REVIEW OF OIL SANDS TAILINGS POND CONTAMINANTS WITH FISH TAINTING POTENTIAL

by

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The literature on tainting of fish by petroleum-derived compounds has been reviewed for information specifically relevant to the potential for tainting of fish in the Athabasca River. Major classes of compounds which are known to be present in oil sands wastes and which have been studied for fish uptake include: alkylated benzenes, alkylated naphthalenes, polynuclear aromatic hydrocarbons, polynuclear aromatic sulphur heterocycles, polynuclear aromatic nitrogen heterocycles and naphthenic hydrocarbons. Threshold odor levels in water for many of these compounds occur in the 1-100 ppb range. A need for more background data on the occurrence of these types of compounds in the oil sands region and in oil sands effluents has been identified.

ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

Experience with fish tainting in the Athabasca River raises concerns with the chemical composition of possible future treated discharges from oil sands plant tailings ponds. Regulation of such discharges based upon conventional petroleum refinery effluent parameters will not address fish tainting potential. Several waste sources within conventional oil sands plants contain a variety of organic, hydrophobic contaminants. While such contaminants are included in the conventional oil and grease parameter, the latter is neither sensitive nor specific enough to deal with fish tainting potential.

The data base on characterization of oil sands wastewaters is limited considering the extreme variety and complexity of contaminants which can be present. Likewise, the data base on background contaminant levels for the Athabasca River is also limited. Waste characterization indicates a variety of alkylated aromatics and heterocyclic compounds with substantial quantities of organic sulphur compounds.

Information on fish tainting by petroleum-derived organic contaminants is limited relative to the wide range of contaminants which can be present in oil sands wastewaters. Tainted fish from the Athabasca River in 1982 were found to contain polynuclear aromatic hydrocarbons and polynuclear aromatic sulphur heterocycles, but direct correspondence

between identified compounds and those primarily responsible for sensory taint was not established. Experimental data has been reported from several sources for bioconcentration of alkylated benzenes and polynuclear aromatic hydrocarbons. Limited bioconcentration data has been obtained for polynuclear aromatic sulphur and nitrogen heterocycles.

Threshold odor levels of a few relevant contaminants have been reported. These indicate threshold odor levels as low as 0.5 ppb (for diesel fuel). General monitoring techniques are not specific to the more relevant oil sands contaminants. Available techniques are generally tedious and complex. Control options for oil sands wastes have not been explicitly evaluated for control of tainting contaminants. Such evaluations have been limited by the inadequate characterization of specific contaminants in oil sands waste streams and their specific fish tainting potential.

A better understanding of baseline conditions for petroleum-derived compounds with fish tainting potential is required for the oil sands region. As well, better characterization of wastewaters, potential effluent discharges and treatment performance is also required.

water and fish need not arise only from oil sands sources. Other industries, such as pulp and paper or intensive agriculture could discharge substances capable of causing fish tainting. The scale of such activities as they may affect water quality in the oil sands region of the Athabasca River is very limited. However, sound management of Athabasca River water quality in the face of tailings pond discharges or increased oil sands development will require being able to distinguish and manage potential tainting contributions from oil sand sources from other industrial or natural sources. The conventional petroleum refinery parameters will not provide an adequate basis to draw such distinctions. Consequently, there is a need to explore the nature of potential fish tainting contaminants which may arise from oil sands processing facilities to determine which contaminants pose a concern, what concentrations are relevant, what measures are available for monitoring and what technology can remove potential problem compounds.

1.2 PROCESS DESCRIPTION

Oil sands are mined in open pits and transported to extraction facilities by conveyor systems. After rough screening to remove oversize material, the oil sand is mixed with hot water, steam, and caustic in a conditioning drum (Figure 1). From here the mixture is discharged to separation cells, where gravity segregates the mixture into skimmable float, middlings, and bottoms. The bottoms discharge to the

1. INTRODUCTION

1.1 PROBLEM STATEMENT

The treatment and discharge of tailings pond wastewaters is one of several different options for eventual site reclamation at surface mining oil sands operations. As a result, criteria for approving discharge of tailings pond supernatants are being considered by Alberta Environment. Conventional parameters (oil and grease, ammonia, sulphides, phenol, suspended solids and chemical oxygen demand) which have been used for the regulation of petroleum refinery effluents will provide little specific information on the potential for tailings pond contaminants to taint fish or cause taste and odor in water supplies. The possibility of oil sands effluents leading to fish tainting is a valid concern. Walleye in the Athabasca River were tainted during the 1981-82 winter season coincident with upset conditions at the Suncor oil sands plant which led to the discharge of substantial quantities of oil to the Athabasca River (R. v. Suncor 1984).

Many of the specific contaminants which could be expected in oil sands plant tailings ponds can pose environmental problems at very low concentrations. Bioaccumulation can lead to much higher concentrations of some contaminants in fish tissue than found in water (Eastmond et al. 1984). Many of these contaminants cause taste and odour in water at extremely low concentrations Zoeteman et al. (1971). However, taste and odor problems in

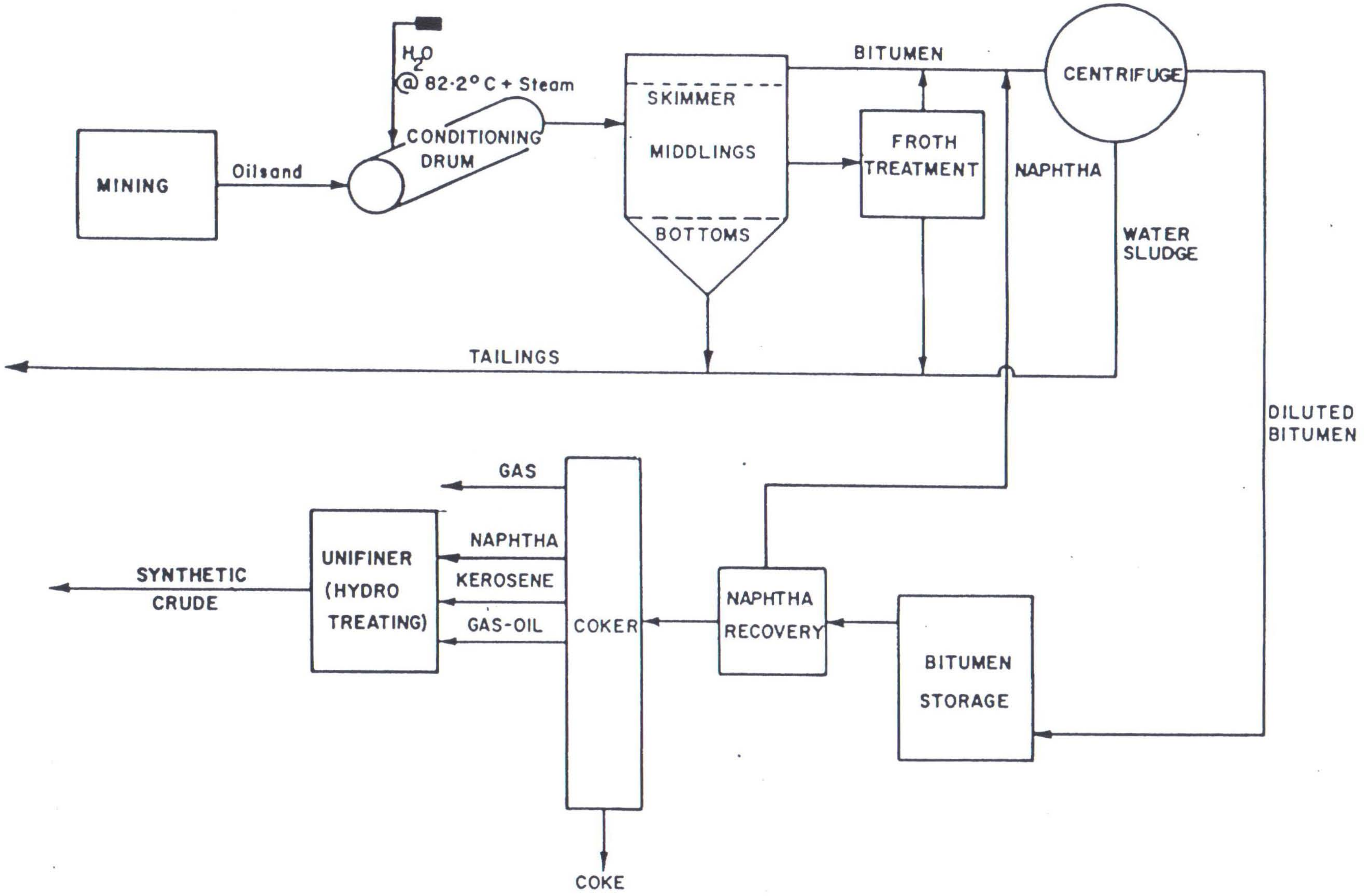

Figure 1. Schematic of a typical surface mining oil sands plant

tailings pond as wet tailings. These have a water content of about 50% by weight and contain about 7.5% of the bitumen feed to the plant (Monenco 1983). This stream was estimated at 325 000 m^3/d for a plant producing 20 000 m^3/d of synthetic crude (Monenco 1983).

