result it was dropped in favor of a site on the Athabasca River near the Horse River confluence.

The southern crew operating out of the AOSERP camp at Mildred Lake, carried out field studies on Stations 7-11 during the period October 4-12, 1975. The primary method of transportation was a 24 foot aluminum boat powered by two propeller driven 40 hp motors. The same crew carried out studies on Stations 12-16 over the period October 20-27, 1975. During this second phase more emphasis was placed on obtaining samples from the tributaries rather than the Athabasca River proper.

The northern study crew, based out of Fort Chipewyan, carried out sampling at Stations 1-5, over the period October 6-22, 1975. Transportation was by Cessna 185 float plane and boat and local guide.

METHODOLOGY

Fish Collection

A Smith-Root Type VII backpack electroshocker, adapted for boat use, and variable mesh gill nets were utilized by the southern crew during the initial phase of the field studies. A high output electroshocking unit designed specifically for boat use was to be the primary collecting tool, however, it was rendered inoperative early in the study due to a defective transistor. It was however functional for work on Sites 12-17. The northern crew relied entirely on test nets for fish collecting.

Table 1. Areas sampled during the fall 1975 AOSERP aquatic studies.

NORTHERN SECTOR

Station 1	Slave River (at the Peace-Rocher River confluence)	Sec. 23 - Tp. 115 - Rge. 9 - W4
Station 2	Lake Athabasca (at Fort Chipewyan)	Tp. 111, 112 - Rge. 8 - W4
Station 3	Lake Claire	Tp. 110 - Rge. 12 - W4
Station 4	Richardson Lake	Tp. 108 - Rge. 8 - W4
Station 5	Athabasca River (near Embarras)	Sec. 11 - Tp. 108 - Rge. 10 - W4

SOUTHERN SECTOR

Station 7 *	Steepbank River (at the North Steepbank River)	Sec. 32 - Tp. 90 - Rge. 7 - W4
Station 8	Athabasca River (at Clarke Creek)	Sec. 5 - Tp. 90 - Rge. 9 - W4
Station 9	Athabasca River (At MacLean Creek)	Sec. 17 - Tp. 91 - Rge. 9 - W4
Station 10	Clearwater River (at Christina River)	Sec. 33 - Tp. 88 - Rge. 7 - W4
Station 11	Athabasca River (at Horse River)	Sec. 17 - Tp. 89 - Rge. 9 - W4
Station 12	Muskeg River (at Athabasca River)	Sec. 6 - Tp. 94 - Rge. 10 - W4
Station 13	MacKay River (at Athabasca River)	Sec. 24 - Tp. 94 - Rge. 11 - W4
Station 14	Ells River (at Athabasca River)	Sec. 2 - Tp. 96 - Rge. 11 - W4
Station 15	Steepbank River (at Athabasca River)	Sec. 36 - Tp. 92 - Rge. 10 - W4
Station 16	Firebag River (at Athabasca River)	Sec. 12 - Tp. 101 - Rge. 9 - W4

* No area was designated as Station 6.

All fish were measured and given a position within a size interval, separated by station and species (in most cases) and then stored in unused heavy gauge plastic bags. Fish samples from the southern study were immediately placed on dry ice for freezing. Northern samples were placed in a rented freezer following sorting and labeling. The Fort McMurray samples were taken to Edmonton by the field crew at the termination of the field studies. The samples were placed on dry ice and shipped in styrofoam insulated wooden boxes. Fort Chipewyan samples were shipped on dry ice in insulated boxes by Pacific Western Airlines to Edmonton. The latter samples were stored in freezers in Edmonton for shipping at a later date to Winnipeg. The southern samples were shipped to the client immediately following termination of the field studies. In all cases fish were maintained in a suitably frozen state during the transfer period.

Benthos Collection

Several types of conventional invertebrate collection gear were available to both field crews. These included Surber samplers, dip nets and Ekman dredges. Due to sampling constraints the only feasible method of collecting in northern sector (Stations 1-5) was dredging. At Stations 7-16 kick sampling with a dip net was found to be the only practicable technique. Although the physical constraints of kick sampling were few the method was generally not effective in producing a sample. This was due in most cases to the presence of unproductive substrates. Adult Hemiptera and Coleoptera were collected rather effectively by the Fort McMurray crew during the fish shocking program. These insects showed a definite propensity to become attracted to the immersed anode and were easily retrieved. Invertebrate samples were weighed, placed in plastic bags and frozen.

