AQUATIC FATE OF FISH TAINTING COMPOUNDS
IN THE ATHABASCA RIVER

RESEARCH MANAGEMENT DIVISION

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AQUATIC FATE OF FISH TAINTING COMPOUNDS IN THE ATHABASCA RIVER

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for

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PREFACE

Syncrude Canada Ltd.'s Fort McMurray oil sands mining operation has been operating under the concept of zero discharge or total containment of wastewaters since start up in 1978. Recently, Syncrude requested that Alberta Environment establish standards/guidelines for treated wastewater discharge from the plant to the Athabasca River. The request was made in recognition of Syncrude's eventual need to decommission the site and tailings pond area.

In considering such a request, Alberta Environment requires that the best practicable wastewater treatment technology be implemented and that downstream impacts be environmentally acceptable. Because of the unique nature and volume of the extraction wastewaters, the lack of proven treatment technology, and the sensitive downstream water uses, considerable research is required before discharge criteria can be established and such a request granted.

Discharge criteria would focus on pollutants outlined in the Alberta Petroleum Refinery Effluent Guidelines. Effluent standards for the oil sands discharges must also address, among other things, acute and chronic toxicity of pollutants and their fish tainting potential.

The motivation for examining this fish tainting issue arises from the knowledge that several compounds, singularly or in combination, have been shown to taint fish at low concentrations. Some of these compounds are present in tailings pond wastewaters. However, much contradiction and confusion exists as to how and at what level these and other compounds would behave within the actual effluent matrix. Whether these compounds would be taken up by fish or other aquatic life and how long the chemicals would be retained are other areas yet to be explored.

To compound the problem of an incomplete knowledge base on fish tainting, there are limited existing regulations to control industrial discharges based on taint potential. In addition there does not appear to be any wastewater treatment technology specifically developed to reduce the fish tainting substances.

Alberta Environment is further addressing research into fish tainting through support of a companion report entitled Review of Oil Sands Tailings Pond Contaminants with Fish Tainting Potential. Fish taint experiments are also being conducted by Syncrude on site with the assistance of the Department. In addition, three graduate student projects are concerned with this issue under the direction of Dr. Steve Hrudey at the University of Alberta.

Prepared by: Research Management Division

EXECUTIVE SUMMARY

This report investigates the relationship between certain hydrocarbons that are present naturally, or could be introduced due to surface oil sands mining and upgrading activities, and their potential bioaccumulation and tainting of the commercial fishery in the Athabasca River. This includes defining the contaminants of concern, reviewing their bioavailability and bioconcentration properties and consideration of their persistence in the aquatic environment of the Athabasca River. A water management approach for setting ambient surface water objectives and effluent standards for fish tainting compounds is discussed within the context of basin-wide water resource planning.

The scientific literature regarding petroleum related compounds that could cause off-flavour in fish is often confused and contradictory. This results from inconsistent testing protocols and lack of analytical precision. However, it is generally concluded that low molecular weight compounds, i.e., dibenzothiophenes, naphthenic acids, mercaptans and methylated naphthalenes are petroleum related compounds which can taint fish. Phenolics are also of concern.

Detailed chemical characterization of wastewaters originating from oil sands extraction is lacking. Those data which are available indicate that the general composition of the wastewaters is the same as the raw bitumen, but relative concentrations are drastically altered. The oil in natural bitumen deposits is deficient in water-soluble components, saturated hydrocarbons (n-paraffins) and low molecular weight aromatic compounds, while being enriched in asphaltenic and nitrogen-, sulfur-, and oxygen-containing compounds (NSO compounds). The process effluents (e.g., upgrading wastewaters and tailings pond discharge) resemble more the synthetic crude than the parent bitumen, being enriched in aromatic and alipathic compounds, including those which have the potential to taint fish flesh.

Cross comparison between compounds known to taint fish and those which could exist in oil sand wastewaters results in identification of the following major compound groups:

1. alkylated naphthalenes;
2. alkylated benzothiophenes;
3. alkylated dibenzothiophenes;
4. naphthenic acids; and
5. phenols.

This list should be revised once the wastewater characterization is more complete.

The uptake and bioaccumulation of tainting compounds is dependent upon the fish species of interest and the physico-chemical characteristics of the compound. Of the three potential uptake pathways, transfer across the gills will probably be more significant than epidermal adsorption. There is also some potential for uptake through the alimentary canal. The rate of uptake is dependent upon the compound, the exposure time, water temperature and fish species. Mechanisms may vary depending upon whether the fish feeds on plankton and bottom organisms, or is a predator. Lipophilic compounds tend to bioaccumulate more so than water soluble compounds, and the octanol-water partition coefficient of the compound can be used to define the approximate uptake potential. Fish metabolism will result in degradation of the compound once absorbed, and the rate of depuration is a key factor in defining a hydrocarbon's tainting potential.

The aquatic fate of wastewater hydrocarbons must be considered in any management scheme. Hydrocarbons with tainting potential are not conservative and therefore would be subject to physical, chemical and biological processing if discharged to the Athabasca River. Abiotic factors would include surface spreading, photolysis, volatilization, dissolution, emulsification, adsorption and sedimentation. Since many of the compounds of concern are low molecular weight aromatics, photo-oxidation and volatilization would be major processing pathways. In the Athabasca River this would be tempered by ice-cover for much of the year. The larger molecular weight hydrocarbons would tend to adsorb to suspended or bottom sediments. NSO compounds would be the most soluble and tend to stay longer in solution.

The natural microbiological community in the Athabasca River should be adapted to hydrocarbon degradation. The most readily degradable wastewater hydrocarbons are the n-alkanes and the low molecular weight aromatics. In the Athabasca River biotic degradation may be restricted much of the year by low water temperatures and minimal concentrations of nitrogen and phosphorus. There is some indication that the most active hydrocarbon degrading flora is associated with sediments.

In addition to anthropogenic sources of compounds with a tainting potential, there is a possibility that tainting could occur secondarily due to microbial processing of wastewater discharges to the river or in the alimentary canal of the fish. This potential is poorly understood and requires considerable research to identify its significance.

There are numerous computer models which simulate the aquatic fate of organic chemicals, and this is an active development area. Models range in complexity from relatively simple to extremely detailed, and require varying amounts of input data. These data can be derived from the scientific literature, laboratory studies or field experimentation. A relatively simple model should be used first to screen compounds of potential concern. Special considerations that must be incorporated in any modelling of the Athabasca River include:

1. Low river water temperatures for much of the year;
2. Prediction of very low concentration levels;
3. Ice cover conditions;
4. Mixing zone characteristics; and
5. Extremely variable sediment regime.

The present petroleum effluent guidelines would probably not provide adequate protection against fish tainting. Site-specific surface water objectives and effluent standards should be developed, using either the whole-effluent or chemical-specific approach. The whole-effluent approach involves the direct measurement of effluent tainting with test organisms under laboratory or controlled field experiments. Once the threshold concentration of the effluent for tainting has been defined, this information would be used to calculate the required river dilution which would permit appropriate protection of the fishery.

The chemical-specific approach to setting of receiving water objectives and effluent standards is the classical method and involves managing the specific chemical attributes of the wastewater. The chemical characteristics of the wastewater are evaluated and screened for parameters of concern. Desired concentrations of each parameter are defined for the receiving water based upon published criteria or site-specific field or laboratory experiments. After the receiving water objectives are set the effluent standards can be defined based upon probable future streamflow conditions, upstream quality, other point and non-point source loadings and in-stream assimilation.

With respect to effluents with potential fish tainting hazard, there is currently no clear rationale for selecting either approach. This report discusses the merits of each and gives direction as to the kinds of data which must be collected prior to definition of the appropriate wasteload allocation procedure.

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ABSTRACT

A water management approach for setting ambient surface water objectives and effluent standards for oil sands mining and upgrading activities is discussed. The review examines the relationship between hydrocarbons that are present naturally, or introduced from mining activities, and their potential for bioaccumulation and tainting of a commercial fishery.

Information from an incomplete data base suggests that certain constituents in oil sands effluent, such as aromatic and aliphatic compounds, including some with tainting potential, and more likely to reflect the composition of upgraded-synthetic crude than raw bitumen. The raw bitumen is deficient in water-soluble components, saturated hydrocarbons and low molecular weight aromatic compounds. Low molecular weight compounds such as alkylated naphthalenes, benzothiophenes and dibenzothiophenes, and naphthenic acids may be present in oil sands wastewater and can taint fish.

The uptake and bioaccumulation of tainting compounds is dependent on the fish species, their feeding habits, the physico-chemical characteristics of the specific compound, exposure time and temperature. Lipophilic compounds were noted to bioaccumulate more readily than water soluble compounds, suggesting the utility of octanol-water partition coefficients in defining approximate uptake potential. However, compound degradation through fish metabolism is a key factor in defining a hydrocarbon's tainting potential. Selected computer models which simulate the aquatic fate of organic compounds in river systems are described. The merits of using either or both of the whole effluent or chemical-specific approaches for setting site-specific surface water objectives and effluent standards are examined. Future research recommendations include chemical characterization of the raw and treated effluent,

screening for background levels of potential fish tainting compounds in the receiving stream, and biomagnification studies.

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1. INTRODUCTION

1.1 BACKGROUND AND TERMS OF REFERENCE

This report investigates the relationship between certain hydrocarbons that are present naturally, or could potentially be present as a result of surface oil sands mining and upgrading activities, and their potential bio-accumulation in the commercial fishery of the Athabasca River. Emphasis is placed on those compounds which have the potential to cause tainting of fish flesh. This includes defining the contaminants of concern, reviewing their bioavailability and bioconcentration properties, and considering their biodegradation and persistence in the aquatic environment of the Athabasca River. A water management approach for setting ambient surface water objectives and effluent standards for fish tainting compounds is discussed within the context of basin wide water resource planning.

Specific project tasks include the following:

1. Compilation of pertinent scientific and technical literature.

2. Screening of natural and synthetic tar sand related hydrocarbons with physical and chemical properties appropriate to accumulation in muscle tissue of adult lake whitefish and adult walleye. Including consideration of:
   - mechanisms for uptake from the aquatic environment
   - probable target tissues
   - metabolism of compounds once absorbed
   - synergistic effects of multiple compounds.

3. Definition of instream fate and degradation processes, including:
    - partitioning of hydrocarbons between water and sediment phases;
    - abiotic factors like photolysis, volatilization, dispersion, dissolution, emulsification and sorption;
    - biotic degradation factors and how they relate to controlling factors like oxygen, nutrients, temperature, pH etc.;
    - end products of biodegradation and their fish tainting potential.

4. Reviewing existing environmental fate models and how they might facilitate water quality planning activities in the tar sands area. Factors considered in the review include:
    - pertinent fate process included in the model;
    - type of mathematical formulation;
    - complexity of data requirements and application;
    - success of previous applications;
    - ease of modification;
    - availability;
    - computer system requirements;
    - prediction reliability;
    - data requirements.

5. Recommendations for field and laboratory data collection or experimental programs necessary to develop aquatic fate modelling capabilities for fish tainting compounds in the Athabasca River.

1.2 THE ATHABASCA RIVER

The Athabasca River originates in the Columbia Icefields and flows northeast for 1464 km before discharging to Lake Athabasca. The Athabasca River Basin has a total area of 157,000 km^2, of which about 15% (23,500 km^2) lies downstream of Fort McMurray. The river has four major tributaries, the McLeod, Pembina, Lesser Slave and Clearwater Rivers, of which only the last enters below Fort McMurray. However, ten smaller tributaries, including Poplar Creek and the Steepbank, Mackay, Ells and Firebag Rivers enter the Athabasca River in the 114 km between Fort McMurray and Lake Athabasca. Detailed physical-chemical data on these tributaries are presented in (Walder et al. 1980).

The Athabasca River has an average channel slope of 0.86 m/km, but from Fort McMurray to the mouth the slope is reduced, being only 0.12 m/km; elevational drop for this entire reach is only 32 m, compared to 1,254 m for the whole river (Kellerhals et al. 1972). In the tar sands area, the river is comparatively straight, free from the developed meanders and oxbows which are typical of tributaries in the area (Walder et al. 1980), with a few islands and mid-channel sand bars. The river channel under average flow conditions is wide (up to 500 m), shallow (1.5 m mean depth) and flow is sluggish (approximately 1 m/s). Under bankfull or flood conditions, channel width increases about 20% (590 m), depth more than doubles (3.4 m) and velocity increases only slightly (1.4 m/s) (Kellerhals et al. 1972). Long-term mean discharge at Fort McMurray is about 645 m^3/s, and is strongly seasonal; peak flows occur in May-July and lowest flows occur in winter (Hamilton et al. 1985). The river flows through a wide, shallow, stream-cut valley, with erodible clay and silt banks and usually complete forest cover. The river in the Fort McMurray area flows over sedimentary bedrock, mostly Lower Cretaceous sandstones and oil sands, overlain by glacial deposits of gravel, sand, silt and clay (Hamilton et al. 1985). Soils are predominantly grey wooded and muskeg. Bottom sediments of the river are composed entirely of gravel, coarse and fine sand, and silt, with a mean particle diameter (D_{50}) of 0.17-0.25 mm (Kellerhals et al. 1972).