The middlings are transferred to a scavenger cell which uses air flotation to recover further bitumen. This is combined with the skimmable float to constitute bitumen froth. The bitumen froth is diluted with raw diluent naphtha before centrifugation. The latter stage produces a bottoms stream, which goes to tailings, and the diluted bitumen, which goes to storage prior to upgrading. The wet tailings stream produced is 77% water by weight, but contains about 1.8% diluent naphtha by weight (Monenco 1983). This stream contains less than 2% of the bitumen feed to the froth treatment and was estimated at 20 000 m^3/d for a plant producing 20 000 m^3/d of synthetic crude.

The diluent naphtha is recovered from the diluted bitumen by distillation immediately prior to charging the bitumen into the cokers. This process is a high-temperature thermal cracking process, which converts the predominantly high molecular weight bitumen molecules into smaller more useful hydrocarbons. The cokers produce five streams: non-condensible gases, naphtha, kerosene, gas oil, and solid coke. The middle three comprise the raw materials for blending to produce synthetic crude. However, these streams contain substantial quantities of unsaturated hydrocarbons and sulphur and nitrogen heterocycles, when they come directly from the coker. These materials are undesirable in petroleum products, so the coker distillate (refers to all three streams combined) is hydrogen treated in separate hydrotreating stages (three at Suncor, producing naphtha, kerosene and gas oil; 2 at Syncrude, producing naphtha and gas oil). The hydrogen treating saturates the unsaturated hydrocarbons and removes sulphur and nitrogen compounds. The hydrotreated product is blended to produce synthetic crude.

Wastewaters resulting from the extraction processes are discharged to the tailings pond. These are contaminated with unextracted bitumen and raw, diluent naphtha carried over from the centrifugation stage as noted previously.

Wastewaters resulting from the upgrading stage include sour condensates, coke cutting waters (at Suncor), and miscellaneous oily process waters. The sour condensates arise from steam stripping of the coker and hydrotreating process distillates. This steam comes in direct contact with the distillate materials and contains oils and dissolved polar organics, including phenolics. The condensates are termed "sour" because they also are enriched in odorous sulphur compounds. This stream is discharged to the tailings pond and was estimated by Monenco (1983) to comprise 4200 m^3/d for a 20 000 m^3/d synthetic crude plant.

The coking drums at Suncor are run in a batch mode and after each run the coke formed must be hydraulically cut out of the drum with high-pressure water jets. This process produces a wastewater with some potential for oil and dissolved sulphur compound contamination. At Suncor, the coke cutting waters are discharged, after settling, to a wastewater pond for ultimate discharge to the Athabasca River. Although future plants are unlikely to use coke cutting water, sluice water to transport coke should be considered. Monenco (1983) estimated this stream to be 366 m^3/d, with a typical oil and grease concentration of 10 mg/L for a 20 000 m^3/d synthetic crude plant.

The upgrading section of the plant, like any petroleum refinery, uses process water for pump and equipment cooling, area washup, and a variety of intermittent applications. Such process wastewaters can come in contact with oily materials to varying degrees to produce an oily waste stream. At Suncor, these oily wastes are processed through two oil-separation settling basins in series before travelling through a series of three holding ponds, a final underflow dyke, and on to a submerged outfall to the Athabasca River.

At Syncrude, the equivalent wastewaters are collected in a wastewater pond before being pumped to the tailings pond. Under upset conditions, substantial quantities of oily material can reach these oily wastewater streams. Monenco (1983) estimated oily process waste streams for a 20 000 m^3/d synthetic crude plant as:

tank bottoms	41 m^3/d @ 5.75% oil and grease
building drains	1308 m^3/d @ 1000 mg/L oil and grease

in-plant runoff 4489 m^3/d @ 200 mg/L oil and grease.

Finally, non-contact cooling water is required in the power plant and process areas. Leaking heat exchangers can lead to substantial oily contamination of these cooling waters. Suncor has a cooling water pond that may be operated in once-through mode during warmer summer months (direct discharge back to the river). During the winter, this system is intended to be run in a recirculated mode, with no discharge back to the river. During the winter of 1982, the system was found to be discharging directly to the river while containing substantial contamination (several hundred mg/L) of kerosene-like material (R.vs Suncor 1984). The cooling system at Syncrude is designed for no discharge to the Athabasca River.

Monenco (1983) estimated condensate leakage for a hypothetical plant as 259 m^3/d @ 1000 mg/L of oil & grease and cooling tower blowdown (if recirculated cooling is being practised) as 4870 m^3/d @ 10 mg/L of oil & grease.

1.3 CONTAMINANT CLASSIFICATION

Wastewaters from the various oil sand extraction and bitumen upgrading processes can contain a wide range of water pollutants, both organic and inorganic. This review is focused on those contaminants that pose a potential threat to aquatic resources at very low concentrations, particularly by means of fish tainting. Such contaminants are likely to be both organic and hydrophobic in nature. These characteristics coincide with those which make substances appear as part of the oil & grease parameter (APHA 1985). This parameter, by itself, is inadequate as a measure of tainting substances because its detection limits are poor and because it can respond to compounds which may be innocuous (i.e. chlorophyll as well as innocuous hydrocarbons). Discharge limits set for a potent tainting compound, but measured as oil & grease, would have to be unacceptably high to allow for the interference from non-tainting substances. For many tainting substances, the oil & grease parameter cannot provide an adequate detection limit to allow regulation to levels low enough to avoid problems.

2. REVIEW OF RECENT RESEARCH

2.1 IDENTIFICATION OF CONTAMINANTS

Relatively little work has been published that is useful for identifying the occurrence of contaminants with tainting potential in oil sands tailings ponds. Hrudey (1975) conducted a survey of the Great Canadian Oil Sands (now Suncor) plant in 1974. Samples of upgrading plant wastewater, licensed for discharge through the plant's wastewater pond, and drainage from the riverside dykes of the tailings pond were collected. The wastewater pond discharge was non-acutely lethal in a 96 hour flow through bioassay with rainbow trout. Chemical parameters were all very low and well within the licensed discharge levels. Consequently, analysis was limited to the standard license parameters, and no followup analysis was pursued on this source at that time. The tailings pond dyke drainage was acutely toxic to rainbow trout in static bioassay, with an estimated LC_{50} of approximately 10% by volume. This drainage also exhibited relatively high total organic carbon (77 mg/L), which suggested that further work to characterize the organic content of this wastewater was warranted. Preliminary fractionation and gas chromatography / mass spectrometry (GC/MS) analyses were performed on a grab sample collected at the same location. This analysis found a total of 98 mg/L of ether soluble material, which was sub-fractionated to suggest the presence of fatty acids; a complex mixture of unsaturated, saturated, cyclic, and aromatic acids; an unresolved complex mixture (UCM) of paraffinic hydrocarbons, including some normal alkanes with a majority as unsaturated, branched and cyclic compounds; and a range of aromatic and substituted aromatic compounds. Tentative GC/MS identifications of some phthalate esters were given.

Strosher and Peake (1976) conducted a more detailed survey of the same wastewaters in 1975. They found that the tailings pond dyke drainage contained 100 to 120 mg/L of total organic carbon, of which 69% was extractable with organic solvents. The extractable carbon was mainly (92%) oxygenated compounds, comprised of 79% organic acids, 4.5% phenols, 2.7% ketones, 1.9% aldehydes, 1.5% organic acid esters, 1% amides, and 0.2% quinones. The remainder was characterized as 5.3% organic sulphur compounds, 1.1% organic nitrogen compounds, and 0.04% hydrocarbons.

With the upgrading plant wastewater, Strosher and Peake found an average of 36 mg/L of total organic carbon, of which only 42% was solvent extractable. Some of this high loss may have been caused by loss of volatiles in the solvent extraction / residue drying operation. Of the extractable material, 30% was oxygenated organics, 17% organic sulphur compounds, 7% organic nitrogen compounds, and 7% hydrocarbons. Forty percent of the extractable organic carbon was unaccounted for, and may have included asphaltenes. Compounds tentatively identified in the upgrading plant wastewater included:

alkyl substituted benzenes

alkyl substituted naphthalenes
alkyl substituted biphenyls
alkyl substituted anthracenes
alkyl substituted benzothiophenes
alkyl substituted dibenzothiophenes

The benzothiophenes and dibenzothiophenes were also tentatively identified in the dyke drainage samples. In all samples and fractions, gas chromatograms had significant UCM character.

Strosher and Peake (1978) analyzed more upgrading plant wastewater samples and found that, for an average of 36 mg/L of organic carbon, 47% was extractable. Of this portion, 24% was organic sulphur compounds (mainly substituted benzothiophenes), 17% oxygenated organics, 16% hydrocarbons (C8 to C30 n-alkanes, branched and cyclic aliphatics, substituted naphthalenes to multi-ring aromatics), 10% asphaltenes and 7% nitrogen compounds. These proportions differ substantially from those found in their 1976 study, but the scale of variation is not surprising given the complexity of the analyses involved and the large portion of organic matter which cannot be accounted for.

An important aspect of this work (Strosher and Peake 1978) is the information it offers on background hydrocarbons in the Athabasca River. Extensive Alberta Oil Sands Environmental Research Program (AOSERP) monitoring data using the standard freon extraction - partition/gravimetric "oil & grease" method (APHA 1985) has produced a theory (R.

vs Suncor 1984) that background hydrocarbon levels are abnormally high in the Athabasca River. The freon method, which has a usable detection limit of >1 mg/L (APHA 1985) and which is not recommended for levels below 10 mg/L, has been reported for Athabasca River samples to 0.1 mg/L (IWD 1981). These data for Athabasca River sites are summarized in Table 1; sample locations are illustrated in Figure 2.