Plankton Collection

Plankton sampling was carried out at Station 2(Lake Athabasca), Station 3 (Lake Claire), and Station 4(Richardson Lake). Plankton collection involved horizontal towing with a Wisconsin plankton net behind either a boat or float plane. Use of the aircraft was necessary in some cases due to the distance of the sample sites from Fort Chipewyan. An attempt was made to keep the speed of the boat and aircraft approximately equal in order to determine the volume of water filtered. Vertical tows were carried out at the beginning and end of each tow session which varied from 10 to 30 minutes in length. This procedure was considered to be adequate to ensure that plankters from all depths were represented in the sample, particularly because of the shallow nature of sampled lakes and the continual turbulence during the study period. The samples were strained, placed in plastic bags, weighed and then frozen.

Sediment Collection

The methods of sediment collection utilized in the study did not correspond exactly with those specified in the terms of reference. A more practicable approach had to be adopted to overcome certain physical constraints at sample areas and to allow use of shallow water core samplers. Use of Ekman dredges was not considered due to possible contamination of samples with metal filings.

Stream velocity and depth at some river sites precluded the collection of sediment from mid-stream locations. On lake sites rough water necessitated the taking of samples in less turbulent open water areas and in protected bays.

Sediment corers constructed by Renewable Resources Consulting Services Ltd. personnel were utilized in both study areas. A hand-held plexiglass sampler (length 22.7 cm, outside diameter 4.8 cm) was used in the Fort McMurray area. A corer constructed of PVC material (length 36.8 cm outside diameter 4.8 cm) mounted on a 2 m pole was used in the Fort Chipewyan region. From 3 to 10 cores, depending on the particular substrate, were composited to form a single 200 g sample. Cores taken with the hand-held sampler varied in depth from 0.5 to 0.7 m. The pole mounted sampler was capable of sampling effectively at depths of up to 1.5 m.

Water Collection

In the southern sector water samples were taken from a boat at mid-stream locations as prescribed in the terms of reference. In contrast samples collected at Stations 1-5 were taken from a float-equipped aircraft. Due to landing difficulties at the various sites however, samples were taken at quarter point locations on rivers and sheltered locations in lakes.

Acid rinsed plastic bottles (1 quart capacity) were used at all stations. Two bottles were filled at each site and prepared according to the terms of reference. All filtration equipment was rinsed with distilled water following use to prevent sample contamination.

All samples collected in the Fort McMurray area were prepared and frozen in the field. Due to operating difficulties with the Millipore Filter apparatus in Fort Chipewyan all water samples from Stations 1-5 were collected in one morning and shipped immediately to Edmonton by Pacific Western Airlines Ltd. The samples were prepared and frozen within approximately 10 hours of their being taken.

RESULTS

Northern Sector (Stations 1-5)

Fish Collection

A total of 262 fish from Stations 1-5 were sampled and frozen during the period October 6-22, 1975.

Approximately 350 other sampled fish were considered to be surplus to the needs of the study and were given to local Indian families.

Seven species were represented in the catch. By far the greatest percentage was comprised of northern pike and lake whitefish (Table 2). In the course of the study a number of local fishermen were queried as to the makeup of their catch. In most cases pike were most numerous followed by lake whitefish. This provides further evidence that these species were the most abundant fish in the sampled areas during the study period.

Walleye were most abundant at Station 5 (Athabasca River near Embarras), however they were never present in large numbers. Indications are that the period of maximum abundance for this species was well past by the time this study was initiated. The same holds true for suckers which were poorly represented in the catch. Burbot were encountered only at Station 1, the Slave River. Apparently they are commonly in the area. No Arctic grayling were encountered in the northern sector. However, a local resident indicated that the occasional specimen is taken in the Athabasca River at Station 5. These are apparently downstream migrants from Pine Creek (local name).

A number of lake whitefish at Station 5 were externally examined to determine sexual condition on October 15. There was no release of sexual products upon handling which might indicate that spawning had been completed. Ten mature whitefish from the Richardson Lake area were examined internally on October 19 and all were spent.

Table 2. Numbers and size intervals (*) of fish sampled during the 1975 AOSERP studies, Fort Chipewyan and Fort McMurray, Alberta.

Sample Area	SPECIES								STATION TOTAL
	YW	NP	AG	GE	LW	WS	LS	BT	
Station 1. Slave River (at Peace-Rocher R. confluence)		2		1			3	5	11
Station 2. Lake Athabasca (at Fort Chipewyan)		28(7)			2(2)				30
Station 3. Lake Claire (at Prairie River)		36(5)			3(3)				39
Quatre Fourches	1				13(4)	2			16
Station 4. Richardson Lake (at Jackfish Creek)	4	32(7)			80(9)				116
Station 5. Athabasca River (near Embarras)	10(5)	24(7)			9(2)	7(4)			50
Sub-total (Northern section)	15	122	0	1	107	9	3	5	262
Station 7. Steepbank River (at N. Steepbank)	3(2)	8(3)	8(4)		4(3)	17 (6)	6(4)		46
Station 8. Athabasca River (at Clarke Creek)	15(7)	1(1)	4(3)		15(4)	2(2)	11(8)		48
Station 9. Athabasca River (at MacLean Creek)	24(7)	1(1)	6(3)		15(5)		2(2)		48
Station 10. Clearwater River (at the Christina River confluence)	1(1)	3(3)					23(5)		27