Climate of the area is continental, characterized by long, cold winters and brief, cool summers. The Athabasca River at Fort McMurray usually freezes near November 5 to 9, and the average ice break up, date is April 28 (Standard deviation: 7 days). Freeze-up in late October, and break-up later than the first week in May are rare occurrences (Kellerhals et al. 1972; Hamilton et al. 1985). Median water temperature in the open-water season is 12 to 16°C.

As is typical of rivers flowing over limestone, waters of the lower Athabasca are moderately hard, alkaline and dominated by calcium among cations, and bicarbonate among anions. Total dissolved solids, a measure of salinity, remain near 150 mg/l all along the river and pH is near 8.0. The river is generally rich in sulphate (near 20 mg/l) and below Fort McMurray it is high in sodium and especially chloride, due to naturally saline inflows from the Clearwater River (Hamilton et al. 1985).

The lower Athabasca River is turbid, with levels of non-filterable residue (suspended solids) in excess of 150 mg/l; much higher levels (> 500 mg/l) may be observed during spring peak flows. Associated with these suspended solids are high levels of phosphorus, nitrogen, iron and manganese (Hamilton et al. 1985). Natural concentrations of certain trace metals are also comparatively high.

2. FISH TAINTING COMPOUNDS

2.1 REVIEW OF FISH TAINTING COMPOUNDS

Volumes have been written about the toxic effects of various chemicals (especially organics) on aquatic biota, including the lethal effects on fish. However, sub-lethal effects on fish have proved more difficult to assay, especially an effect as subjective as an off-flavour, either taste or odour. Nonetheless, the tainting of some fish stocks has occurred to the detriment of commercial and sports fisheries. Tainting of fish flesh, as detected by taste test panels, can be caused by concentrations of volatile substances that are at the lower limit of analytical detection.

Fish tainting is often difficult to study, and even more difficult to prove, because it may result from many different sources - including substances which naturally occur in freshwaters and certain phytoplankton species. Chemical analyses for suspect chemicals are highly specialized and often cannot be used to unequivocally identify those compounds which may be imparting taste or odours to fish flesh.

Hence, it is often difficult to relate fish tainting to a specific source and, because fish are capable of significant movements, precise location of contacts with tainting chemicals are difficult to determine. Other sources, such as thermal decomposition of certain food organisms also may impart distinct odours to fish flesh, hence complicating the types and sources of origin for investigators to resolve in tainting incidents.

The problem of fish tainting has been extensively studied for marine fisheries, especially in areas such as the Gulf of Mexico, East Coast Canada, the Beaufort Sea, and the North Sea, which are also areas of offshore hydrocarbon development. The effects of petroleum hydrocarbons on marine organisms have been reviewed by Lee (1977), Scarrat (1980) and the National Research Council - U.S.A. (1985). Tainting of fin-fish is not thought to be a major problem from large oil spills, because of the ability of the fish to swim away, but is more likely in restricted spill incidents as in bays and estuaries. The precise route of entry of the tainting substances is uncertain, but probably includes both the respiratory process and uptake through tainted food. Little is known of the actual substances responsible for the tainting of marine fish meat. No exact identification of substances in crude oil exists which matches the taint profile in contaminated fish products. It is thought that aromatic hydrocarbons, substituted benzenes and naphthalenes, napthenic acids, and organo sulfur compounds are involved.

Another source of tainting of marine fish has been found at coastal sites which receive chronic oil inputs from refineries. Mullet collected off the Queensland Coast, in the outfall area of refinery effluent, had a strong kerosene-like taint. It was thought possible that the kerosene-like flavour could be linked to the thermal decomposition of naturally occurring components of the tissue to produce dimethyl sulphide (Vale et al. 1970), but upon detailed analysis the mullet flesh had a series of hydrocarbons similar to those found in kerosene, including several alkylated naphthalenes (Shipton et al. 1970). Ogata and Miyake (1973) studied tainted mullet taken from an oil polluted harbour in Japan, and the objectionable odour was shown to be due to the presence of toluene in the flesh. The mullet only had a concentration of toluene of about 5 mg/kg flesh. Sites of chronic pollution which impinge upon fish resources can often cause problems in pinpointing the source of tainting. The source of the off-flavour can be due to a number of contaminants, and different sources can give rise to similar signs of tainting.

Neff et al. (1976) considered the accumulation of petroleum-derived aromatic hydrocarbons in marine animals, including fish. They found that the aromatic hydrocarbons were accumulated to a greater extent (mainly due to their higher water solubility) and retained longer than the alkanes. The binding of hydrocarbons to tissue lipids was by hydrophobic interactions, rather than covalent bonding, and dependent on the octanol-water partitioning of the hydrocarbons. Because of metabolic breakdown, the fish were able to depurate the hydrocarbons to undetectable levels in 2 to 60 days, but the higher molecular weight aromatic hydrocarbons were released more slowly than lower weight alkane hydrocarbons. Ogata et al. (1977) found that eels exposed to crude oil solutions accumulated paraffins, organic sulphur compounds and aromatic hydrocarbons, and that some paraffins (particularly the C_{13} to C_{15} compounds) in the petroleum were transferred to the fish flesh. Nulton and Johnson (1981) considered fish tissue contamination in the Gulf of Mexico, particularly of aromatic hydrocarbons. The most frequently found aromatic material in pelagic fishes were pyrene, 1,3-dimethylnaphthalene and 1-methylnaphthalene. Aromatic compounds were detected in selected tissues at levels less than 30 mg/kg flesh in over 60% of samples. These compounds were alkylated benzenes, naphthalene, alkylated naphthalenes, phenanthrenes, alkylated 3-ring aromatics and pyrene.

Woodward et al. (1981) exposed trout to various concentrations of crude oil. It was found that the accumulation of total hydrocarbons in fish tissue was directly related to water concentration, except for the highest concentration selected which may have been close to the lethal level. Alkylated mono- and dicyclic aromatic hydrocarbons were accumulated most readily. Because it was the dominant aromatic component in both the oil and the water column, naphthalene was also detected at the highest flesh concentrations. However, the study concluded that the six aromatic hydrocarbons which had the greatest propensity for accumulation by fish were as follows:

> Alkylated benzene > alkylated indane > alkylated biphenyl > Alkylated tetraline > fluorene > alkylated naphthalene.

Cravedi and Tulliwz (1982) studied the accumulation of branched alkanes and cycloparaffins in trout flesh. The compounds were fed to the fish. Steady-state tissue concentrations were achieved after three months for the cycloparaffins and six months for the alkane. The adipose tissue (fatty) retained the largest proportion of both hydrocarbons. However, hydrocarbons were detected in every tissue examined, and generally, the cyclic aliphalic fractions were retained to a greater extent than branched alkanes.

Although the effluents from petroleum refineries are not directly analogous to those produced by the bitumen upgrading process, the tainting effects of refinery wastewaters may have relevance to the oil sands. Sprague et al., (1978) studied the sub-lethal effects of treated refinery effluent, but did not consider tainting. Cote (1976) reviewed the effects of refinery wastewaters with respect to the Canadian environment. The mechanisms by which a fish takes up tainting material are through the gill and gut membranes into the bloodstream, absorption through the skin, and absorption to the mucosa. Investigations dealing with the tar constituents of wastes suggested that the taste change was not due to the storage of phenols in the body of the fish, but rather to the non-phenolic substances such as aromatic and aliphatic hydrocarbons accompanying the phenols in the wastewater. Another study, referred to by Cote, used threshold odour tests on drinking water sampled below a refinery effluent input, and revealed that the major odorants in the receiving water were aliphatic and aromatic hydrocarbons and cyclic sulphur compounds.

However, also reported in Cote is a study by Winston (1959) in which fish held for seven days in a tank contaminated with phenolic compounds revealed an ability to assimulate minute concentrations which were enough to produce an off-flavour. The detectable threshold level of chlorophenol was observed at concentrations as low as 0.005 mg/l. The particular causative agents of tainting, and their mode of action, were not resolvable. However, minute concentrations (in the ppb range) of organic chemicals create taste and odour problems in fish flesh. Table 1 is taken from Winston (1959), as presented in Cote (1976), and presents a list of some of the organics implicated in fish tainting, and their threshold concentrations. Krishnaswami and Kupchanko (1969) confirm the low threshold values; they found that petroleum refinery effluent diluted 1:100 produced an oily taste in fish after a 24 hour exposure, and this diluted concentration is only 1/4 of the minimum odour detection concentration. Interestingly, fish tainting was also projected as a potential problem from petrochemical effluent wastes in Canada (Smith, 1974), often from similar compounds to those in refinery wastes.

Alabaster and Lloyd (1982), in a compilation of EIFAC reports, considered the effect of one group of hydrocarbon compounds on fish, namely phenols. While short-term exposure to 25 mg/l phenol, and four days exposure at 2.5 mg/l phenol did not cause flavour change in fish, and 10 mg/l cresol only caused a slight taint, some other constituents of phenolic wastes were very effective tainters. Xylenols, naphthols and quinols tainted bream and common carp at concentrations between 0.5 and 5.0 mg/l. An undesirable taint was produced in common carp by only 0.06 mg/l of p-chlorophenol and 0.015 mg/l O-chlorophenol. It was considered

Table 1. Fish taste thresholds.

Material	Concentration[a] (mg/l)
2,4-Dichlorophenol	0.005
o-Chlorophenol	0.015
p-tert-Butylphenol	0.03
p-Chlorophenol	0.05
Diphenyl oxide	0.05
Kerosene	0.1
"Insecticide" oil (heavy aromatic naphtha)	0.1
Cresylic acid ("meta-para")	0.2
Isopropylbenzene	<0.25
Ethylbenzene	<0.25
Styrene	0.25
α-Methylstyrene	0.25
o-Dichlorobenzene	0.25
Toluene	0.25
o-sec-Butylphenol	0.3
Acetophenone	0.5
Phenol	1.0
o-Phenylphenol	1.0
β, β'-dichlorodiethyl ether	1.0
"Cutting" oil (emulsifiable)	>15.0

[a] Minimum concentration that imparted an "off-flavour" to the fish being held for 7 days.

Source: Winston (1959) as presented in Cote (1976).

likely that these were the responsible taint agents in fish caught in the Rhine River when 0.02 to 0.03 mg/l phenols were present. Some phenolic taints may persist in fish flesh for several weeks when fish are kept in clean water, unlike other taints, for example, those produced by actinomyces which may be lost within one day under these conditions (see below).

Branson et al., (1979) exposed rainbow trout for seven days to substantial concentrations of diphenyl oxide (DPO), and the trout flesh was then analyzed for taste and residue concentration. The taste threshold was found to be related to a residue concentration of 7.5 mg/kg DPO. The concentration of DPO in trout flesh increased 1.75 times upon cooking, possibly due to a transfer of DPO from the skin to the flesh during baking.

The examples shown above are of tainted fish resulting from industrial effluents, but many odours in surface waters are of biological origin, and may be attributed to the decomposition of organisms, or to microbial metabolites. These odours can be absorbed and concentrated in the tissues of aquatic animals. Blevins (1980) reported on the major odorous metabolites of microbial origin, and fish-tainting potential. Aquatic actinomycetes (filamentous bacteria) of the genera Micromonospora, Nocardia, and especially Streptomyces are known to produce a variety of volatile metabolites, many of which are odorous. The major odorous substance produced by numerous actinomycetes is an earthy smelling compound and this has been identified as geosmin. This volatile terpenoid can also be produced by a few species of blue-green algae. Geosmin is a clear, neutral oil that has an extremely low odour threshold concentration of 0.2 ppm or less. Geosmin has been extracted from the flesh of fish having a muddy or earthy taint, where the threshold taste level was established at 0.6 ug of geosmin/100 g flesh.

Blevins reports on several other biologically produced odorous compounds. Two odorous sesquiterpene monoalcohols have been identified with an earthy or woody odour, and 2-methylisoborneol has a similar earthy or muddy flavour. There are other less complex microbially produced compounds that may contribute to environmental odour and taste problems. These are butyric acid and other fatty acids, aldehydes, alcohols, esters, amines, hydrogen sulfide, isopropyl mercaptan and other sulphur-containing compounds.

Yurkowski and Tabachek (1980) reported on a problem of tainting in a commercial freshwater fishery in Cedar Lake, Manitoba. The muddy flavour and odour was detected in walleye and lake whitefish among other species, and the taint was indicated to be the result of geosmin and 2-methylisoborneol in the flesh. The source of these compounds was thought to be the decomposition of blue-green algae. Other studies on geosmin are reported in Yurkowski and Tabachek (1974), Persson (1980) and Brownlee et al., (1984).