These values appear erratic and they are misleading if taken as reliable measures of hydrocarbons. At most, only one or two samples are in the recommended range for this method (i.e., >10 mg/L), and at least one of these values is either an error or a contaminated sample. In that case, the oil and grease reported at 176 mg/L would represent a massive level of oil contamination. If the Athabasca River was carrying oil concentrations this high, the flux of oil would range from 470 kg/hr to 10 000 kg/hr (using 1976 and 1977 flow data) depending on the time of year this high value was collected. At the high end of the range (10 t/hr) the river would be carrying commercial (pilot) scale production quantities of oil. However, in all but one case, median river concentrations were 1 mg/L or less, with most sites reporting median values below 0.1 mg/L. The latter value is 1/10 of the detection limit specified for this method (APHA 1985).

Notwithstanding the questions which may be raised about this data base, the few values that are reported in the 1 to 10 mg/L range, combined with the knowledge that bitumen is exposed on the banks of the Athabasca and some

Table 1 Athabasca River oil and grease data

Site Name	Site Number	Low	High	Mean	Median	Number of Samples	Number Below Detection Limit
McDonald Island	00AT07DA0035	<0.1	5	0.6	<0.1	15	9
OSERP Site 3	00AT07DA0036	<0.1	7	1.9	0.5	7	3
OSERP Site 4	00AT07DA0038	<0.1	2	0.4	<0.1	7	6
Old OSERP Dock	00AT07DA0039	<0.1	4.4	0.7	<0.2	11	7
OSERP Site 6	00AT07DA0040	<0.1	0.9	0.3	<0.1	6	4
Upstream of Muskeg R.	00AT07DA0041	<0.1	<0.2	<0.1	<0.1	5	5
Ft.Mackay	00AT07DA0042	<0.1	2.6	1	0.9	24	1
Upstream of Tar R.	00AT07DA0043	<0.1	0.4	0.2	<0.1	7	5
Upstream of Firebag R.	00AT07DA0044	<0.1	<1	0.4	<0.2	7	6
13 mi. below Firebag R.	00AT07DA0045	<0.1	0.7	0.2	<0.1	7	5
Tar Island	00AT07DA0046	1	3	2	1	26	5
Ft. Mackay	00AT07DA0051	<1.0	5	2	2	11	4
Bitumont	00AT07DA0053	<1.0	176	30	1	6	3
Embarras	00AT07DD0001	0.1	2.4	0.8	0.6	14	0
Big Point Channel	00AT07DD0004	0.3	1.4	0.8	0.8	11	0

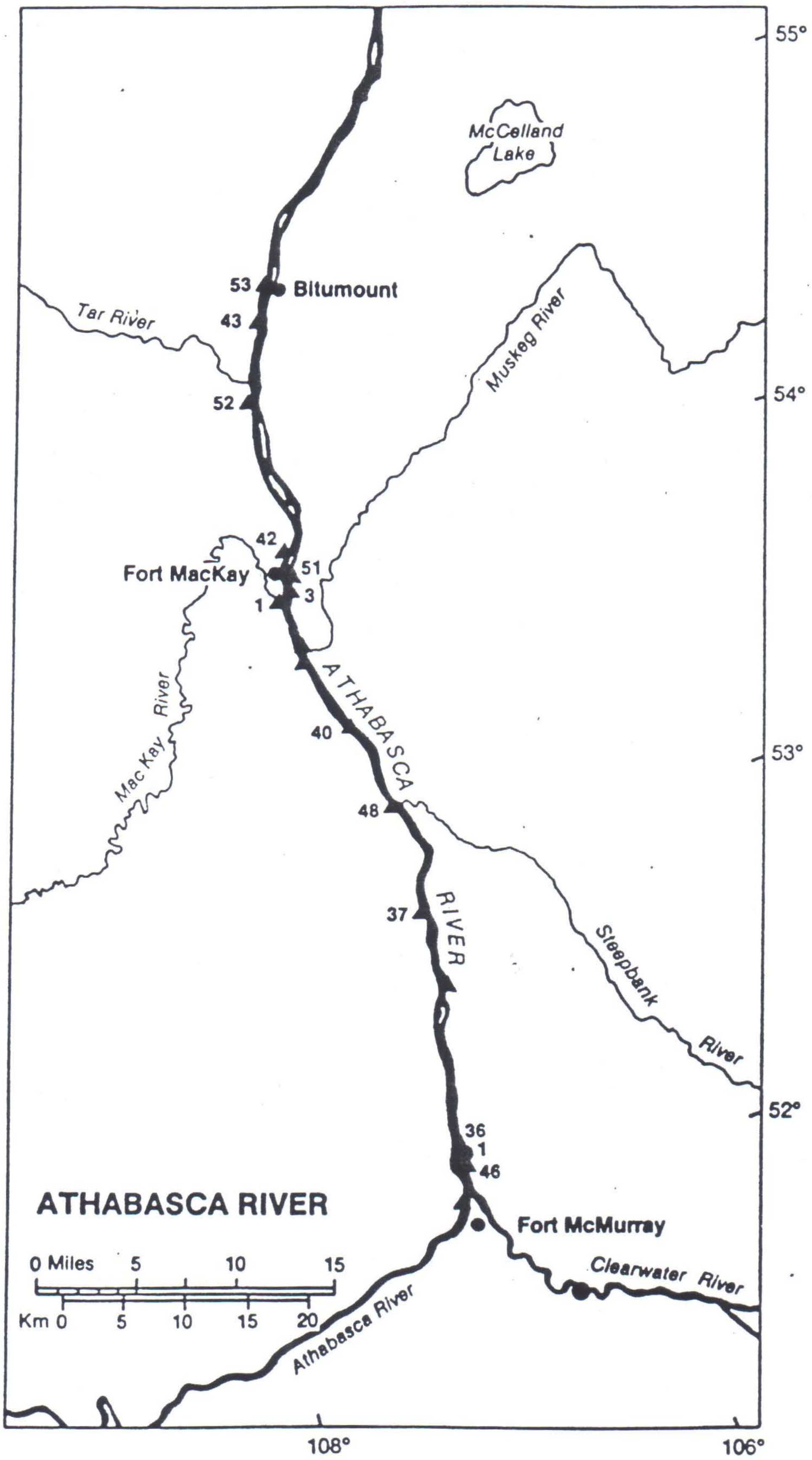

Figure 2. Location of Athabasca River sampling sites

tributaries, has provided the basis for a theory that uniformly high "background" hydrocarbon level exist in the Athabasca River, downstream from Ft. McMurray. These data are not a valid basis for that supposition.

Unfortunately, an adequate data base to prove or disprove theories on background hydrocarbon levels in the Athabasca River has not been gathered. An example of the type of data required is illustrated by the approach taken by Strosher and Peake (1978). They collected river samples both upstream and downstream from the the Suncor (then called GCOS) outfall as well as wastewater samples from the outfall line. Both the aliphatic and aromatic hydrocarbon GC profiles of the wastewater extracts corresponded qualitatively with downstream river samples, while differing substantially from upstream river samples. The aromatic character, in particular, was notably deficient and different in character for the upstream river samples. On a quantitative basis, they found typically about 3 to 4 mg/L of extractable matter (which would roughly correspond to the oil and grease test) in river samples, but GC analyses showed aliphatic plus aromatic hydrocarbons to be generally less than 0.010 mg/L in the same samples. The latter finding casts serious doubt on the accuracy inherent in assuming that extraction gravimetric methods represent hydrocarbons for river samples.

Unfortunately, their work has apparently not been replicated at these sites or elsewhere in the oil sands region of the river. A subsequent report (Strosher and Peake 1979) reported similar low hydrocarbon levels at three sites upstream of Ft. McMurray. Consequently, all that can be said with certainty is that there are insufficient data to support a theory of high "background" hydrocarbon levels in the Athabasca River and the limited useful data that are available suggest that there is a substantial difference in the character of background hydrocarbons from those contained in upgrading plant wastewaters.

Park and Maynard (1980) conducted a survey for U.S.Environmental Protection Agency priority pollutants on three samples from a "Canadian tar sands operation". They analyzed water from a coke storage area, tailings water (no other details given), and solids settled from a tailings pond sample. Very few of the priority pollutants were identified in any of the samples. Specifically, only benzene (.42 mg/L), ethylbenzene (.23 mg/L), toluene (1.09 mg/L), dimethylphthalate (.65 mg/L) and bis (2-ethylhexyl) phthalate (.015 mg/L) were identified in the tailings water sample. Traces were detected for fluoranthene, fluorene, naphthalene, and phenanthrene. A number of other alkanes and alkenes were tentatively identified in the purgeable sample. The base/neutral extract of the tailings solids sample [which would contain the polynuclear aromatic hydrocarbons (PAH)] revealed a complex response indicative of substituted PAH that are not explicitly on the EPA list. As well, some substituted dibenzo- and benzo/naphtho-thiophenes were tentatively identified with the tailings solids.

MacKinnon and Retallack (1981) reported characteristics of the Syncrude tailings pond. This included classification of the major organic compounds identified by GC/MS as summarized in Table 2.

A series of studies by Zenon Environmental Inc. (1984, 1985) focused on characterization and treatment of toxic constituents in tailings pond water, but no detailed GC/MS component analysis of tailings supernatant was reported. An empirical method using dichloromethane extraction at pH 4 and UV absorbance measurement at 227 nm (reported as tar sands acid) was found to possess an infrared (IR) spectrum very similar to commercial grade naphthenic acids. This parameter correlated well with acute toxicity for the samples tested. Schramm et al. (1984) reported the simplified structure (Figure 3) and properties of these components of bitumen.