Table 2. continued

Sample Area	YW	NP	AG	GE	LW	WS	LS	BT	Station Total
Station 11. Athabasca River (at Horse River)	7(6)	1(1)	2(2)		28(5)	1(1)	16(4)		55
Station 12. Muskeg River (at Athabasca River)	3(2)	8(3)	8(4)		4(3)	17(6)	6(4)		46
Station 13. MacKay River (at Athabasca River)	2(2)	4(3)			7(3)		12(4)		25
Station 14. Ells River (at Athabasca River)			1(1)						1
Station 15. Steepbank River (at Athabasca River)		1(1)	10(6)		3(2)	3(3)			17
Station 16. Firebag River (at Athabasca River)									0
Sub-total (Southern section)	55	27	39	0	76	40	76	0	313
Grand Total	70	149	39	1	183	49	79	5	575

YW - Yellow Walleye
NP - Northern Pike
AG - Arctic Grayling
GE - Goldeye
LW - Lake Whitefish
WS - White Sucker
LS - Longnose Sucker
BT - Burbot

Fish appeared to be moving rather extensively in the delta area. This was particularly evident in the Richardson Lake - Jackfish Creek vicinity with respect to pike and whitefish. Juveniles of the latter species were extremely abundant. The general movement trend appeared to be downstream and out of Richardson Lake. Water levels throughout the delta were observed to be dropping steadily during the latter stages of the study.

Benthos Collection

As indicated in Table 3 benthic invertebrates were difficult to collect at Stations 1-5. In fact only Richardson Lake yielded a significant sample, largely consisting of chironomids. Numerous dredges were taken in Lake Athabasca and Lake Claire however no benthic invertebrates were observed. No effective method was available to sample the river sites.

Plankton Collection

Only Richardson Lake and Lake Athabasca yielded significant plankton samples. Approximately one hour of towing produced only 16 g of plankton in Richardson Lake. A similar level of effort in Lake Athabasca produced considerably less. Several concerted attempts at plankton collection in Lake Claire were carried out but were largely unsuccessful. Sampling of the lower end of the Birch River was also carried out. However, plankton populations were likewise extremely limited.

Sediment Collection

Sediment samples were collected at all sites with a minimum of difficulty (Table 3). However as previously pointed out it was necessary to collect the samples near the banks at river sites and in less turbulent areas in lakes.

Water Collection

Water samples were collected at all sites and no problems were encountered (Table 3). All samples except that from Station 5, Athabasca River at Embarras, were heavily laden with suspended sediment. River water at Station 5 though it was free of silt exhibited a dark brown coloration.

Table 3. Summary of sampling success in AOSERP field studies fall of 1975 (excluding fish)

Sample Area	Benthos	Plankton	Sediment	Water
Station 1 - Slave River (at Peace-Rocher River confluence)	-	N/A	+	+
Station 2 - Lake Athabasca (at Fort Chipewyan)	-	+(1)	+	+
Station 3 - Lake Claire	-	-	+	+
Station 4 - Richardson Lake	+(1)	+(1) (16g)	+	+
Station 5 - Athabasca River (near Embarras)	-	N/A	+	+
Station 7 - Steepbank River (at North Steepbank River)	-	N/A	+	+
Station 8 - Athabasca River (at Clarke Creek)	+	N/A	+	+
Station 9 - Athabasca River (at MacLean Creek)	+	N/A	+	+
Station 10 - Clearwater River (at Christina River)	+(1)	N/A	+	+
Station 11 - Athabasca River (at Horse River)	+(1) (10g)	N/A	+	+
Station 12 - Muskeg River (at Athabasca River)	+(38g)	N/A	+	+
Station 13 - MacKay River (at Athabasca River)	-	N/A	+	+
Station 14 - Ells River (at Athabasca River)	-	N/A	+	+
Station 15 - Steepbank River (at Athabasca River)	-	N/A	+	+
Station 16 - Firebag River (at Athabasca River)	-	N/A	+	+

(1) Indicates that the sample did not completely fulfill the terms of reference.

Southern Sector (Stations 7-16)

Fish Collection

A total of 313 fish of six species were sampled in the southern sector (Table 2). Most abundant were lake whitefish and longnose sucker followed by walleye. Present in smaller numbers were Arctic grayling, white suckers and northern pike. In general, most species appeared to be represented by a few individuals at most sites. At sites such as the Athabasca River at Horse River (Station 11) where lake whitefish were congregating (in near spawning condition), collection of the required sample was relatively easy. In general however, it was not possible to fulfill the terms of reference at most sites due to the timing and short duration of the study.