Thus, although it is difficult to quantify fish tainting, since it is essentially subjective as measured by taste panels, and tainting often results from body burden concentrations at the low end of analytical detection, it is apparent that many compounds are implicated. Blevins (1980) presented a partial list of industrially produced odorous compounds. Phenol and its chlorinated products constitute the best known examples of taste and odour compounds of industrial origin. Among other important odorous compounds of this type are methylamine, naphthalene, various chlorinated and non-chlorinated terpenes and sesquiterpenes, alkyl-substituted benzenes and bicyclic aromatic hydrocarbons.

Klein (1962) was concerned with wastes from coal carbonization processes, especially the phenols, nitrogenous organic compounds and hydrocarbons, which he felt could cause the tainting of fish flesh. The information he presented is shown here as Table 2. He observed that quite low concentrations of phenolic compounds could affect the taste of fish adversely. Significantly, mixed wastes appeared to affect fish taste more than simple compounds (possible synergism).

Thomas (1973), in a study of tainting of catfish in the Ohio River, presented an extensive listing of compounds that imparted an off-flavour to fish, based on data published to 1970. This is shown as Table 3. The compounds range from single, unsubstituted components, through complex compounds to mixed wastes. He stated that chlorinated, organic compounds were particularly involved in causing tainting. The extremely low threshold odour concentrations shown for some compounds, especially chlorophenols, indicates the seriousness of the tainting problem.

Persson (1984) reported on more than 50 substances that he identified as having fish-tainting potential. Many of these were hydrocarbon compounds, among them were phenolic derivatives, benzene compounds or other hydrocarbons. However, less well defined, but more complex contaminants, such as oils, refinery effluents and pulp and paper wastewater were also identified as taint producers in fish. There were also non-hydrocarbons. His listing is shown here as Table 4.

Most of the work on tainting has been directed towards identifying the tainting substance as detected in tissue or organ residues, and relating the residue concentration to the contaminant concentration in the water source. This tends to produce two threshold values, the water concentration that leads to tissue residue and the threshold concentration within the tissue that leads to an 'off-flavour'. Some of the available threshold data have been presented in tables above, for both effluent and flesh concentrations.

Table 2. Concentrations of phenols and other organic compounds present in coal carbonization effluents having adverse effects on taste of fish.

Compound	Fish Tested	Toxicity to fish (threshold value) ppm	Approximate Concentration (threshold value) at which fish flesh is tainted ppm
Phenol	trout, carp	9.5	25
Cresols	trout, carp	10-15	10
Coke oven wastes	freshwater fish	3-5	0.02-0.1 Phenols
in polluted river	minnows	0.08	0.02-0.15
1:3:4-xylenol	carp	10	5
1:3:5-xylenol	rudd	18	1
1:2:4-xylenol	rudd	5	1
Pyrocatechol	carp	15	2.5
Resorcinol	carp	35	30
p-toluidine	rudd	50	20
Pyridine	carp, rudd	160-200	5
Quinoline	carp	10	0.5-1
Naphthalene	rudd	--	1
α-naphthol	rudd	2	0.5
β-naphthol	carp, rudd	2	1
α-naphthylamine	rudd	6	3

Source: Klein, L. (1962).

Table 3. Compounds imparting off-flavor to fish flesh.

Compound	Threshold Odor Concentration mg/l
Acetophenone	0.5
Benzkatechin	2.5
o-sec Butylphenol	0.3
p-tert. Butylphenol	0.03
p-Chloride Phenol	0.06
Chlorophenol	0.01
o-Chlorophenol	0.015
o-Chlorophenol	0.015
p-Chlorophenol	0.05
Coal-Coking Wastes	0.02
Coal-Tar Wastes	0.1
Cresylic Acid ("meta para")	0.2
Cresols	10.0
Cresol	10.0
"Cutting" Oil (Emulsifiable)	15.0
o-dichlorobenzene	0.25
β, β-Dichlorodiethyl Ether	1.0
2,4-dichlorophenol	0.01
2,4-dichlorophenol	0.005
Diphenyl Oxide	0.05
Ethylbenzene	0.25
Gasoline	0.005
Simple petroleum hydrocarbon	1.0
"Insecticide" Oil (Heavy Aromatic Naphtha)	0.1
Isopropylbenzene	0.25
Kerosene	0.1
Kerosene	0.5
Kraft Mill Effluent-raw	1.0 (percent by volume)
α-methylstyrene	0.25
Naphthalene	1.0
α-Naphthol	0.5
β-Naphthol	1.0
α-Naphthylamine	3.0
Outboard Motor Exhaust Wastes	0.5
Petroleum Refinery Effluents	0.25 (threshold odor number)
Aromatic, neutral substances of phenols	2.6-3.4
Phenols in Polluted River	.02-.15
Phenol	.02-.1
Phenol	1.0
Phenol	15-25
Phenol	25.0
o-Phenyl phenol	1.0
Phlorogluci n	100.0
Pyridine	5.0
Pyrogallol	20-30
p-quinone	0.5
Quinoline	.5-1.0
Resorcin	30.0
Sewage containing phenols	0.1
Styrene	0.25
Toluene	0.25
p-Toluidine	20.0
Xylenols	1-5

Source: Thomas, N.A. (1973)

Table 4. Compounds impairing the flavour of fish. Data from the literature. Source: Persson (1984).

COMPOUND	FISH SPECIES	ETC (mgl^{-1}) RANGE (geom.mean)	CONC. THAT DID NOT IMPAIR THE FLAVOUR (mgl^{-1})	EXPOSURE TIME (h)	TOC IN WATERS (mgl^{-1}) (geom.mean)
Acetophenone	Yellow perch	0.5	-	168	0.105
Acetone (2-propanone)	Rainbow trout	-	1000	48	55.4
Acetonitrile (ethanenitrile)	Carp	-	550	-	-
Acrylonitrile (2-propenenitrile)	Rainbow trout	18	5.8	48	18.6
Amylacetate (pentyl acetate)	Rainbow trout	-	10	48	0.02
Aniline	Rainbow trout	-	10	48	458
Benzene	Rainbow trout	-	5.8	48	8.55
n-Butanol	Rainbow trout	10	100	48	3.1
Butanethiol	Rainbow trout	0.055-0.040 (0.047)	0.008	96	0.008
o-sec-Butylphenol	Yellow perch	0.3-0.5 (0.39)	-	168	-
p-tert-Butylphenol	Yellow perch	0.03	-	168	0.8
Chlorophenol	Eel	0.0001	-	264	0.01
m-Chlorophenol	Rainbow trout, carp, bluegill	0.08	1.0	48-72	0.01
o-Chlorophenol	Rainbow trout, carp, yellow perch	0.015-0.08 (0.024)	0.1	48-168	0.05
p-Chlorophenol	Rainbow trout, carp, yellow perch	0.045-0.08 (0.051)	0.021	48-168	0.06
Cresol (methylphenol)	Rainbow trout, eel	0.07-10 (0.84)	0.005	48	-
m-Cresol (3-methylphenol)	Rainbow trout	0.2	0.05	48	0.8
o-Cresol (2-methylphenol)	Rainbow trout	0.4-2.0 (0.45)	0.1	96	1.4
p-Cresol (4-methylphenol)	Rainbow trout	0.12	0.05	48	0.2
Cresylic acid (meta-para)	Yellow perch	0.2	-	168	-
o-Dichlorobenzene	Yellow perch	0.05-0.25 (0.11)	-	168	0.01
β,β'-Dichlorodiethylether	Rainbow trout, yellow perch	0.088-1.0 (0.30)	0.080	48-168	-
2,3-Dichlorophenol	Rainbow trout	0.084	0.032	48	0.03
2,4-Dichlorophenol	Rainbow trout, large-mouth, bass, bluegill, yellow perch	0.0004-0.014 (0.0023)	0.00001-0.01	48-168	0.04
2,5-Dichlorophenol	Rainbow trout	0.023	0.01	48	0.03
2,6-dichlorophenol	Rainbow trout	0.001-0.035 (0.006)	0.01	48	0.2
1,2-Dihydroxybenzene(brenzkatechin)	Carp	2.5	-	-	-
Dimethylamine	Rainbow trout	6.8	5.8	48	23.2
Dimethylsulphide (methylthiomethane)	Channel catfish	25	-	0.17	0.0014
Diphenylether (diphenyloxide, phenoxybenzene)	Yellow perch	0.05	-	168	0.015
Ethanethiol	Rainbow trout	0.24	0.10	48	-
Ethylacrylate (ethyl-2-propenoate)	Rainbow trout	0.08	0.01	48	0.0067
Ethylbenzene	Yellow perch	0.25-0.5 (0.35)	-	168	0.14
2-Ethyl-l-hexanol	Rainbow trout	-	5.8	48	0.59

Connell and Miller (1981) considered the sub-lethal effects of petroleum hydrocarbons in the aquatic environment, including the available information on fish tainting. They stated that the organoleptic sensation (the properties by which chemicals act upon organs of sensation) experienced on consuming petroleum hydrocarbons was due to the volatile components which generated a flavour aroma within the food which in turn was described as a taint by taste panels. The organoleptic response to hydrocarbon compounds is influenced mainly by two factors:

(i) the amount of the volatile compounds present, and
(ii) the intrinsic strength of its flavour or aroma.

They present a list of substances which have been known to cause tainting, in terms of threshold concentrations in water, shown here as Table 5. Not all of these compounds are components of petroleum. However, the major tainting components of petroleum are stated to be phenols, dibenzothiphenes, naphthenic acids, mercaptans, tetradecans and methylated naphthalenes. Also, minor components of a petroleum substance may be major contributors to its aroma, and a flavour aroma almost always consists of complex mixtures of substances which exhibit synergistic or antagonistic effects. Caution is required in applying data from Tables 4 and 5, since the "taste" threshold is quite subjective. It is recognized that food preparation techniques, fish flesh and hydrocarbon species will each influence reported values. What is important is the relative "orders of magnitude" between chemical groups and their roles in determining subsequent taste thresholds.

Other important reviews that included work on fish tainting by hydrocarbons are found in Persson (1984) and E.V.S. (1985). The latter is particularly relevant to this work because tainting was considered in an overall assessment of freshwater impacts possible from the Norman Wells oilfield development. They reported on studies carried out in response to fish tainting and

Table 5. Concentrations of chemical compounds in water that can cause tainting of flesh in fish and other aquatic organisms.

Chemical	Estimated Threshold Level In Water (μ g/l)	Chemical	Estimated Threshold Level In Water (μ g/l)
Acetophenone	500	Kerosene	100
Acrylonitrile	18,000	Kerosene plus kaolin	1,000
N-Butylmercaptan	60	2-Methyl-4-Chlorophenol	75
o-Chlorophenol	0.1 to 15	2-Methyl-6-Chlorophenol	3
p-Chlorophenol	10-50	Naphtha	100
Cresol	70	Naphthalene	1,000
m-Cresol	200	Naphthol	500
o-Cresol	400	2-Napthol	300
p-Cresol	120	Oil, emulsifiable	15,000
o-Dichlorobenzene	250	Phenol	1,000-10,000
2,3-Dichlorophenol	84	Phenols in polluted rivers	20-150
2,4-Dichlorophenol	1 to 14	o-Phenylphenol	1,000
2,5-Dichlorophenol	23	Pyridine	5,000-28,000
2,6-Dichlorophenol	35	Pyrocatechol	800-5,000
Dimethylamine	7,000	Pyragallol	20,000-30,000
Diphenyloxide	50	Quinoline	500-1,000
Ethylbenzene	250	p-Quinone	500
Ethanethiol	240	Styrene	250
Ethylacrylate	600	Toluene	250
Formaldehyde	95,000	2,4,6-Trichlorophenol	3-50
Quaiacol	82		

Source: Connell & Miller (1981)

quality complaints, in which the source of off-flavour was not identified specifically, but was thought to be associated with elevated levels of hydrocarbons in the river water. Also, a general statement was made to the effect that those refinery effluents which had the highest concentrations of oil and grease, total organic carbon and total phenolics (i.e. those standard water quality parameters associated with hydrocarbons) were also the highest with respect to more toxic organic parameters such as phenol, benzene, toluene, naphthalene, etc., which are not included on usual water quality surveys.

Tsui and McCart (1979) studied the residues of chlorinated hydrocarbons in several fish species from the Cold Lake area. The compounds were DDT and its metabolites and PCB, resulting from pesticide spraying. The fish species were chosen to represent different ecological niches, i.e. pike = predator, cisco = plankton feeder, whitefish = bottom feeder, and sucker = omnivore. The chlorinated hydrocarbon residues were higher in fatty tissues than muscles, a reflection of the oleophitic (fat soluble) nature of these compounds. Among fish species the rank order for fat residues was the same for DDT and PCB i.e. pike > whitefish > cisco > white sucker > bottom feeder > plankton feeder > omnivore. They concluded that the concentrations in the flesh of various species are influenced by their ecological role and particularly their feeding habits. Smith et al. (1980) fed trout fixed concentrations of trichlorobenzene. The fish assimilated more than 60% of the available chemical, but were able to depurate more than 90% of the residue in a week. They did not report upon total clearance, but did detect unidentified compounds late in the experiment, assumed to be metabolites.