Given the limited specific compound characterization of tailings pond waters, evaluation of compounds that could reach the tailings pond may be inferred from information on the properties of bitumen and various process intermediates. There has been considerable research done on bitumen properties by experienced hydrocarbon chemists seeking relevant process information. That data base should be considered to help compensate for the inadequate data base available on oil sands wastes.

Table 2. Organic compound classes identified in the Syncrude tailings pond.[a]

HYDROCARBONS	aliphatic	- straight chain alkanes nC_{16} nC_{28} range - complex mix of substituted, unsaturated, cyclic, and branched chain
	aromatic	- simple, alkylated and substituted benzenes - polyaromatics from naphthalenes to substituted benzanthracene
PHENOLS	low molecular weight	- simple and alkylated phenols
	high molecular weight	- complex mix including phenolic acids and polyphenols
ORGANIC ACIDS	most abundant organic group	- few individual compounds identified
OTHER CLASSES	asphaltenes	- about 10% of organic carbon
	organic S compounds	- complex mix, mainly thiophene substituted compounds
	organic N compounds	- low concentrations
	phthalates	- dibutyl and diethylhexyl phthalates

[a]After MacKinnon and Retallack, 1981

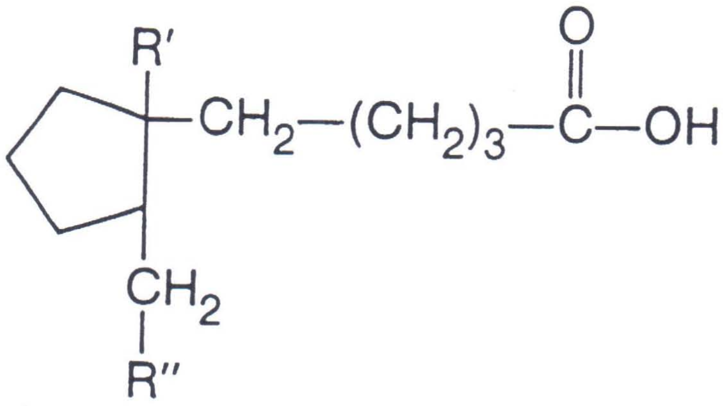

Figure 3. Structure of naphthenic acid

Selucky et al. (1977) and George et al. (1977) reported general composition categories for Athabasca bitumens (summarized in Table 3). The bitumen is often sub-classified into asphaltenes and maltenes, the former being large molecular weight hydrocarbons which are insoluble in pentane, the latter being pentane soluble. Selucky et al. (1977) report the average molecular weight of the asphaltenes as 4500, compared with maltenes at 435. The asphaltenes also contain higher sulphur (7.5% vs. 3.9%), nitrogen (1.1% vs. 0.07%), and oxygen (2.8% vs. 0.85%) than the maltenes. Athabasca asphaltenes have been further characterized by sequential elution solvent chromatography by Jacobs and Filby (1983). Their results are summarized in Table 4.

Hepler et al. (1986) noted that water soluble substances can be present in bitumen or formed during processing. Classes of compounds that may be found are listed in Table 5. Unfortunately, no relative quantity or approximate prevalence was specified.

No analyses of chemical characteristics of components produced during bitumen upgrading, at either Syncrude or Suncor, have been published to our knowledge. Some expectations for likely composition can be deduced from experimental work with bitumen fractions. Ritchie et al. (1979) pyrolized Athabasca bitumen asphaltene at 350, 500, and 800°C, and performed GC/MS analysis on the condensible volatiles. Specific compound classes identified are summarized in Table 6. The sulphur heterocycles (thiophenes,

Table 3 Gross composition of Athabasca bitumen (weight %).[a]

Asphaltenes	Saturates	Mono-aromatics	Di-aromatics	Poly-aromatics & polars	Acids	Bases	Neutral nitrogen	Reference
16.6	18 to 21	8.6 to 9.0	3.8 to 4.4	24	14	6.5	1.3	Selucky et al. (1977)
15.3	21	7.8	11.0	39.1	N.R.	5.7	N.R.	George et al. (1977)

N.R. = not reported

[a] after Selucky et al. (1977); George et al. (1977)

Table 4. Characterization of Athabasca bitumen asphaltenes.[a]

Fraction	Compound Types Eluting	Weight %	Empirical Formula
1	saturates	2.9	$C_{100}H_{164}S_{1.8}O_{0.3}N_{0.1}$
2	aromatics	2.2	$C_{100}H_{143}S_{2.6}O_{1.2}N_{0.4}$
3	polar aromatics, non-basic N, S, O heterocyclics	24.5	$C_{100}H_{121}S_{3.2}O_{4.9}N_{1.1}$
4	monophenols	29.5	$C_{100}H_{127}S_{3.8}O_{7.0}N_{1.1}$
5	basic N-heterocycles	1.6	$C_{100}H_{128}S_{3.8}O_{7.3}N_{1.1}$
6	highly functional molecules with 10 % heteroatoms	11.6	$C_{100}H_{132}S_{5.7}O_{16}N_{1.2}$
7	polyphenols	12.8	$C_{100}H_{122}S_{3.9}O_{9.2}N_{1.3}$
8	functional species with increasing O,N content	7.0	$C_{100}H_{129}S_{3.3}O_{7.6}N_{1.0}$
9	increasing N-basicity	6.2	$C_{100}H_{115}S_{3.8}O_{6.5}N_{1.9}$
10	highly functional species	2.2	$C_{100}H_{124}S_{3.9}O_{11}N_{3.4}$
Whole asphaltene		100	$C_{100}H_{131}S_{3.3}O_{3.6}N_{1.0}$

[a] after Jacobs and Filby (1983)

Table 5 Classes of organic compounds in bitumens and aqueous production streams[a]

hydrocarbons
carboxylic acids
humic and fulvic acids
asphaltic acids
sulphonic acids
phenols
esters
alcohols
aldehydes
ketones
sulphoxides
thiophenes
mercaptans
sulphides
carbazoles
imines
quinolines
porphyrins (V, Ni)

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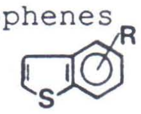
[a] after Hepler et al.(1986)

Table 6. Volatile chemical classes from the pyrolysis of Athabasca asphaltene.[a]

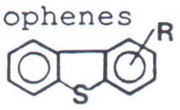
alkyl benzenes

alkyl thiophenes

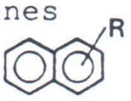
alkyl benzothiophenes



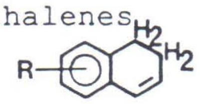
alkyl dibenzothiophenes



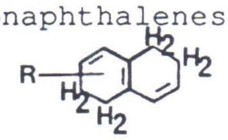
alkyl naphthalenes



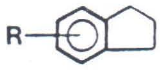
alkyl dihydronaphthalenes



alkyl tetrahydronaphthalenes

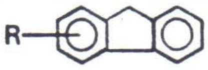


alkyl indans



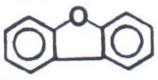
alkyl indenes

alkyl fluorenes

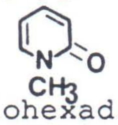


biphenylene

dibenzofuran

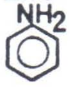


methylpyridone

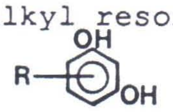


cyclohexadiene

aniline



alkyl resorcinols



alkyl phenanthrenes or anthracenes

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[a]after Ritchie et al., 1979

etc.) were the most prevalent (number of compounds), although the alkylated benzenes were the most abundant (amount). The variety of possible heterocycle isomers is staggering. Nishioka et al. (1986) report studies with 62 possible thiophenic structures involving up to five aromatic rings, but without adding alkyl substitutions. These are depicted in Figure 4.

Moschopedis et al. (1981) studied the nitrogen functional groups present in Athabasca bitumen and concluded that the predominant groups are carbazole structures, although indole structures cannot be ruled out (Figure 5). A class of nitrogen compounds that includes potent mutagens, the aromatic amines, has been reported for other synthetic fuels and petroleum (Tomkins and Ho 1982), but not explicitly for synthetic crude from bitumen (except for aniline). These consist of an amine substitution on benzene, naphthalene, or higher-ring aromatics and include: aniline, toluidine, aminonaphthalenes, aminobiphenyls, aminoanthracenes, etc.