Fish appeared to be more abundant at Sites 7-11 which were sampled in the initial field studies (October 4-12). Although the subsequent field studies began approximately two weeks later the type of habitat available at stations 12-16 was probably the cause of the reduced catch.

Benthos Collection

As was the case of the Fort Chipewyan region, benthic invertebrate sampling was extremely difficult in the southern sector (Table 2). The type of sampling constraints varied however and included high flows (Station 7), and unproductive substrates (Stations 13-16). A good benthic sample (38 g) was obtained in the lower Muskeg River in an area of productive gravel-rubble substrate. Partial samples were also obtained from Station 10 and Station 11 through the use of the electroshocker. An additional sample of invertebrates (30g) was collected from the east bank area of the Athabasca River near the MacKay River confluence.

Sediment and Water Collection

Sediment and water was collected at each of the 10 sites (Stations 7-16) (Table 3).

8.2 APPENDIX II - Quality Assurance:

National Bureau of Standards Reference Materials 1577 bovine liver) and 1571 (orchard leaves) were analyzed routinely with each set of fish samples; the former for copper, zinc, lead, cadmium and selenium, the latter for arsenic. The following results were obtained:

Element	Our Value	NBS Certified Values
	Mean ± Standard Deviation (μg/gm)	
Copper	191±9(19)	193±10
Zinc	125±6(19)	130±10
Lead	0.42±0.05(8)	0.34±0.08
Cadmium	0.25±0.04(17)	0.27±0.04
Selenium	1.11±0.07(21)	1.1±0.1
Arsenic	9.7±0.71(20)	11±2

where the number in brackets is the number of times the sample was analyzed.

Neither of the above samples is certified for chromium, vanadium, or nickel.

Two "in-house" samples were routinely analyzed for mercury with each set of fish samples. These samples are composites of previously analyzed samples and have expected values of 0.55 and 0.45 μg/gm. Our results based on six trials were 0.53±0.02 and 0.43±0.03 μg/gm.

Because all pesticide - PCB values were at or near the detection limit, no confirmatory tests were done.

8.3 APPENDIX III - Precision and Detection Limits

Precision in determination of metals in sediment, invertebrates, and plankton.

	Conc. Level μg/g	S.D.	R.S.D.%
As	9.7	0.7	7.2
Cr	16.2	0.48	3.0
Cu	4.1	0.24	5.8
Fe	10,800	280	2.6
Mn	279	8.7	3.1
Zn	24.8	1.0	4.0

Detection Limits	Water μg/ℓ	Fish μg/g
Arsenic	0.4	0.01
Cadmium	0.002	0.01
Chromium	0.05	0.1
Copper	0.04	0.03
Iron	0.5	-
Manganese	0.25	-
Nickel	0.2	0.1
Vanadium	0.5	0.04
Zinc	0.1	0.01
Lead	0.2	0.05
Mercury	-	0.01
Selenium	-	0.01

Detection limit is defined as twice the peak to peak variability of the background.

LIST OF PUBLICATIONS

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	Preliminary Vegetation Survey of the AOSERP Study Area
5	HY 3.1	Evaluation of Wastewaters from an Oil Sands Extraction Plant
6		Housing for North--Stackwall System Construction Report
7	AF 3.1.1	Synopsis of the Physical and Biological Limnology and Fishery Programs within the Alberta Oil Sands Area
8	AF 1.2.1	Impact of Saline Waters upon Freshwater Biota (A Literature Review and Bibliography)
9	ME 3.3	Preliminary Investigation into the Magnitude of Fog Occurrence and Associated Problems in the Oil Sands Area
10	HE 2.1	Development of a Research Design Related to Archaeological Studies in the Athabasca Oil Sands Area (at print)
11	AF 2.2.1	Life Cycles of Some Common Aquatic Insects of the Athabasca River, Alberta
12	ME 1.7	Very High Resolution Meteorological Satellite Study of Oil Sands Weather, "A Feasibility Study"
13	ME 2.3.1	Plume Dispersion Measurements from an Oil Sands Extraction Plant
14	HE 2.4	Athabasca Oil Sands Historical Research Project (3 volumes) (at print)
15	ME 3.4	Climatology of Low Level Air Trajectories in the Alberta Oil Sands Area (at print)
16	ME 1.6	Feasibility of a Weather Radar near Fort McMurray, Alberta (at print)
17	AF 2.1.1	Survey of Baseline Levels of Contaminants in Aquatic Biota of the AOSERP Study Area

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For information regarding any of these publications or the Alberta Oil Sands Environmental Research Program, please contact the Program office.

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