The Alberta Environment Centre at Vegreville is undertaking a program to study chemical residues in fish from a variety of compounds which are of concern in oil sands mining operations, and only after a full characterization of each type, with exposure testing, will one be able to adequately narrow down this extensive list. Phenols, undoubtedly, should be high on any list for consideration as would any kerosene or naphtha related products of the oil sands upgrading process.

2.2 POTENTIAL TAINTING COMPOUND SOURCES

2.2.1 Oil Sands Extraction

The nature of the Athabasca Oil Sands has been described by Berkowitz and Speight (1975) and Strom and Dunbar (1981). According to the Alberta Energy Resources and Conservation Board, crude bitumen is defined as:

> "A naturally occurring viscous mixture, mainly of hydrocarbons heavier than pentane, that may contain sulphur compounds, and that in its naturally occurring state is not recoverable at a commercial rate through a well."

Strom and Dunbar (1981) further characterize this bitumen as typically containing 4.5 weight percent of sulphur, and small amounts of dissolved methane and traces of hydrogen sulphide. Also, as a hydrocarbon material, bitumen is notable for a deficiency of hydrogen in relation to carbon (midway between medium crude oil and sub-bituminous coal). Thus, the upgrading processes available to convert bitumen to synthetic crude oil are either hydrocracking (hydrogen addition) or coking (carbon reduction).

More details on the chemical composition of Athabasca bitumen are available in Selucky et al. (1977), Starr et al. (1981) and Strausz (1981). Starr et al. discuss the physical and chemical properties of Athabasca bitumen (together with other Alberta bitumen deposits) and provide both elemental analyses and the hydrocarbon types. This bitumen is by percentage weight 83% carbon, 11% hydrogen and 5% sulphur. The breakdown of hydrocarbon types by weight is 39% resins, 22% saturates, 21% aromatics and 18% asphaltenes. Strausz provides a slightly different class composition of Athabasca bitumen in that the aromatic component of the hydrocarbons is increased to 29% and the saturates falls to 18%, and the resins to 35%. Strausz also provides details on the composition of the aromatic fraction of Athabasca bitumen.

The chemical composition of the bitumen changes radically upon being upgraded to synthetic crude oil; this is shown in Speight and Moschopedis (1981) where a comparison of the properties of bitumen and synthetic crude is presented. The synthetic crude shows an increase in carbon and hydrogen and a decrease in sulphur. Also, the hydrocarbon structure is significantly different in that synthetic crude has no asphaltene or resins, being composed of 79% saturates (up from approximately 20% in bitumen) and 21% aromatics (down from approximately 30% in bitumen).

Oil sands are mined in open pits and transported to extraction 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, Suncor; Figure 2, Syncrude). 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 tailings pond. 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 naphtha is recovered from the diluted bitumen by

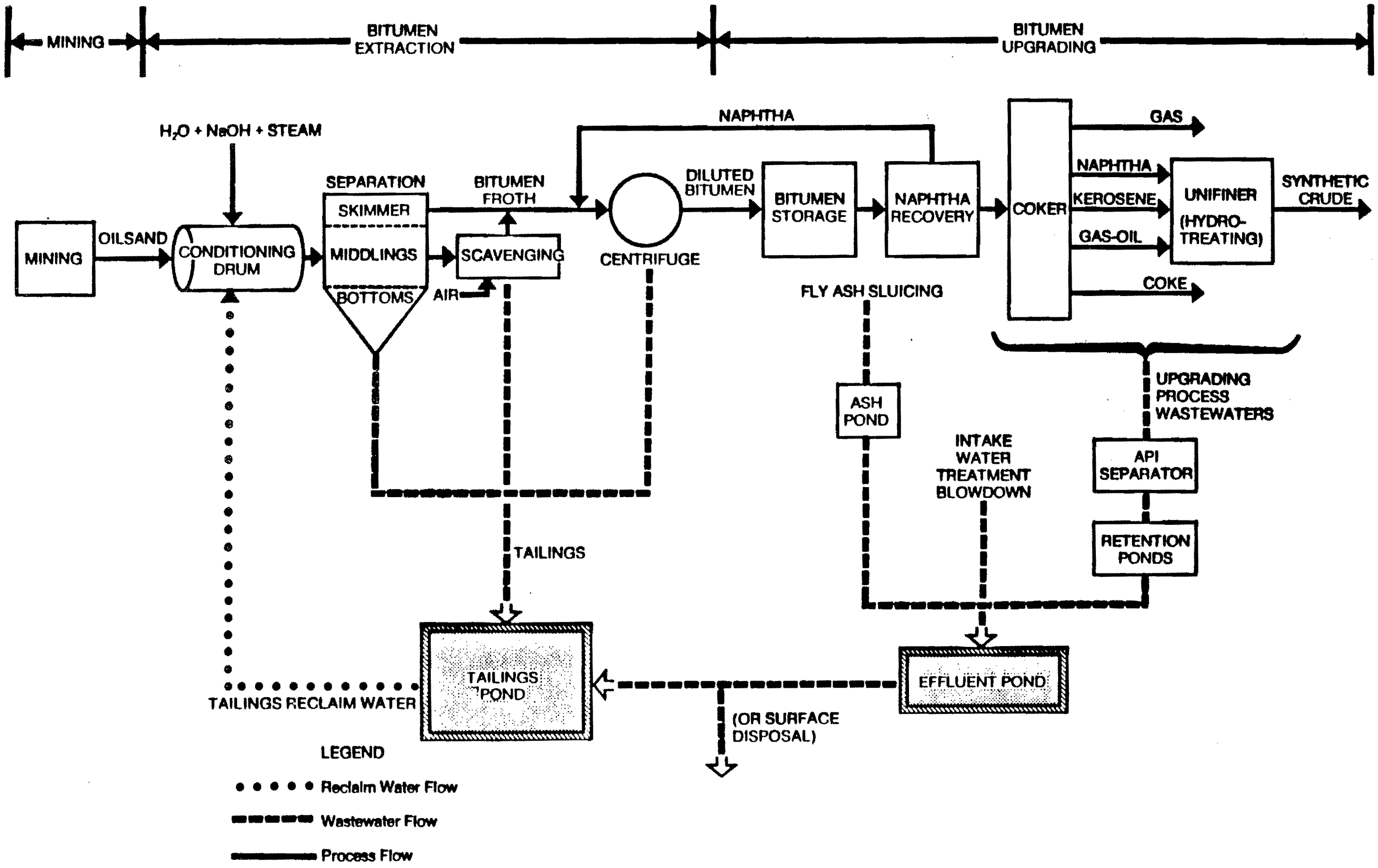
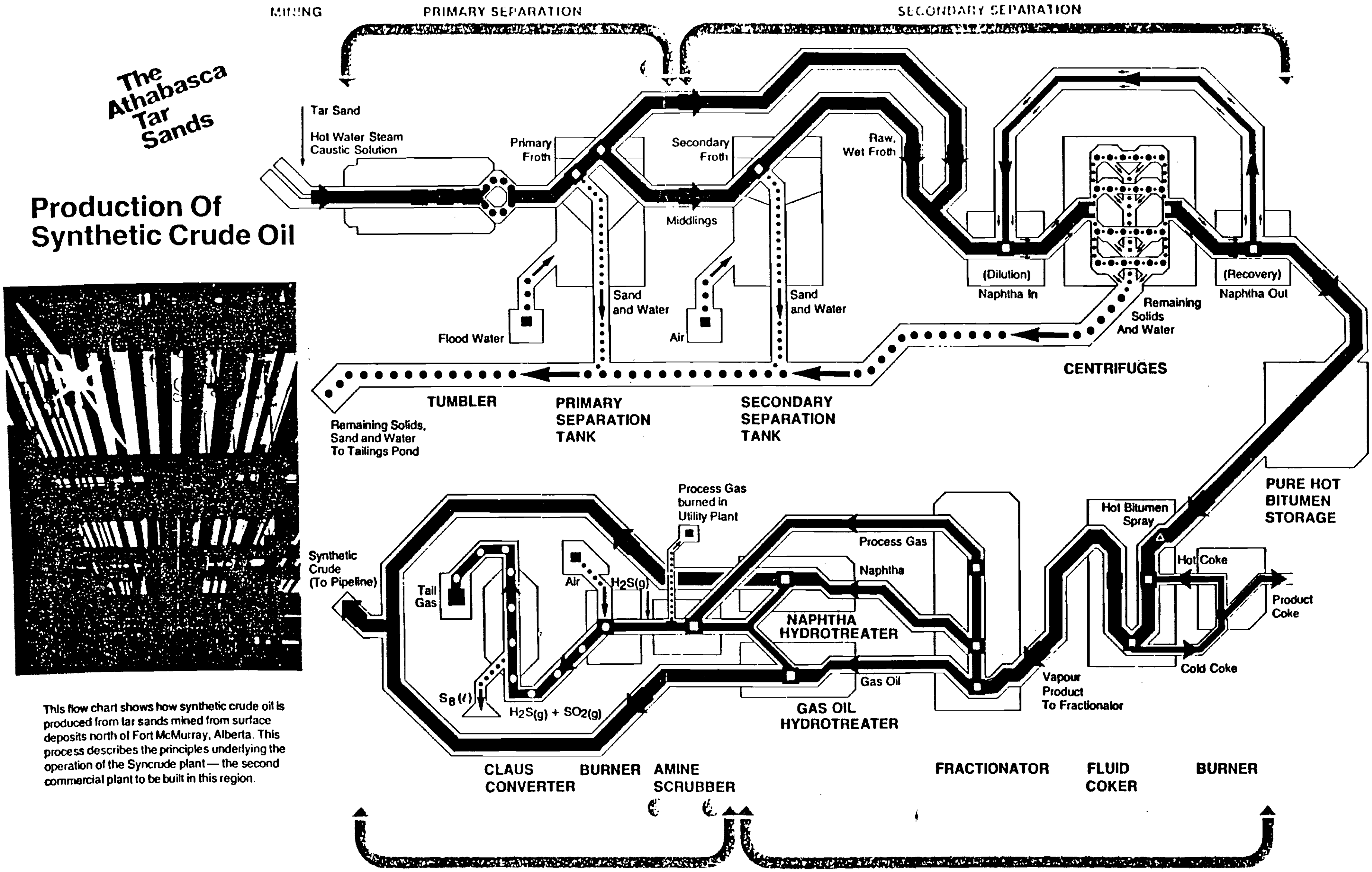


FIGURE 1 Oil Sands extraction process used at the Suncor Plant.



The Athabasca Tar Sands

Production Of Synthetic Crude Oil

This flow chart shows how synthetic crude oil is produced from tar sands mined from surface deposits north of Fort McMurray, Alberta. This process describes the principles underlying the operation of the Syncrude plant — the second commercial plant to be built in this region.

FIGURE 2 Oil Sands extraction process used at the Syncrude Plant.

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 sulfur and nitrogen heterocycles, 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, naphtha, kerosene and gas oil; two at Syncrude, naphtha and gas oil). The hydrogen treating saturates the unsaturated hydrocarbons and removes sulfur and nitrogen compounds. The hydrotreated product is blended to produce synthetic crude.

Wastewaters arising from the extraction processes are discharged to the tailings pond. These will be contaminated with unextracted bitumen and raw diluent naphtha carried over from the centrifugation stage.

Wastewaters arising 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 will contain oils and dissolved polar organics, including phenolics. The condensates are termed sour because they also are enriched in odoriferous sulfur compounds. This stream is discharged to the tailings pond.

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 sulfur compound contamination. At Suncor, the coke cutting waters are discharged, after settling, to their wastewater pond for ultimate discharge to the Athabasca River.

The upgrading section of the plant, like any petroleum refinery, uses process water for pumps and equipment, cooling, area washup and various intermittent purposes. 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 three holding ponds, and a final underflow dyke to a submerged discharge 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 additional oily material can be found in these wastewater streams.

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 which 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. The cooling system at Syncrude does not involve any discharge to the Athabasca River.

A considerable amount of effort has been expended in analysing and characterizing the organic constituents contained within the effluents produced from the Suncor (GCOS) project, e.g. Hrudey (1975), Lake (1976) and Strosher and Peake (1976, 1978). In their first report, Strosher and Peake compared the organic constituents of wastewaters from both the upgrading plant effluents and tailings pond dyke filter drainage, and found that they differed in amounts of extractable carbon and types of carbon compounds. The tailings drainage contained 75 mg/l extractable carbon made up of 92% oxygenated compounds, (79% organic acids, 5% phenols), 5% organic sulphur compounds, and only 0.04% hydrocarbons. The upgrading plant effluent contained 15 mg/l extractable carbon, made up of 30% oxygenated compounds, 17% organic sulphur compounds, 7% nitrogen compounds and 7% hydrocarbons. The hydrocarbon composition resembled that of synthetic crude and was likely contributed from the upgrading process rather than being indigenous to the bitumen. Although the tailings drainage water has more organic carbon than the upgrading plant effluent, because of flow differences it was the upgrading plant effluent that discharged the majority of the carbon load to the river (almost 90%).