Birkholz et al.(1986) conducted exhaustive analysis of the water soluble extract obtained from an oil sample collected from the Suncor wastewater pond during a plant upset. The oil exhibited properties indicative of partially upgraded bitumen (i.e., raw coker distillate). Gas chromatography / mass spectrometry analysis was conducted following various sample cleanup procedures aimed at providing cleaner mass spectra. The classes of compounds identified are listed in Table 7. Because the focus of this

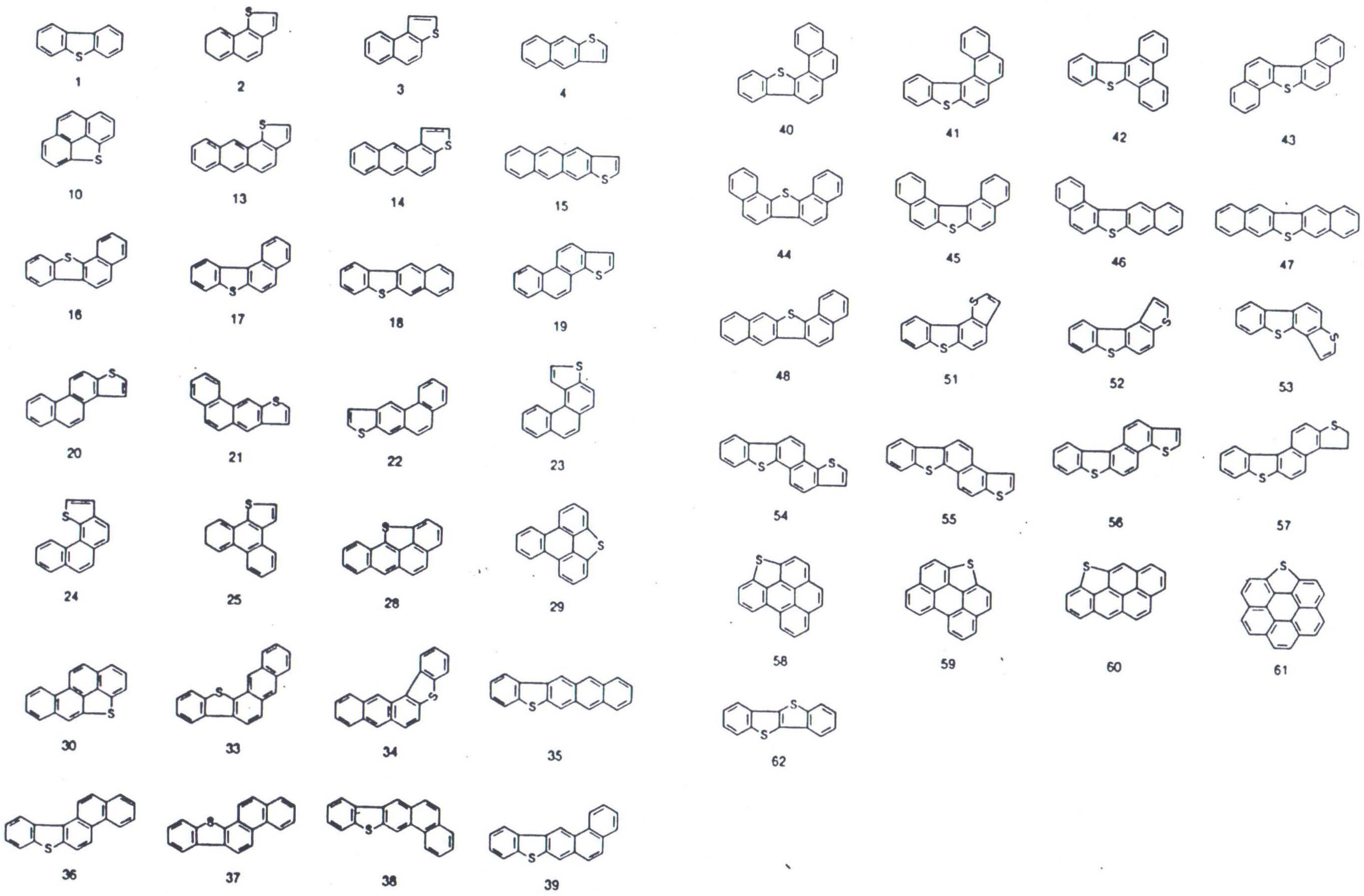


Figure 4. Sampling of sulphur heterocycle (PASH) structures

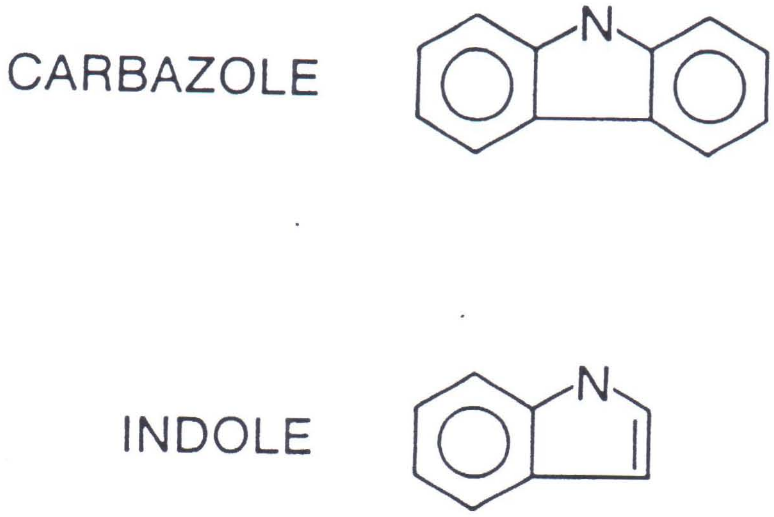
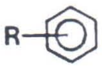
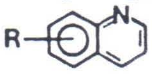
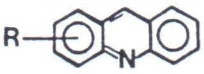
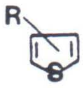
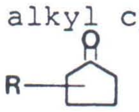
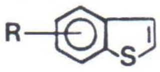
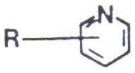
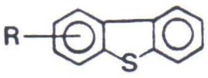


Figure 5. Structures of carbazole and indole

Table 7. Classes of compounds identified in a water soluble extract from a waste oil derived from raw coker distillate[a]

alkyl benzenes 	alkyl quinolines 
alkyl naphthalenes 	acridine 
alkyl thiophenes 	alkyl cyclopentanones 
alkyl indans 	alkyl benzothiophenes 
alkyl pyridines 	alkyl dibenzothiophenes 
alkyl furans 	ketones

[a]after Birkholz et al. (1986).

study was to obtain unequivocal identification of some prevalent compounds for a court case, many other constituents were not pursued for cleanup and identification.

2.2 CONTAMINANT UPTAKE BY AQUATIC ORGANISMS

Oil tainting of aquatic organisms has been a concern for decades. Unfortunately limitations in analytical techniques and the lack of common terminology among disciplines and nations has led to considerable confusion about this subject. This situation is reflected by Stansby (1978), who reviewed the literature on petroleum tainting of fish and concluded:

> The area of research in this field which has been most neglected and which more work should certainly be undertaken is a definitive evaluation of the maximum concentration of different kinds of petroleum in water in which fish can reside without picking up petroleum types of flavors. In what few reports on this matter exist in the literature there is such a complete disagreement among levels found which are said to lead to petroleum flavors or odours in the fish that we really know nothing definite.

He noted discrepancies in the petroleum exposures required to taint, ranging from only 10 ppb in 24 h to greater than 10 ppm for 13 days.

More recent reviews have been conducted by Connell and Miller (1980, 1981), Malins and Hodgins (1981), Motohiro (1983), Persson (1984), and Vandermeulen (1986). The work reviewed by Vandermeulen (1986) and by Malins and Hodgins (1981) is mainly useful for consideration of bioconcentration. The former cites work by Southworth et al.(1978) that documents bioconcentration of di-, tri-, and polyaromatics by *Daphnia pulex* (Table 8).

Malins and Hodgins (1981) cite the work by Roubal et al. (1978) with Coho salmon and starry flounder. They observed 9000 times bioconcentration into muscle for C4- and C5-substituted benzenes for the starry flounder. Other noteworthy observations were:

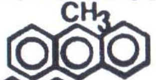
1.the demersal (bottom-dwelling) flounder accumulated more hydrocarbons than the pelagic salmon,

2.alkyl substituted aromatics accumulated to a greater degree than unsubstituted aromatics,

3.salmon depurated within a week in clean water while flounder retained parts per million concentrations of substituted benzenes and naphthalenes over the same period.

Much of the literature reported by Persson (1984) is old and difficult to reconcile with modern analytical data. For example, threshold taint levels for compounds relevant to oily taint extracted from his Table 2 were derived from references dated as follows: ethylbenzene (1959), isopropylbenzene (1959), methylnaphthalene (1959), naphthalene (1955, 1959), naphthylamine (1958), quinoline (1955), toluene (1953, 1959), and methylaniline (1958). Because gas chromatography was not in widespread use in the 1950s and was certainly not reliable for quantitative trace analytical work, these data do not represent a reliable basis for current decisions.

Table 8 Bioaccumulation of aromatic hydrocarbons by *Daphnia pulex*[a]

Compound	Molecular Weight	Ring Number	Bioconcentration factor (24 h)	Uptake rate (h^{-1})	Elimination rate (h^{-1})
naphthalene 	128	2	131 +/- 10	197	1.667
phenanthrene 	178	3	325 +/- 56	203	0.543
anthracene 	178	3	917 +/- 48	702	0.589
9-methylanthracene 	192	3	4583 +/- 1004	561	0.144
pyrene 	202	4	2702 +/- 245	1126	0.343
benz(a)anthracene 	228	4	10 109 +/- 507	669	0.144
perylene 	252	5	7191 +/- 804	752	0 139

[a]after Southworth et al.(1978)

Connell and Miller (1981) cite Kerhoff (1974) for threshold tainting levels for various compounds, but comparison of the numerical values cited shows that most correspond to the old references cited by Persson (1984). Connell and Miller cited two references (Moore and Dwyer 1974; Nitta 1972) that suggested that very low levels of oil (0.001 to 0.01 ppm) were sufficient to taint oysters. Connell and Miller (1981) also summarized a series of references on oily taints of fin fish. Most of this work was in marine environments, and very little quantitative information was provided. Because there has been no integrated parameter to measure and express total hydrocarbon-related compounds, cases of tainting have been judged largely on specific compound analyses and sensory evaluation.