However, the extra carbon load only amounted to about 1% of the natural organic load of the river. Nonetheless, problems may still be posed by the tailings drainage since little is known of the toxic or tainting effects of the complex mixtures of compounds such as the organic acids, as well as the synergistic effects when combined with other wastewater components such as phenols and low molecular weight hydrocarbons.

Aleksiuk et al. (1982) described the management procedures for waste waters at the Syncrude project. Unlike Suncor, Syncrude has adopted a zero discharge approach, with retention of all processes and diversion waters in tailings ponds. Unfortunately, detailed chemical characterization of the Syncrude tailings pond is not available. However, based upon the extraction and upgrading process we do know that compounds which can impart unpleasant taste or odour to fish and which can be readily taken up and bio-concentrated by fish are being generated. Coker distillate fractions contain a wide range of compounds with these characteristics (Birkholz et al, in press). These are listed in Table 6. The compounds containing sulfur, nitrogen or oxygen will be present to a much lesser degree in hydrotreated products. Consequently, the major problem wastewaters would be those which contact raw coker distillate. However, the alkylated benzenes, naphthalenes, and phenanthrenes, which also have substantial tainting potential, will be present as major constituents of the product synthetic crude.

At present the Syncrude tailings pond is acting as a repository of all plant wastes. This includes raw naphtha used as bitumen diluent, sour condensates from the refining process and process oily wastes.

2.2.2 Natural Sources and Degradation Products

Compounds present in the extraction and refinery wastes also occur naturally in the Athabasca River due to erosion of the surficial bitumen and its incorporation into the water column and bed material. Tainting of fish populations has also occurred due to in situ biological production of tainting compounds. Furthermore it is possible that relatively innocuous compounds in oil sand wastewaters, with little or no tainting potential on their own, could be transformed through bio-metabolism into compounds of concern.

In the 1978 study Strosher and Peake tested wastewaters from the Suncor mine depressurization program, runoff from the coke and sulphur storage areas, and the Athabasca River up and downstream of the processing plant. The mine depressurization water was found to be similar in composition to that of tailings drainage, i.e. high in organic acids and low in hydrocarbons. The storage runoff was high in asphaltenes, oxygenated and sulphur compounds and low in hydrocarbons. It was concluded that the main

Table 6. Compounds in coker distillate with tainting potential.

alkylated benzenes
alkylated naphthalenes
alkylated phenanthrenes
alkylated benzothiophenes
alkylated dibenzothiophenes
alkylated quinolines
alkylated acridines
alkylated indans
alkylated tetralins
alkylated furans
alkylated benzofurans
alkylated dibenzofurans

PAH's

acenaphthene
anthracene
benz(a)anthracene
benzo(a)pyrene
benzo(e)pyrene
benzofluoranthene
biphenyl
chrysene
dibenz(a,h)anthracene
fluoranthene
fluorene
perylene
pyrene

source of light hydrocarbons in the section of the Athabasca River adjacent to the oil sands processing site is the upgrading plant (effluent), whereas the oxygenated compounds may be derived from the tailings pond dyke filter drainage or natural sources, of which mine depressurization water may be representative.

Strosher and Peake (1979) expanded their study to more carefully analyze the organic carbon composition of Athabasca River water above the processing site. They found major differences between effluent composition and natural river water, in terms of type of carbon product, the solubility, and the amounts. River water had only 1 mg/l extractable carbon compared to 13 to 89 mg/l extractable from Suncor effluent sources, and river organic carbon is mostly highly water-soluble, and generated over a long time. Those major wastewater compounds - organic acids, phenolic compounds and sulphur compounds - total less than 0.01 mg/l in undisturbed river water. There are small quantities of hydrocarbon in the river, presumably derived from the oil sands deposit by natural leaching, and these hydrocarbons are generally of a higher molecular weight than those found in process effluents.

The microbial community in the Athabasca River has the potential to degrade tainting compounds derived naturally from the bitumen or via effluent discharges from the extraction and refining process. At the same time there is the possibility that new ones may be produced.

All natural organic compounds can undergo some form of microbial degradation. However, if the compound is chemically complex or has bacteriostatic properties, then degradation may be slow or incomplete. Intermediate metabolites may be produced by a structural change to the parent compound. These metabolites are often less resistant to further decomposition than the parent compound, and their potential for tainting fish flesh may be altered.

Table 7 lists potential tainting compounds derived from bacterial metabolism of petroleum products. In general, biodegradability of metabolites tends to be the same as, or greater than, parent compounds. However, the tainting potential of metabolites is variable and not so easily predicted.

Bacterial metabolism of natural plant compounds also proceeds within the river, and this may also produce tainting compounds. For instance, starch and cellulose, common and innocuous plant products, may be degraded through a number of simpler carbohydrates, some of which may taint fish flesh (Table 7).

Finally, microbes themselves produce a wide variety of structural or metabolic compounds which, when degraded, constitute a second natural source of possible fish tainting compounds. Prominent examples from this source are also listed in Table 7.

2.2.3 Summary of Probable Fish-Tainting Compounds Associated With Tar Sands Extraction

In the Athabasca River compounds with fish tainting potential could be derived from natural instream biological processes, weathering of natural bitumen deposits and direct or indirect discharge of wastewaters from the tar sands upgrading, extraction and refining process. These latter inputs include treated wastewater (i.e. Suncor), tailings pond dyke drainage and future discharges of treated tailings water (i.e. Syncrude).

The compounds found in the process wastes are the same as those occurring naturally in the surficial bitumen and the Athabasca River. However, the relative quantities in process and tailings wastes are altered relative to the raw bitumen, in particular the lower molecular weight compounds are accentuated (PAH'S) and the sulfur and nitrogen compounds are concentrated.

Table 7. Bacterial metabolites with fish-tainting potential.

Potential Tainting Compounds	Relative Biodegradability[a]	Tainting Metabolic Intermediate or Product	Relative Biodegradability
PETROLEUM DERIVED			
Aliphatics			
n-alkanes	+++++	alcohols, fatty acids	+++++
isoprenoids	+++	branched fatty acids	+++
alicyclics	+	naphthenic acids	
		n-alkyl-odd	++
		n-alkyl-even	+
Aromatics			
monocyclic[b]	+++++	oxygenated (e.g.phenolics)	+++++
diaromatics[b]	+++++	oxygenated (e.g.naphthols)	+++++
triaromatics[b]	+++	oxygenated aromatics[d]	++
polycyclics (PAH'S)	+/-[c]	oxygenated aromatics[d]	+/-[c]
Heterocyclics			
sulfur-containing	+	oxygenated	+/-[c]
nitrogen "	+++	oxygenated	++
oxygen "	+/-[c]	unknown	+/-[c]
PLANT DERIVED			
lignin	+	benzenoid nuclei	++
starch[e]	+++++	carbohydrates	+++++
cellulose[e]	+++	carbohydrates	+++
lignosulfonates	+/-[c]	unknown	+/-[c]
MICROBIALLY DERIVED			
various natural compounds	variable	volatile fatty acids	+++++
		mercaptans	+
		sulfides (and thiols)	+
		butanol	+++
		organic acids	+++
		acetone	++
		phthalates	+
		geosmin	unknown

[a] +++++ (very biodegradable) to + (relatively resistant to biodegradation)

[b] if an alkyl side chain is present it may be attacked before the aromatic ring is cleaved

[c] an hydroxyl or a carboxyl group (or both) are introduced into the aromatic ring

[d] biodegradation probably proceeds via a consortium of microorganisms

[e] these parent compounds do not cause tainting but their metabolites may.

Both of these groups have a high tainting potential. For this reason the fishery resource risk of wastewater discharges or accidental spillage of tailings or refined product cannot be taken lightly.

Table 8 is a summary list of compounds which are associated with tar sands extraction and have tainting potential based upon cross-referencing with the literature on fish tainting. Birkholz et al. (in press) maintain that the alkylated naphthalenes, alkylated benzothiophenes and alkylated dibenzothiophenes are the compounds which pose the greatest risk. Reasons for this conclusion are: (1) they are abundant in the process wastes; (2) they have a high bioconcentration potential; and (3) they have a low threshold odour level. While the naphthalenes are quite easily degraded, the heterocyclic compounds are relatively resistant to microbial breakdown. The latter are also much more water soluble than many of the mono and polycyclic aromatic hydrocarbons. The naphthenic acids are very abundant in the process waste waters but their tainting potential is suspect. Phenols have been implicated in many tainting literature reports and are common components of petroleum wastewaters.

This list should by no means be considered exhaustive. The scientific literature on compounds which cause tainting is incomplete and often contradictory. At the same time the chemical characterization of wastewaters at Suncor or Syncrude is by no means completed. To our knowledge there has not been a systematic wastewater or river background characterization using current analytical techniques.

It is not possible at this time to include metabolic byproducts in Table 8. Not enough is known about the actual process pathways nor the amounts of material which could be produced.

Table 8. Compounds related to tar sands refining and wastewaters which have potential hazard for fish tainting.

Aromatic Hydrocarbons

Biphenyl
Anthracene
Benz(a)anthracene
Pyrene
Benz(a)pyrene
Benz(b)pyrene
Chrysene
Fluorene
Pyrene
Perylene

Substituted Simple and Polynuclear Aromatic Hydrocarbons

Alkylated Benzenes
Alkylated Naphthalenes[a]
Acenaphtene
Alkylated Indans
Alkylated Tetralins
Alkylated Phenanthrenes

Substituted Oxygen, Nitrogen and Sulfur Heterocycles

Alkylated Benzothiophenes[a]
Alkylated Dibenzothiophenes[a]
Alkylated Furans
Alkylated Benzofurans
Alkylated Dibenzofurans
Alkylated Quinolines
Alkylated Acridines

Other Compounds

Naphthenic Acids[b]
Phenols[c]

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[a] Recommended by Birkholz *et al*. (In press.).

[b] Very abundant in refined product and wastewaters but little is known about tainting potential.

[c] Additional compounds from literature with high tainting potential.

3. BIOLOGICAL PROCESSES OF TISSUE ACCUMULATION

3.1 BIOAVAILABILITY

This term is used to describe the contaminants in wastewater and natural river waters that are available for biological uptake. Data on bioavailability can be found in specific studies on wastewaters, and in general chemistry/quality surveys. For the Athabasca Oil Sands area some of the relevant data can be found in Strosher and Peake (1976, 1978, 1979) and Tsui et al. (1980) for wastewaters; and Akena and Christian (1981), Corkum (1985), Nix et al. (1979) and Wallis et al. (1980) for water surveys, and Wallace (in press) for biota.

Anderson (1977) considered that knowledge of bioavailability, as represented by the exposure concentration in the sea, was vital to an understanding of marine fish tissue contamination. The time of exposure was another important factor of bioavailability, as well as the hydrocarbon composition. Hydrocarbons can be dissolved or dispersed in the water column, as well as being adsorbed to bottom sediments. Thus, fish can acquire hydrocarbons from diverse sources, and it is difficult to obtain an accurate estimate of the total availability of hydrocarbons from any one water measurement. Different fish species will be affected by different hydrocarbon source areas. Also, the chemical composition of the hydrocarbon is an important variable, some are more or less water soluble, volatile or degradable by microorganisms (Wallace, in press; Southworth, 1979). Staples et al. (1985) found that sorption to abiotic or biotic solids was an important factor in reducing bioavilability of organic compounds in freshwater. A similar result had been reported by Lockhart et al. (1982) using radioactive labelling.

If adsorption to sediment can reduce the hydrocarbon concentration in solution, the presence of an ice cover can have an opposite effect. A total ice cover on a river, such as the Athabasca, will reduce or eliminate evaporation especially of the lighter molecular weight hydrocarbons, thus magnifying the concentration of dissolved hydrocarbon components. This can be a very important factor, since these components are usually volatilized rapidly in open-water conditions and are, therefore, not available as a potential taint source.

3.2 BIOACCUMULATION

This is taken to be the increase in concentration of a chemical in or on a fish due to uptake of the chemical directly from the water, or the ingestion of chemicals through food or sediments. It is measured by the residue or body burden, which can be associated with tainting. The processes involved are: uptake, metabolism and depuration. Other considerations are persistence and synergism.

The principal uptake processes in fish appear to involve direct absorption of hydrocarbons which may be in dissolved or dispersed (particulate) forms via gills, or from drinking water, or indirectly through ingestion of food or sorbed sediments. Absorption on and through the skin is probably not an important route of uptake for freshwater fish, because of the relative impermeability of the skin. Jones (1962) also tends to eliminate drinking as a source of contaminants in freshwater fish, and is therefore in agreement with Persson (1984) that the gills are the primary route of hydrocarbon uptake for freshwater fish, with the alimentary canal providing an additional uptake route during feeding. This has been confirmed from many studies on tissue residues of hydrocarbons which found the greatest concentrations of certain substances, such as phenol, in the liver and gills.

The rate of uptake of odorous (and hydrocarbon) compounds by fish can be very rapid. The rate can be affected by the compound concentration, exposure time, water temperature, and perhaps most importantly, the species and physiological state of the fish. The species of fish can also affect the route of uptake, in that bottom feeders might ingest more hydrocarbons (both in food and sediment particles) than would planktonic feeders or predators. There have been several studies on the fish species to be found in the Oil Sands area, some of them are Bond (1980), Bond and Machniak (1979), Jones et al. (1978), Kristensen et al. (1976), Machniak and Bond (1979), Machniak et al. (1980), Sekerak and Walder (1980), Tripp and McCart (1979) and Tripp and Tsui (1980). The important fish species, in terms of commercial and domestic fishing, as well as tainting potential are whitefish and walleye, and their migration routes and spawning periods have been identified. Walleye are predators, and whitefish bottom feeders, and hence, one might expect differences in uptake of odorous compounds and tainting potential.

There have been numerous studies on the uptake of hydrocarbons by marine fish. Lee et al. (1972) traced the uptake of radioactive-labelled polycyclic aromatic hydrocarbons through the gills to the liver and gall bladder and then the flesh. The uptake was rapid for both naphthalene and benzopyrene. Lee (1977) stated that hydrocarbon uptake from water was through the gills, but some oil, including tar particles, entered during feeding. Teal (1977) proposed that liver residue hydrocarbons came mainly from the food (entered bloodstream from gut) while muscle hydrocarbons are absorbed through the gills from the water. This was based upon the carbon number distribution: even numbers in the alkanes in muscle, and odd number predominance in the liver. Malins and Hodgins (1981) reviewed the literature on the biological processes associated with marine fish and petroleum. Majewski and Scherer (1985) and Biddinger and Gloss (1984) studied the potential for food chain (trophic transfer) accumulation of hydrocarbons but were mainly concerned with marine invertebrates. The latter study concluded that only a few of these substances were capable of biomagnification.

Reports on the uptake route or uptake rates of hydrocarbons in freshwater fish are also plentiful. Many are concerned with pesticides, particularly chlorophenols. Jones (1984) found that the study fish had rapid uptake of PCP. Macek et al. (1979) and Rodgers et al.(1983) both investigated the potential for biomagnification of various hydrocarbons in freshwater fish, and found that uptake from water (mainly by gills) was far more dominant than uptake by feeding, thus making trophic level biomagnification inconsequential. Hansen (1980) investigated the uptake of a chlorinated hydrocarbon and final tissue disposition. He found a high content in the gills, after rapid uptake from the water, but found uptake from food to be relatively slow.

The bioaccumulation of petroleum hydrocarbons is related in large part to their affinity for certain components in biological membranes and cellular materials, especially those lipophilic components. A good predictor of the potential for a particular hydrocarbon to accumulate in an organism is its octanol-water partitioning coefficient (K_{OW}). This is based upon the ratio of the hydrocarbon tendency to concentrate in either n-octanol or in water, when exposed to a mixture of these two solvents. A wide range of petroleum hydrocarbons (including effluents from synthetic fuel production) have high octanol-water partitioning coefficients, and are readily bioaccumulated by aquatic organisms. This also explains why fattier parts of fish tend to reveal higher concentrations of hydrocarbon residues, e.g. Connell and Miller (1981) reported that there was a greater storage of aromatics and PAH's in lipid-rich than in lipid-poor fish species.

In general, lipophilic organic molecules present in a fish must undergo biotransformation to more polar derivatives, and greater water solubility, before excretion can occur. A detailed review of hydrocarbon metabolic processes in fish is given in Bend et al. (1980). Malins (1977) outlines the process for marine organisms. Cravedi and Tulliez (1982) and E.V.S. (1985) describe metabolism of petroleum hydrocarbons in freshwater fish. The general process usually starts with oxidation at one or more carbon atom in the molecule, and the oxidized xenobiotic may then react with small endogenous molecules such as water, glucoronic acid or small peptides, either through hydroxylation or conjugation. Either reaction renders the lipophilic compounds more water soluble, and therefore, more readily excreted.

Malins and Hodgins (1981) report that the metabolic products of some hydrocarbons tend to accumulate in the tissues of fish, often differentially from parent compounds. Melancon and Lech (1979) found that the metabolites of two naphthalene compounds had considerably different elimination kinetics, being much slower to depurate than the untransformed compounds. The E.V.S. (1985) study reported that many metabolites of petroleum hydrocarbons are not detected by the same analytical methods or conditions as the parent compounds. Accordingly, it was concluded that total depuration of oiled tissues had occurred in fish, when, in fact, a broad range of undetected hydrocarbon metabolites still persisted. Also, although metabolism is generally thought of as a detoxification procedure, it is possible that more toxic metabolites could be produced, especially from polycyclic aromatic hydrocarbons. Some parent compounds cannot be metabolized, and thus, can fail to achieve excretion and become persistent. This is especially true of halogenated aromatics, in which the halogens on the aromatic ring prevent metabolism (Lee et al. 1972).

Thus, it can be seen that fish take up parent hydrocarbons, and metabolize many, if not most, of these compounds. Eventually, most of these products are depurated. Slow depuration leads to accumulation in the organism as a residue for some period of time. If incomplete, and no depuration occurs (as with halogenated products) then these residues can persist and possibly lead to biomagnification through the food chain (Karazawa, 1980). There are three major routes of excretion (Bend et al., 1980). The respiratory surfaces of the gills permit gas exchange, but is of limited importance in the excretion of most xenobiotics or metabolites. The secretions of digestive organs, especially the liver, play the most significant role in the excretion of foreign compounds, as well as being a major centre of metabolism. The kidney, through the urine, is capable of excreting small molecules which are able to pass through the filtration units.

Depuration was thought to occur rapidly upon the removal of the fish from contaminated water. This was found to vary by species and compound. However, more studies now recognize that depuration is often biphasic, with metabolites being excreted more slowly, as seen in studies by Smith et al. (1980) and Jones (1984). Since many fish have rapid uptake rates for a range of hydrocarbons, but have decidedly different depuration rates by species and compounds, it has been postulated that it is the depuration rate that is the critical factor in controlling the bioconcentration factor and persistence, e.g. Rodgers et al. (1983). Macek et al. (1979) further state that depuration rates may be the best test of whether an organic chemical is likely to undergo persistence and biomagnification.

3.3 SYNERGISM

Hynes (1966) pointed out that many aquatic poisons have been shown to increase one another's toxicity either by forming more toxic compounds, or by enhancing each other's physiological activity. Thus, since an effluent rarely contains only a single contaminant, and a river may receive several effluents, synergistic effects must be considered in any contamination or tainting study. Persson (1984), in direct reference to fish tainting, stated that the presence of other compounds in the water may influence the intensity of off-flavours produced by a specific compound. Reece and Burks (1985) isolated and identified eleven polycyclic aromatic hydrocarbons at extremely low concentrations in petroleum refinery wastewaters. Although these compounds were each at sub-lethal concentrations, the combination proved lethal to Daphnia magna because of the additive or synergistic effect. Parkhurst et al. (1979) tested the toxicity of fractions of untreated process water effluent from a synthetic fuel plant in the USA. It was found that the toxicities of the four fractions of the whole effluent were additive. Anderson et al. (1979) found synergism, which they designated as supra-additive, between vanadium, nickel and phenol, chemicals expected to be found in oil sands process waters. Finally, Connell and Miller (1981) stated that studies of the flavour aromas of a wide variety of foods had indicated that these are rarely due to single components or to simple mixtures. Therefore, the chemically accurate composition of a flavour aroma usually consists of complex mixtures of substances which exhibit synergistic and antagonistic effects.

3.4 SUMMARY

Predictions of organic accumulation in fish must be tempered with consideration of the species under study, and the physico-chemical characteristics of the chemical, particularly partition coefficients. Long-term predictions are particularly difficult to reach since they must consider depuration, metabolism and synergistic effects of related compounds.

Clearly, direct hydrocarbon uptake mechanisms through gill tissues represent the most vulnerable portion of fish physiologic characteristics. Compounds with high octanol-water partitioning coefficients are predicted and found to have high bioaccumulation potentials for aquatic species. Lipid tissues, such as occur in fat-rich species, are likewise known to maintain higher concentrations of hydrocarbon residues.

Since uptake and depuration rates may vary widely between fish and chemical species, caution must be exercised in reaching broad generalizations regarding risks from particular chemicals. Once a compound of relevance for tainting is identified, the full range of uptake, metabolism and depuration must be studied before long-term conclusions could be successfully attempted.

4.0 FATE OF COMPOUNDS IN AQUATIC SYSTEMS

The compounds which have the potential to taint commercial fish species in the Athabasca River are all organic. Unlike many inorganic chemicals (i.e. salt) once they are discharged to the Athabasca River they will be subject to chemical, physical, and biological transformation processes (Fig. 3). These will degrade the compound and reduce its concentration in the river relative to that anticipated from straight dilution and dispersion. These aquatic fate processes will be chemical specific and must be accounted for in the setting of ambient water quality objectives and the wasteload allocation process.

The products of oil sand upgrading are different in chemical and physical nature from both the parent bitumens and conventional crude oils. The oil in the natural bitumen deposits is deficient in water-soluble components, in saturated hydrocarbons (n-paraffins) and low molecular weight aromatic compounds (e.g., naphthalene) and enriched in asphaltenic and nitrogen-, sulfur-, and oxygen-containing (NSO) compounds (Westlake 1984). That is, those hydrocarbons which readily support microbial growth have been mostly removed from the bitumens, leaving compounds which are less susceptible to microbial attack.

The process effluents (e.g. upgrading wastewaters and tailings pond discharge) resemble more the synthetic crude than the parent bitumen, being reduced in asphaltenes and enriched in aromatic and aliphatic compounds (Fig. 4) (Strosher and Peake 1976). This change in composition will affect the fate of process products or effluents spilled into the Athabasca River, compared with a spill of conventional crude or a seep of natural bitumen. The processed material, because of its greater content of low molecular weight hydrocarbons, will be more environmentally active than the parent bitumen which is primarily composed of high molecular weight, insoluble compounds. In addition, the increased

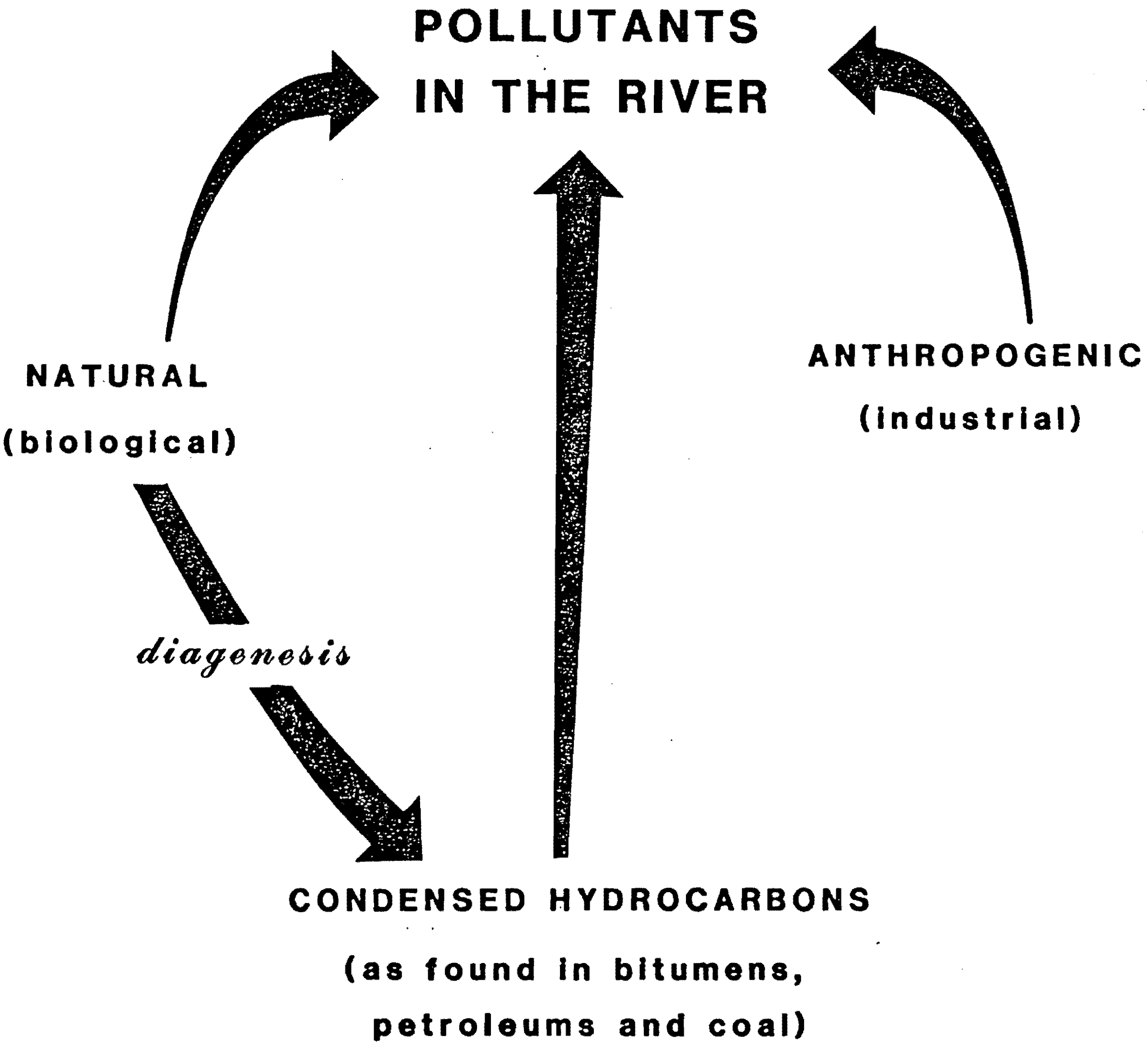

Figure 3. Sources and types of pollutants for microbial degradation.