Wellington Environmental (1983) conducted a series of analyses on tainted walleye from the Athabasca River. Their initial work provided very rough quantitative estimates of tissue levels of hydrocarbon contaminants for five walleye collected by Alberta Fish and Wildlife. They reported aliphatic hydrocarbons ranging from 40 to 150 ppb, polynuclear aromatic hydrocarbons (PAH) ranging from 50 to 1600 ppb and polynuclear aromatic sulphur heterocycles (PASH) ranging from 30 to 1500 ppb. Subsequent work focused on qualitative matching of specific compounds found in the fish tissue with those identified in the Suncor waste oil described by Birkholz et al. (1986). Compounds that were rigorously matched included dimethylbenzenes, tetramethylbenzene, and dimethylnaphthalene. Several other compounds corresponded to those in the oil, but were not confirmed with authentic standards. Many other compounds were identified by GC/MS, but only tentatively in the fish extracts, including some alkyl- substituted thiophenes.

2.2.1 Alkylated Benzenes

Ogata and Miyake (1973, 1975) and Ogata and Ogura (1976) implicated toluene and xylenes as contributors to objectionable odours in fish exposed to petroleum. Their quantitative analysis was rudimentary by current standards and is not judged to be sufficiently reliable as a basis for current interpretation. For these compounds, the work of Roubal et al. (1978), discussed previously, likely provides the most useful data.

2.2.2 Alkylated Naphthalenes

Alkylated naphthalenes, naphthalene in particular, have received considerable attention in well-documented experimental investigations. Lee et al. (1972) examined the uptake, metabolism, and discharge of ^{14}C-naphthalene and ^{3}H-3,4-benzopyrene. They found that the entrance of these compounds into the fish was via the mouth and gills, metabolism by the liver, transfer of the hydrocarbon and metabolites to the bile, and excretion. The gall-bladder was a major storage site, while the urine appeared to be the major route of discharge. The fish readily take in these hydrocarbons from sea water, but also are able to efficiently detoxify and remove these compounds from most tissues, although removal from flesh appeared to be slowest. Major metabolites produced were: ^{3}H-7,8-dihydro-7,8-dihydroxybenzopyrene and ^{14}C-1,2-dihydro-1,2 dihydroxy-naphthalene.

Varanasi et al.(1979,1981a) provided exposure of H-1-naphthalene to flounder, and found significantly higher concentrations in the tissues of flounder kept at 4°C compared with those maintained at 12°C. This retention effect was even more marked after one week, when the muscle and liver of fish at the cooler temperature contained levels that were 26 to 34 times higher. Increases in concentrations of naphthalene at the lower temperature were much more pronounced than for its metabolites, which were primarily dihyrodiol and its conjugates.

Melancon and Lech (1978) studied the distribution and elimination of naphthalene and 2-methylnaphthalene in rainbow trout. They found that elimination of ^{14}C from radio-labelled naphthalene was much slower after long-term exposure (four weeks) than after short-term exposure (@40 hours). Furthermore, long-term exposure resulted in a greater percentage of metabolites in the muscle, increasing from 1% of ^{14}C present after short-term exposure to 24% after long-term exposure. These results are consistent with the theory of differential rates of elimination of 2-methylnaphthalene and its metabolites. They indicate that short term exposures may be misleading in predicting long-term tissue levels of certain chemicals.

Woodward et al.(1983) studied the accumulation and sublethal effects of a refined oil in cutthroat trout. Fish were kept in concentrations of total hydrocarbons ranging from 24 to 183 ppb in water for 90 days. Napththalenes were the dominant component of the aromatic fraction of the oil, and were readily taken up by the cutthroat trout. Those fish in the 183 ppb (total oil) accumulated 4.6 ppm total naphthalenes and responded adversely to seven tests of biological response (i.e., survival, growth, gill pathology, liver pathology, caudal fin erosion, caudal fin pathology, and swimming performance). Fish exposed to 39 ppb total oil accumulated 2.7 ppm of naphthalenes and responded negatively to two of the seven biological tests, while fish in 24 ppb total oil accumulated only 1.2 ppb of naphthalenes and had a response toward the seven tests that was similar to that of the control fish. Growth was retarded in those fish exposed to the highest concentration, with decreasing effect as the concentration was reduced.

Extreme hypertrophy of the gill epithelium and necrosis of the liver occurred at 183 ppb. They found a levelling off of naphthalene accumulation in flesh above 56 ppb total oil; however, this may be due to an inability of fat tissue to accumulate any more, or mixed function oxygenase (MFO) activity transforming the napthalenes into soluble metabolites.

2.2.3 Polynuclear Aromatic Hydrocarbons (PAH)

Polynuclear aromatic hydrocarbons PAH have received considerable attention because some of them are known carcinogens. In particular, several studies have been directed at 3,4-benzopyrene (or benzo[*a*]pyrene) (Mallet 1967; Mallet and Louise 1967; Malanoski et al. 1968; Howard and Fazio 1969; Diamond and Clark 1970; Pancirov and Brown 1977; Payne and Penrose 1975; Capone et al. 1976; Kurelic et al. 1977;Dunn and Fee 1979; von Hofe et al. 1979; Ilnitsky et al. 1979; Varanasi and Gmur 1980; Varanasi et al. 1981b; Hose et al. 1982; Thornton et al. 1982; Lawrence and Weber 1984). This particular compound is not known to be a specific problem for oil sands wastes, and these studies will not be discussed further as they relate to 3,4-benzopyrene.

Dunn and Fee (1979) found that some commercial seafoods were contaminated with PAHs at concentrations ranging from 10 to 215 ppb. In particular, they demonstrated that lobsters held in tidal ponds made of creosoted lumber became contaminated with PAH. Lawrence and Weber (1984) also documented the occurrence of PAH in seafood products.

Niimi and Palazzo (1986) reported the biological half-lives for eight PAHs based on a single oral dose experiment with rainbow trout. They found values of nine days for phenanthrene, seven days for fluorene and anthracene, and six days for fluoranthene. No values were determined for the remainder (benzo[*a*]pyrene, benz[*a*]anthracene, chrysene, or pyrene) because low or non-detectable values were determined at the first sample interval. The data suggest that these PAH are poorly absorbed by trout, although the overall experimental approach was not very realistic compared with likely environmental uptake.

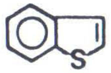
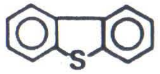
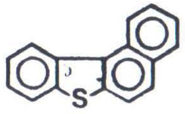
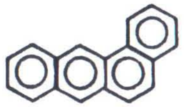
2.2.4 Polynuclear Aromatic Sulphur Heterocycles (PASH)

Ogata and Miyake (1978, 1980) found that eels exposed to crude oil exhibited flesh contamination by alkyl derivatives of benzothiophene and dibenzothiophene. Ogata and Fujisawa (1983) found accumulation of alkylated dibenzothiophenes (C_1 - C_3) to tissue concentrations of 6 ppb in oyster and 9 ppb in mussel. These corresponded to bioconcentration factors from 1845 to 28 500.

Paasivirta et al. (1981) and Sinkkonen (1982) measured a range of parts per million concentrations of alkyl dibenzothiophenes in fish and mussel from the Baltic. They found a good correlation between total oil residues and residues of dimethyldibenzothiophenes.

Vassilaros et al. (1982) analyzed sediment near a coking plant outfall and tissue from catfish for PAH and PASH. They found part per billion concentrations of specific compounds in each class. They also argued that the environmental significance of the PASH would be greater because of their higher water solubility relative to the corresponding PAH (Table 9).

Table 9 Comparison of octanol/water partition coefficient and water solubility for Selected PASH and PAH[a]

PASH	Log P	Water Solubility	PAH	Log P	Water Solubility
thiophene 	1.6	1430.	benzene 	1.6	1515.
benzothiophene 	3.1	113.	naphthalene 	3.4	30.
dibenzothiophene 	4.4	1.7	anthracence 	4.4	0.04
benzo[*b*]naphtho-[1,2-*d*]thiophene 	5.6	0.06	benz[*a*]-anthracene 	5.6	0.01

[a] after Vassilaros et al.(1982)

Eastmond et al. (1984) measured the uptake and elimination of PASH by *Daphnia magna* and compared bioconcentration with the corresponding PAH analogue. Their results are summarized in Table 10, and they suggest a greater degree of bioconcentration for the PASH than for the corresponding PAH.

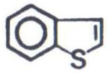
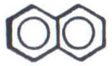
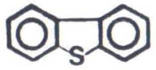
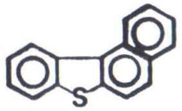
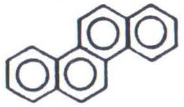
2.2.5 Polynuclear Aromatic Nitrogen Heterocycles (PANH).

Polynuclear aromatic nitrogen heterocycles (PANH) which are believed to be generally more toxic than PASH or PAH have received very little attention with regard to uptake. Southworth et al. (1978) studied the bioconcentration of benz[*a*]acridine, acridine, and isoquinoline by *Daphnia magna*. They found bioconcentration factors of 350, 30, and 2.5 respectively for these compounds. Southworth et al. (1981) studied the accumulation of benz[*a*]acridine by fathead minnows and found a value of 106 $^+/-$ 17, which was about one-tenth that predicted by correlation models based upon the octanol water partition coeffient.