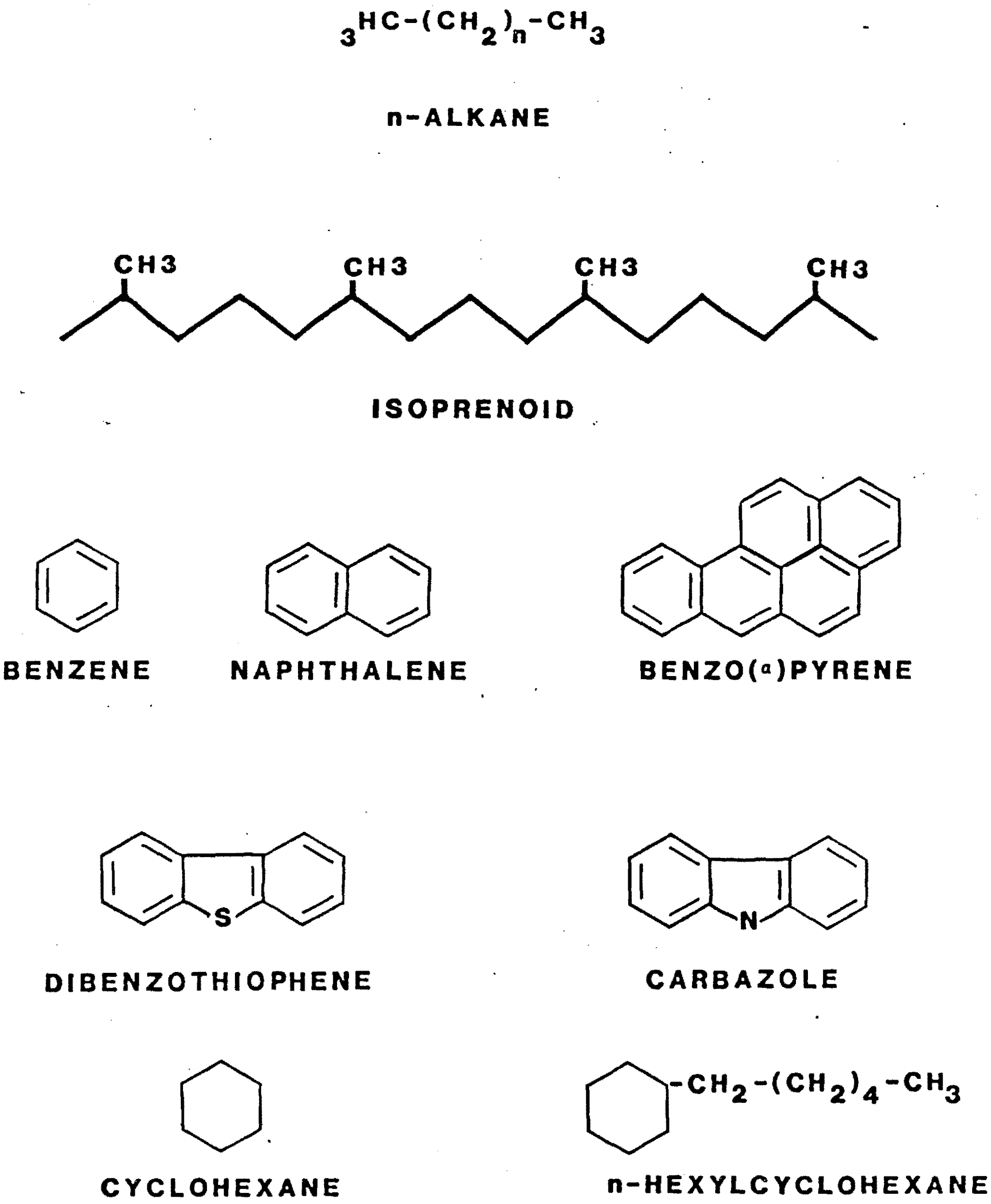

Figure 4. Structures of some common petroleum constituents.

concentrations of polar organics, found especially in the tailings pond, will influence both abiotic fates (e.g. through solubility effects) and biotic fates (e.g. through degradative attack and toxicity considerations).

4.1 ABIOTIC FATES

4.1.1 Processes Affecting Abiotic Fates

Petroleum introduced into an aquatic environment may undergo a number of chemical and physical alterations. The spreading of hydrocarbons over the surface of the water begins immediately after the oil is introduced into the system and results in the formation of hydrocarbon films and slicks of varying thickness. The rate of spreading is related to the physical properties, such as density, viscosity and pour point, of the oil spilled and the energy level of the environment receiving the hydrocarbons. The greater the surface area covered by the hydrocarbons the more susceptible they will be to "weathering" processes such as photolysis, volatilization, dissolution, dispersion and emulsification, adsorption and sedimentation (Baugham and Burns 1980). Lighter hydrocarbon mixtures such as found in some process effluents, spread quickly, and are more affected by these processes than heavy hydrocarbon mixtures such as found in bitumens.

The photo-oxidation of hydrocarbons in or on water leads to the introduction of functional groups such as hydroxyls into hydrocarbon molecules and ultimately may produce alcohols, aldehydes, ketones, etc. (Bossert and Bartha 1984). These chemical changes can result in a darkening of the oil, an increase in water solubility of oxidized compounds and greater toxicity of the water soluble fraction. However, such oxidized compounds are more likely to be degraded by microbes than the parent hydrocarbon compound; thus the biodegradability of petroleum hydrocarbons may be increased by photo-oxidation. Photo-oxidation is important in the activation of polycyclic aromatic hydrocarbons (PAH) and has been shown to be a major pathway for flux of anthracene from artificial streams (Bartell et al. 1981) and other PAH's such as benzo(a)pyrene and benzanthracene from marine enclosures (Lee et al. 1978). Photo-activation may lead to generation of polymerized hydrocarbons which are more recalcitrant to microbial degradation (Floodgate 1984). Photo-oxidation has been shown to be effective at depths of five metres in marine enclosures (Lee et al. 1978), but obviously is dependent upon penetration of light and the clarity of the water.

The process of volatilization may be responsible for the rapid transfer of large amounts of hydrocarbons (which can account for 1/3 to 2/3 by weight of a conventional oil) from an aquatic system into the atmosphere. There are many factors which determine the rate of this process, such as the area exposed, the chemical and physical properties of the oil spilled, the temperature of the oil and the energy level of the aquatic system receiving the hydrocarbons (Owens 1978). For example, the rate of volatilization of a heavy bitumen under cold conditions can be expected to be many orders of magnitude less than that of a light oil spilled into warm waters at a high energy level.

As a group, hydrocarbons tend to have low aqueous solubilities. The most soluble hydrocarbons are the low molecular weight n-alkanes and mono-aromatics and, as these are readily lost by volatilization, the solubilization process is significant only during the early stages of an oil spill or under ice cover. Dissolution of poorly soluble materials (e.g. highly condensed hydrocarbons, such as found in bitumens) will depend upon the temperature and flow rate of water over hydrocarbon-contaminated sediments, but will always be low.

The process of vertical dispersion of oil may result in the formation of emulsions (oil-in-water or water-in-oil) of varying stabilities. This process results in the increased likelihood of subsurface biota being exposed to particulate oil. The adsorption of oil droplets on suspended particulate matter or coalescence of oil particles into larger droplets can result in sedimentation and incorporation of oil into sediment. Light oils have less tendency to form emulsions than do heavy oils which are rich in asphaltenes and high molecular weight waxes (NRC 1985). Heavy oils also tend to form very stable water-in-oil emulsions (mousse) particularly in cold aquatic systems. Some microbial products as well as some products of photochemical oxidation can initiate and stabilize emulsion formation (bioemulsification).

Sorption of hydrocarbons onto inorganic or organic particles occurs in aquatic systems, affecting particularly the higher molecular weight compounds (Lee et al. 1978), usually through hydrophobic interactions with suspended solids. This sorption is usually in equilibrium with dissolution, and therefore is affected by water flow and sedimentation rates. Sorption of low-solubility hydrocarbons provides a mechanism for concentration of the compounds through incorporation into sediments; this can result in retardation of biodegradation in anoxic sediments. Such oiled sediments tend to release hydrocarbons slowly, resulting in a chronically polluted water column such as is found with a natural oil seep. Incorporation into sediments also can provide protection from photo-oxidative effects and biocatalytic processes through occlusion.

4.1.2 Relevance to the Athabasca River System

Photo-oxidative effects in the Athabasca River system would be limited to the ice-free season. However, this may be a major fate of the larger PAH's introduced to the river, with the exception of heterocycles which absorb ultraviolet light poorly [e.g., quinoline, benzothiophene; (Mill et al. 1981)]. The humic materials naturally present in tributaries of the Athabasca River (Sekerak and Walder 1980) may act as sensitizers to enhance the photodegradative process (Mill et al. 1981).

Volatilization of toxic, low molecular weight compounds such as benzenes and naphthalenes will occur under ice-free conditions. Strosher and Peake (1978) found that at low molecular weight, dissolved hydrocarbons were present in winter samples under ice, but not in summer samples. However, volatilization processes will have little effect on high molecular weight, bitumen components or the polar, water-soluble compounds in the process effluents.

Similarly, dissolution of non-polar hydrocarbons will be influenced in part by the season, both through temperature effects and flow rates. The polar effluent wastes are more water soluble, and therefore effectively will be removed by water flow and influenced by mixing characteristics of the river. There is evidence that this indeed occurs in the Athabasca River, since Strosher and Peake (1978) found that the bulk of the hydrocarbons discharged with the process effluents were retained in the water column.

Dispersion and emulsification will be influenced by flow rates and mixing characteristics of the river, as well as by the presence of anthropogenic detergents. Sorption and sedimentation also depend on the suspended solids content of the river. At Fort McMurray, the sediment load of the Athabasca River is in the order of several thousands of milligrams per litre, with a composition of 26% clay, 50% silt and 24% sand; silts and clays predominate downstream (Griffiths and Walton 1978). This provides a substrate for sorption of hydrophobic compounds and a mechanism for partitioning of hydrocarbons. Indeed, there is preliminary evidence that organic materials in the process plant effluent are fractionated in the river system; the sediments act as a sink, particularly for the heavier components, while the oily and polar materials are removed by the water (Strosher and Peake 1978). The sediments are found to have increased asphaltenic and aliphatic contents while the N-, S-, and O-containing polar compounds are found in the water column (Strosher and Peake 1978). Also, Nix et al. (1979) analyzed the benzene-extractable fraction of Athabasca River sediments and reported the presence of high molecular weight alkanes. In fact, some of this partitioning may take place before the effluents reach the river, since much of the organic matter in the upgrading plant effluents is not easily extractable, and is presumed to be present as discrete carbon particles or strongly adsorbed to suspended particles (Strosher and Peake 1976). This process probably has a marked influence on a compound's fish tainting potential, since its partitioning in the river system will, in part, determine its bioavailability, both directly, through fish uptake, or indirectly through trophic levels and biodegradation.

4.2 BIOTIC FATES

Micro-organisms have been in contact with molecules derived from natural sources through geologic time and many have developed enzyme systems capable of using such molecules as sources of carbon and energy. Microbes are found to grow readily on molecules from plant and animal sources and also grow, but less readily, on those complex molecules (e.g. low molecular weight aromatic hydrocarbons) arising from diagenetic processes. In contrast, compounds from anthropogenic activities, unless they have structural similarities to natural products, are usually initially resistant to microbial attack. The rate of removal of molecules from an environment will depend on whether that population has been previously exposed to the type of molecule, on its concentration, and on the prevailing environmental conditions. Previous exposure results in a microbial population with an enhanced capability to remove similar molecules (Pfaender and Buckley 1984).

A recent publication of the U.S. Board on Ocean Science and Policy entitled "Oil in the Sea" (NRC-USA 1985) states that microbial degradation is the main mechanism for the elimination of petroleum pollutants from the aerobic marine environment. A similar statement is valid for freshwater systems.