2.2.6 Naphthenic Hydrocarbons

Naphthenic hydrocarbons are part of the saturate fraction, which is a major component of bitumen. The naphthenic acids mentioned in Section 2.1 are believed to be a major portion of the dissolved organic carbon in tailings pond water. Unfortunately very little work has been reported on these compounds. Cravedi and Tulliez (1982) conducted

Table 10. Summary of peak bioconcentration factors and elimination half lives for PASH and PAH in *Daphnia magna*.[a]

PASH	Peak BCF	Elimination half-life (h)	PAH	Peak BCF	Elimination half-life (h)
benzo[*b*]thiophene 	750	27	naphthalene 	50	b
dibenzothiophene 	600	12	phenanthrene 	600	b
benzo[*b*]naphtho-[2,1-*d*]thiophene 	8000	23	chrysene 	5500	18

[a] after Eastmond et al. (1984)

[b] elimination not first order

feeding experiments with rainbow trout using the cyclic paraffin, dodecylcyclohexane. They found that this compound was accumulated to a greater degree than the branched isoprenoid hydrocarbon, pristane. Accumulation was measured on several tissues, but was most notable in the fat tissue of the gut, where concentrations reached over 11 000 ppm.

2.3 AESTHETIC CONSIDERATIONS OF CONTAMINANTS IN WATER

The presence of trace contaminants in the Athabasca River could exert an adverse effect by causing an unacceptable taste or odour in fish or in the water itself. Threshold taste or odour levels for oily contaminants in fish have not been rigorously reported; however, several papers report threshold odour concentrations for specific contaminants in water. These are summarized in Table 11 for the contaminants relevant to this study. An important aspect of odour detection is the relative sensitivity of different individuals which varies over a wide range. Cees et al. (1974) showed that for a series of chemicals including trimethylbenzene, 5% of observers may be expected to detect odours at 0.01 of the group mean threshold odour concentration.

Another concern is whether the source of off-odours or tastes can be determined. Because some of the old literature concerning naturally caused oily taints is continually cited in recent reviews (i.e., Connell and Miller 1981; Motohiro 1983), an impression exists that oily taints

Table 11. Threshold odour levels for oily contaminants in water

Substance	Threshold Odour Level (ppm)	Reference
n-alkanes C_7-C_{12}	10 to 50.	Zoeteman et al.(1971)
branched alkanes	10 to 500.	Zoeteman et al. (1971)
benzene	10. 0.072	Zoeteman et al. (1971) Alexander et al.(1982)
toluene	1. 0.024	Zoeteman et al. (1971) Alexander et al. (1982)
ethylbenzene	0.1 0.14 0.0024	Zoeteman et al. (1971) Rosen et al. (1963) Alexander et al. (1982)
n-butylbenzene	0.1	Zoeteman et al. (1971)
t-butylbenzene	0.05	Zoeteman et al. (1971)
xylenes	1.	Zoeteman et al. (1971)
diethylbenzene	0.0012	Alexander et al. (1982)
cumene	0.1	Zoeteman et al. (1971)
trimethylbenzenes	0.5	Zoeteman et al. (1971)
p-cymene	0.1	Zoeteman et al. (1971)
tetralin	0.01 0.018	Zoeteman et al. (1971) Rosen et al. (1963)
indene	0.001	Zoeteman et al. (1971)
naphthalene	0.005 0.007	Zoeteman et al. (1971) Zoeteman et al. (1971)
1-methylnaphthalene	0.02	Lillard and Powers (1975)
2-methylnaphthalene	0.01	Lillard and Powers (1975)
2,6-dimethylnaphthalene	0.01	Brady (1968) as cited in Zoeteman et al. (1971)
2,6-dimethylanthracene	0.5	Brady (1968) as cited in Zoeteman et al. (1971)
acenaphthene	0.08	Lillard and Powers (1975)

Table 11 Threshold odor levels for oily contaminants in water continued

Substance	Threshold Odor Level (ppm)	Reference
dibenzofuran	0.12 0.003	Lillard and Powers (1975) Alexander et al. (1982)
2-benzothiazole	0.08	Lillard and Powers (1975)
2-mercaptobenzothiazole	1.76	Lillard and Powers (1975)
various crude oils	0.0005 to 0.01	Zoeteman et al. (1971)
gasolines	0.01	Zoeteman et al. (1971)
diesel	0.0005	Zoeteman et al. (1971)
fuel oil (400 Shell)	0.002	Zoeteman et al. (1971)
#2 fuel oil	0.0008	Alexander et al. (1982)
naphtha	0.016	Alexander et al. (1982)

may easily be confused with other taint sources. Experienced researchers who have tested a wide variety of off-odours or flavours do not agree. Specifically, Kuusi and Suihko (1983) state: "The taste of oil is so distinct that it is usually identifiable even when present simultaneously with another off-flavour. The panelists were able to recognize it unambiguously."

2.4 HEALTH EFFECTS

An overview of potential health effects associated with oil sands contaminants in the aquatic environment cannot avoid concern with levels required for carcinogenicity rather than levels necesary for acute health concerns. Short-term health effects would normally require concentrations of contaminants high enough that nuisance conditions arising from taste and odour would also be expected. However, the no threshold, linear model for carcinogenicity specifies some risk, no matter how small, with any exposure to proven carcinogens. Hence, long-term exposure to proven carcinogens at levels too low to be detected by sensory perception may pose an unacceptable risk if contaminant potency is high enough.

Of the chemicals considered in this review, only some of the specific PAH are known carcinogens, and their levels are relatively low and are associated with particulate matter in the tailings pond. However, considerable interest has been generated in the mutagenicity of various compounds and mixtures associated with synthetic fuels production.

Shahin and Fournier (1978) performed the Ames Salmonella / mammalian-microsome assay on seven fractions of oil sands, namely whole bitumen, maltenes, asphaltenes, saturates, monoaromatics, diaromatics, and polyaromatics. None of these materials tested positive in the Ames test, with or without metabolic inactivation. Further testing demonstrated that the polyaromatic fraction actually suppressed the mutagenic activity of the known mutagen 2-aminoanthracene.

Attention has been focused on the aromatic amines because some of the individual compounds are known to be potent mutagens (Guerin et al. 1980). Work with petroleums, shale oils, and coal-derived liquids has shown that mutagenicity of the mixtures can be largely traced to fractions enriched in the primary aromatic amines (Guerin et al. 1980; Wilson et al. 1980). Buchanan et al. (1983) attributed higher mutagenic activity in synthetic fuels (compared with conventional petroleum) to aromatic amines, azaarenes, and hydroxyaromatics. Calkins et al. (1983) found that lower boiling fractions were free of any biological activity, but higher boiling fractions and residues from synthetic crude (shale oil or coal- derived) were mutagenic. Wilson et al. (1981) demonstrated that hydrogenation essentially eliminated the mutagenicity of coal- derived liquids. This finding is consistent with other observations that the more polar fractions are responsible for the mutagenicity. The nitrogen-based mutagens should pose less of a problem with oil sands synthetic crude than is noted in the foregoing references, because the oil sands are not as high in organic nitrogen as those other sources.

Sulphur heterocycles pose a larger concern on the basis of prevalence, because the oil sands are very high in sulphur. Pelroy et al. (1983) tested three- and four-ring PASH compounds with the Ames assay. Of the four three-ring compounds tested, only naphtho[1,2-*b*]thiophene was mutagenic. Of the four-ring compounds seven of 13 were mutagenic, with phenanthro[3,4-*b*]thiophene exhibiting the same potency as 3,4-benzopyrene. The remaining active four-ring compounds exhibited much lower potency.

McFall et al. (1984) tested dibenzothiophene and three isomers of benzo[b]naphthothiophene and found them to be very weak or non-mutagenic. Methylated derivatives of these compounds were more mutagenic, but were still rated as only weak mutagens.

2.5 MONITORING

Procedures for monitoring contaminants from oil sands operations still pose a significant problem. As noted in Section 2.1, the conventional oil and grease parameter based on partition-gravimetric determination provides very little useful information, particularly at low concentrations. Partition-infrared techniques (Gruenfeld

1973,1975; APHA 1985; ASTM 1985) are generally more reliable as gross measures of waterborne oil, but they depend upon calibration by a reference oil and they are biased to determination of aliphatic hydrocarbons because of the absorption bands that are used (Kalbfus in: CONCAWE 1982).

Gas chromatographic (GC) methods can provide substantial information on the character of waterborne oils, particularly if used in combination with mass spectrometry (MS). Unfortunately, the latter is too expensive for routine monitoring. Obtaining maximum useful information from GC methods usually requires substantial sample cleanup to allow resolution of individual peaks from among complex mixtures. Such cleanup procedures are usually too tedious for routine monitoring. In particular, tissue analysis is complicated by interference from biogenic hydrocarbons and specific cleanup measures are necessary (Warner 1976). Likewise, reliable quantitative analysis by GC for specific compounds requires adequate resolution and calibration where elements other than carbon are present in substantial proportion. Gas chromatographic analysis by flame photometric detector is useful for analysis of sulphur containing compounds (Birkholz et al. 1986).

Fluorescence methods have been commonly used for qualitative analysis (identification) of oils with quantitative analysis being less common (Frank 1978; Frank et al. 1979). These methods have the advantage of being very sensitive and responsive to primarily aromatic hydrocarbons.

Because aromatics are more water soluble and generally pose more environmental problems, fluorescence techniques are promising. They have been used to identify oil contamination of aquatic organisms (Zitko 1971; Friocourt et al. 1985).

The combination of fluorescence monitoring with high pressure liquid chromatography (HPLC) offers particular promise for monitoring oil contamination of waters and organisms. This approach has been used very successfully by Krahn et al. (1984, 1986) and Malins et al. (1985a, 1985b). These researchers have demonstrated the utility of this method for the analysis of fish bile to detect metabolites of aromatic hydrocarbons. They have been able to correlate these measures with the occurrence of tumours and lesions in fish livers.

3. CONTROL OPTIONS

3.1 PROCESS SOURCE AND IN-PLANT CONTROLS

Prevention of pollutants from reaching water and removal of pollutants from as simple a matrix as possible are basic principles underlying cost-effective pollution control. Implementation of these principles requires that waste streams should be monitored as close to the source of contamination as possible to identify preventable inputs. On-line monitors for organic carbon, infrared absorbance, or fluorescence would help to identify problem waste streams so that measures to reduce or eliminate unnecessary contamination can be identified. Once waste streams have been allowed to mix, problems for specific contaminant removal are greatly increased. This situation currently exists where all liquid wastes are eventually mixed in the tailings pond. Likewise, diversion of wastes from upset conditions to the tailings pond will only make the ultimate treatment of tailings water more difficult. Separate spill ponds, which allow wastes directed there to be individually treated in batch, will prevent unnecessary mixing of contaminants in the tailings pond. For example, if maximum oil removal is practised on oily waste streams, the resulting water would only be degraded by mixing in the tailings pond, whereas cleaner streams should be exploited for their maximum direct reuse potential.

3.2 EXTERNAL TREATMENT NEEDS

Treatment options to reduce the likelihood of potential fish tainting must be specifically directed at those compounds capable of causing tainting. To date, treatment research has been directed at reducing acute toxicity to fish (Zenon Environmental Inc. 1984,1985; Boerger and Aleksiuk 1986). While this objective is clearly worthwhile, attainment of a non-lethal effluent does not assure that the effluent will not taint fish.

A wide range of compounds that are capable of tainting fish has been identified in oil sands processes. Those compounds that are: prevalent in oil sands waste streams, have high bioconcentration factors for aquatic organisms, and have very low taste and odour thresholds pose the greatest risk. From compounds reviewed in Section 2, the highly alkylated benzenes and naphthalenes and the PASH compounds seem to offer the greatest taint risk. The naphthenic acids are very prevalent, but not enough is known about their bioconcentration or taste and odour properties to judge their taint potential.

Treatment options for such compounds would normally include chemical oxidation, solvent extraction, adsorption, or biological treatment (EPA 1980). Zenon Environmental Inc.(1984, 1985) found some success with acidification for the specific problem of naphthenic acids. The problem which will arise is the large volumes of wastewater which will require treatment if significant removal of water from the tailings pond is to be achieved. Boerger and Aleksiuk (1986) estimated that the Syncrude Tailings pond may eventually contain 200 x 10^6 m^3 of free water. Chemical treatment options evaluated by Syncrude which involved acidfication, flocculation with anionic polyelectrolytes and neutralization were estimated to cost \$0.25/m^3 (Boerger and Aleksiuk 1986). These costs which are regarded as high by Syncrude are much lower than would be associated with most other viable treatment options.

Chemical oxidation is unlikely to be practicable for tailings waste streams because of the high doses of oxidant chemicals that would be necessary to deal with the high organic carbon levels present. Partial oxidation may only create problems through the formation of new compounds, which may pose more problems than the parent compounds.

Solvent extraction is unlikely to be practicable because of problems with emulsion formation and solvent recovery. Solvent extraction processes are usually only economic when used with relatively high strength wastewaters and where solvent recovery and reuse can be practised. If efficient solvent recovery is not achieved, then problems will arise with solvent contamination of the wastewater.

Adsorption processes such as granular activated carbon (GAC) should be applicable to removal of the problem contaminants because the properties that promote high bioconcentration potential also promote adsorption. However, the feasibility of applying adsorption will depend on the rate of exhaustion of the adsorbent. Without substantial reduction in organic carbon by some cost-effective pretreatment, GAC is unlikely to be a feasible alternative. However, this technology may offer the only viable technical alternative for adequate removal of trace contaminants.

Biological treatment options usually are attractive for high-volume waste streams, provided that the contaminants to be removed are biodegradable. Most of the contaminants under consideration have been biodegraded under favourable conditions. Specifically, provision of adequate nutrients and conditions favourable for maximum biomass growth are essential. Aerobic rather than anerobic conditions will likely be more successful. Rates of biological activity dictate that no significant treatment could be expected during winter months. The most cost-effective biological treatment processes should be active rather than passive (i.e., conditions should be engineered to promote maximum biomass growth and substrate removal rather than accepting environmentally limited rates). Two types of process may be promising: overland flow and slow sand filtration.

Overland flow (Overcash and Pal 1979) makes use of plant-soil systems to extract and biodegrade organic pollutants from a thin film of wastewater that is allowed to trickle over the ground surface. Provided that loading rates are controlled and adequate nutrients are supplied, very high quality effluents can be achieved. The land requirements for this option are likely to be a constraint but they would have to be balanced against the existing massive land area occupied by the tailings ponds. Climatic factors are also likely to be limiting, with treatment likely to be viable only for half of the year.

Slow sand filtration (Overcash and Pal 1979) makes use of low- rate infiltration of permeable soils, with the treated wastewater reaching the groundwater table or engineered collection drains. The success of this process depends upon promoting biomass growth within the sand medium. Experience with the high levels of organic carbon observed in tailings pond dyke drainage suggests that biological activity and high-rate bioconversion of organics does not occur spontaneously to a significant degree. This may be caused by inadequate nutrient availablity or inadequate residence time, or both. Performance of filtration for trace contaminant removal could be potentially enhanced by inclusion of an adsorbent, such as activated carbon within the filter medium. This process, like overland flow will suffer from large land area requirements and climatic limitations.

In summary, there do not appear to be any obvious treatment technologies which will insure adequate contaminant removal while meeting the cost limitations considered feasible by the plant operators.

3.3 MONITORING

Regardless of the treatment system used, monitoring successful performance remains a difficult problem. Specific compound analysis on a routine basis is not practical, and even if it were, there is insufficient knowledge to reliably dictate which specific parameters must be monitored. Consequently, some form of pragmatic alternative that could assure the safety of the fishery should be implemented. This could be achieved by running the treated effluent through a holding reservoir stocked with fish that are routinely monitored by a sensitive technique such as the HPLC-fluorescence analysis of bile (Krahn et al. 1984,1986). To account for long-term protection, the reservoir could be also stocked with filter-feeding organisms such as freshwater clams. These would be expected to bioconcentrate contaminants to a high degree, and should serve as an early warning of accumulation in the environment. A key consideration in any such system must be that the monitoring system be more sensitive to the problem contaminants than the most sensitive relevant species in the river.

4. RESEARCH NEEDS

4.1 BASELINE KNOWLEDGE

There is currently no significant knowledge of the status of fish in the Athabasca River with regard to background oil contamination. The upset conditions at Suncor during the winter of 1981-82 led to intensive analytical efforts on a small sample of walleye (Wellington Environmental 1983) which was utlimately accepted as evidence of tainting by the disharged oil. Specifically Judge Dimos of the Provincial Court of Alberta found (R. v. Suncor 1984):

> ...I am totally satisfied that in the result, the tests showed that the panelists were perceiving a petroleum oil base type flavour in the fish, obtained from the Athabasca River and caught May 11th, 1982 downstream from the Suncor plant. I have no doubt that the panel could distinguish levels of intensity and that the Walleye taken from the river were basically found to be unfit by reason of the petroleum taste. A similar result occurred with respect to the Winnipeg whitefish which were exposed to sample 1302..........In considering the evidence, I have no difficulty in accepting that taint occurred in fish as a result of "oil and grease" released by Suncor into the waters of the Athabasca River.

Unfortunately, there has been no coordinated followup on the evidence collected for this trial. This deficiency should be corrected by performing fish sampling surveys during different seasons and establishing background tissue levels for the major compound classes (alkyl benzenes, naphthalenes and PASH). Furthermore, the HPLC-fluorescence method should be applied to fish bile, along with sensory evaluation of fish flesh.

The aforementioned evaluation of the fisheries resource should be co-ordinated with a survey of food organism, sediment, and water column analyses for the same compounds.

Existing data on the composition of tailings water are inadequate to draw final conclusions about which compounds will pose the greatest problem. More specific compound analyses with at least semi-quantitative results are necessary.

Finally, there is a need to determine what levels of exposure to the major compound classes, and complex mixtures containing these compound classes, are necessary to cause tainting over short-term and long-term exposure.

4.2 FATE AND BEHAVIOUR

Basic understanding of the relevant environmental properties of the highly alkylated benzene and naphthalene species and essentially all of the PASH will be necessary before any serious modelling activities can be pursued. These would include water solubility, partition coefficients, vapour pressure, Henry's Law constants, and biodegradation rates under realistic environmental conditions. Properties of these compounds in complex mixture will also need to be considered.

4.3 TREATMENT

Essentially no information exists on the performance of viable treatment options for the removal of the problem compounds discussed in this report. The basic properties delineated in Section 4.2 will help, but specific beaker-scale treatability studies and sensitivity values to environmental conditions for proposed treatment options should be determined. Such information is necessary to assure that optimum treatment performance and cost-effectiveness is achieved.

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