Of the biological species found in aquatic and terrestrial systems, micro-organisms (bacteria, yeast and fungi) play the most important role in the hydrocarbon removal. Under non-stressed environmental conditions oil-degrading bacteria play the major role in hydrocarbon degradation. Although higher biological forms are felt to be active in the transfer of oil within the environment, their role in oil-degradation is unclear, with the exception of benthic invertebrates which are thought to have a role in oil-degradation in sediments. Therefore the following discussion will be concerned with the factors controlling the activities of oil-degrading bacteria.

Hydrocarbon-degrading bacteria can be found in most aquatic environments. In areas where natural seeps (e.g. Athabasca bitumen deposits) or chronic hydrocarbon pollution occurs there will be a greater incidence of such bacteria. In general the number of hydrocarbon-degrading microorganisms in a microbial community is a sensitive index of the degree of exposure of that environment to hydrocarbons. Atlas (1981) states that "in unpolluted ecosystems, hydrocarbon utilizers generally constitute less than 0.1% of the microbial community; in oil-polluted ecosystems they can constitute up to 100% of the viable microorganisms."

Hydrocarbons are usually introduced to the environment in a complex mixture such as petroleum, bitumen, process effluents or seepage. Those compounds which are most readily biodegradable such as n-alkanes and low molecular weight aromatics containing few substituent groups (e.g., biphenyl, alkyl naphthalenes and alkyl phenanthrenes) will be utilized first, followed by more complex molecules such as branched n-alkanes and complex substituted aromatics and heterocyclic compounds such as dibenzothiophenes and carbazoles. Compounds in these groups are easily monitored by gas capillary chromatographic (GC) procedures (Fedorak and Westlake 1983). These generalizations were confirmed in a recent sophisticated study (Miller et al. 1984) using GC - Mass Spectrometric procedures. They reported that the susceptibility of hydrocarbon molecular families in a suite of Oklahoma oils to biodegradation decreases in the order: thiophenes, naphthalenes, n-alkanes, n-alkylcyclohexanes, n-alkylbenzenes, isoprenoids, hopanes with more than 30-35 carbon atoms, moretanes, 18a-trisnorhopane and natural steranes.

There have been several studies on the susceptibilities of hydrocarbons found in conventional oils. Walker et al. (1975) reported the sequential microbial degradation of mono-, di-, tri-, tetra- and penta-aromatics in a south Louisiana crude oil. In a study of the degradation of Prudhoe Bay oil by marine microbes using gas chromatography, Fedorak and Westlake (1981) reported that the simple aromatics (e.g., naphthalenes) were more readily degraded than the n-alkanes. Once the biodegradation of saturates commences, they are very quickly removed from the oil. The aromatic degradation continued to progress from the low to the high molecular weight aromatics in the approximate order C_2-naphthalenes, phenanthrene and dibenzothiophene; C_3-naphthalenes and methylphenanthrenes; then C_2-phenanthrenes. They also noted that microbial utilization of the saturate components was more sensitive to nutrient levels than was aromatic degradation. In a study of the degradation of sulfur heterocycle compounds by marine bacterial populations, Fedorak and Westlake (1983) noted that some degradation took place without nutrient supplementation. The order of susceptibility of the sulfur heterocycles to microbial attack was found to be: C_2-benzothiophenes and C_3-benzothiophenes; dibenzothiophene; C_1-dibenzothiophenes and C_2-dibenzothiophenes. Similar studies (Fedorak and Westlake 1984) showed that C_1, C_2, C_3 and one C_4 isomer of carbazoles (nitrogen heterocyclic compounds) were readily removed from Prudhoe Bay oil by a mixed bacterial population enriched from a fresh water source.

Much of the data in the literature is concerned with the utilization by pure microbial isolates of pure hydrocarbons or mixtures of hydrocarbons such as are found in oils. Such studies suggest that a microbe which utilizes aliphatic components cannot utilize aromatics and one that utilizes aromatics cannot use aliphatics. Pure microbial cultures have been grown on a relatively small number of hydrocarbons under laboratory conditions, yet many other hydrocarbons disappear from oil subjected to attack by mixed microbial populations. Studies on the interaction of microbes and oil led to the development of the concept of co-oxidation where non-growth supporting hydrocarbons are oxidized by a microbe growing on another hydrocarbon. The molecule which has been co-oxidized is now more likely to be susceptible to microbial attack than it was in the unoxidized state.

Different microbes can interact to grow at the expense of a single substrate which neither of them could grow on alone. An example of this is the degradation of cyclohexane by two bacterial strains neither of which can grow on the compound as a pure culture (Perry 1984). One organism when growing on propane oxidizes cyclohexane to cyclohexanone, but cannot grow on either of these compounds, while the other cannot grow on cyclohexane but does grow readily on cyclohexanone, degrading it completely. It also has been reported that another microbe cannot grow on cyclohexane unless there is a microbe present which can supply the vitamin biotin. As suitable microbial techniques are developed, the study of the activities of mixed microbial populations is receiving more attention. It is realized that the interaction of microbes in the environment, e.g., in sediments or on suspended particles, results in the biodegradation of compounds which have not yet been shown to be degraded by a pure microbial isolate. We have to investigate the activities of microbial communities if we wish to understand the total capability of an ecosystem to remove pollutants such as hydrocarbons. As most of the readily degraded hydrocarbons already have been removed from bitumen by microbial action it is likely that further microbial attack on bitumen will occur by the actions of mixed microbial populations.

4.2.1 Processes Affecting Biotic Fates

The rate of removal of hydrocarbons will be determined by many different environmental factors. In particular, the levels of nitrogen and phosphate often have been shown to be one of the major rate limiting factors determining the rate of removal of hydrocarbons from aquatic and terrestrial environments. There are data in the literature which suggest that the addition of iron has a stimulatory effect on hydrocarbon removal (Dibble and Bartha 1979). The nutrient content will vary with the season, the incursion of agricultural runoff, domestic sewage input and surface drainage containing natural organics.

Since oxygen-requiring enzymes carry out the initial attack on hydrocarbon molecules, the aeration level prevalent in an aquatic system is another key factor in controlling the rate of hydrocarbon removal. The oxygen level in aquatic systems is dependent upon the degree of turbulence and usually is sufficient for hydrocarbon degradation to take place in surface slicks and the water column. However, in general, it is probably only the first few millimeters of sediment which can obtain sufficient oxygen for hydrocarbon degradation to proceed.

The pH of most aquatic systems is the neutral range which will support microbial hydrocarbon degradation unless affected by industrial effluents such as sour water from steam stripping processes. Such pH changes can also alter the microbial community structure enhancing the presence of fungi and decreasing the bacterial species diversity index. This change can result in a decreased ability to remove hydrocarbons from such aquatic systems.

The temperature of the aquatic system will vary seasonally and would only be optimal for biodegradation during the warmer periods. Seasonal fluctuations do occur in microbial numbers in aquatic environments, the highest numbers being detected during warm periods with high levels of nutrient and substrate loading. It is doubtful that significant microbial hydrocarbon degradation takes place when aquatic systems are covered by ice.

If sufficient nutrients and oxygen are available, microbial degradation can convert many hydrocarbons to CO_2 and water. However, under environmental conditions it is unlikely that such conditions exist, and the products of microbial hydrocarbon oxidation are going to be oxygenated metabolites containing epoxides, or hydroxyl(s), or carboxylic acid groups.

The biodegradation of hydrocarbons in aquatic systems may be accelerated by the physical process of emulsification. Since microbes adhere to the hydrocarbon-water interface, emulsification may increase hydrocarbon degradation by increasing the surface area of hydrocarbons present. Bioemulsification of hydrocarbons by microbes from freshwater systems has been demonstrated in vitro by Broderick and Cooney (1982); this emulsification process also may result in increased microbial hydrocarbon degradation.

The sorption of hydrocarbons, together with oil-degrading microbes and nutrients, may result in acceleration of the hydrocarbon biodegradation process as long as such particles remain suspended in the aerated water column environment. However, when the flow rate decreases, such particles will be incorporated into the anoxic sediment, and as a result of slow release into the water column, may lead to chronic hydrocarbon pollution. Lee et al. (1978) have shown that methylnaphthalenes and naphthalenes were the first compounds to sediment in experimental marine enclosures, and that this sedimentation was due primarily to sorption of the compounds to living and dead cell material (biosorption), whereas the higher molecular weight compounds were primarily sorbed to inorganic particulates.

Recently Boethling and Alexander (1979) demonstrated that the concentration of the substrate in the environment has an influence on biodegradation. At very low concentrations (e.g., less than 1 ppm, such as those found in the environment), microbial degradation may not be sufficiently induced to initiate degradation, and thus low levels of hydrocarbons may persist or incompletely metabolized products may accumulate. In contrast, higher levels of substrate such as those affected by sorption and/or sedimentation processes may be sufficient to induce metabolism and select for an adapted microflora. However, it is possible that these increased concentrations may result in toxicity to microbes.

The presence of other substrates in the environment, such as readily used carbon sources like sugars and amino acids, can retard degradation of recalcitrant hydrocarbons through the phenomenon of diauxic growth. In this instance, the microbes will utilize the simpler carbon source in preference to the more complex carbon source, which can lead to persistence of hydrocarbons.

The presence of toxic materials such as heavy metals, cyanide, phenolics, etc. can have a detrimental effect on hydrocarbon degradation. Such compounds can kill the hydrocarbon-degrading bacteria or, when they are biodegradable (e.g., phenolics), their degradation by other bacteria can compete with hydrocarbon degrading microbes for available nutrients and oxygen.

4.2.2 Relevance to the Athabasca River System

As the Athabasca River flows through bitumen deposits it is reasonable to assume that there will be an enhanced capability of the microbial flora in this area to degrade hydrocarbons because of naturally adapted populations. However there is very little published information on the hydrocarbon-degrading activities of the microbial communities in this river.

A study on the enumeration of the planktonic microbial populations in this river was carried out by Costerton and Geesey (1979). The numbers of bacteria enumerated by the epifluorescence technique varied from 10^5 to 10^6 cells/ml in the water column; very few algae or fungal propagules were observed. The reported planktonic bacterial populations were larger than those found in many other Alberta rivers and streams, and this increase was postulated to arise from the carbon source provided by natural seeps from bitumen beds in the Athabasca River. Statistical analysis of data generated showed that there was no discernible effect of Fort McMurray or the GCOS plant on the number of bacteria present. They did find a site to site variation as well as a seasonal effect on bacterial numbers, with lower numbers observed in winter samples, as expected. Planktonic bacteria were found to be generally free floating with some colonization of organic detrital materials, but not silt particles, being observed. There was no correlation between bacterial numbers and flow, total organic carbon, kjeldahl nitrogen or conductivity.

Sediment populations from single samples were analyzed by epifluorescent microscopy (Nix et al. 1979) and ranged in size from 10^6 to 10^8/mL. Estimation of hexadecane-oxidizing bacteria by the Most Probable Number method indicated that there were very few hydrocarbon oxidizers among the planktonic populations, but much larger numbers in the sediments. There were more organic acid degraders (i.e., benzoate-degraders) present in water and sediment samples than hexadecane oxidizers at each site sampled.

There is very little information available on the metabolic activities of microbial populations in the Athabasca River. For that reason, reported results from the Syncrude tailings pond are discussed here in addition to those from the Athabasca River.

A study of the heterotrophic assimilation of organic compounds by bacterial populations in the Athabasca River was reported by Nix et al. (1979). They stated that the oil sands mining wastes had no significant effect on the uptake of glutamic acid by planktonic populations of this river. There was a decreasing heterotrophic activity in downstream samples even though the Total Organic Carbon levels increased 33%. There was no reasonable explanation given for these unexpected results.

Nix et al. (1981) using carbon-14 labelled compounds reported a higher degree of mineralization for "natural" compounds such as starch and amino acids than for compounds such as hexadecane and anthracene which are derived from diagenic processes and are associated with the oil industry. It is interesting that neither hexadecane nor anthracene were mineralized to any significant degree, even though hydrocarbon oxidizers were present (Nix et al. 1979), until the river water was supplemented with nitrogen and phosphorus.

Wyndham and Costerton (1981a) reported that the Athabasca oil sands deposits support an active hydrocarbon-oxidizing river sediment population. While this is not reflected in an increase in absolute numbers of hydrocarbon (hexadecane and naphthalene) utilizers, the potential rate of biodegradation of these hydrocarbons and number of micro-organisms capable of growth on oil sands related hydrocarbons increased significantly. Wyndham and Costerton (1981b) reported the in situ colonization of bituminous hydrocarbons by bacteria. Some of these bacteria grown under laboratory conditions were reported to grow on all bitumen fractions except asphaltenes. Fractionation of degraded bitumen revealed that the saturate, aromatic and first polar fractions were preferentially degraded. They concluded that "given suitable aerobic conditions and nutrients, heavy bituminous hydrocarbons can support an active hydrocarbon-degrading community and are therefore potentially available as substrates within the sediments of rivers within the oil sands formation."

Foght et al. (1985) reported that an active microbial population exists throughout the strata of Syncrude tailings pond capable of mineralizing simple organic compounds like glutamic acid, glycolic acid and phenol. However, the hydrocarbon-degrading capability of shallow samples (i.e., 0.5 and 8 m) as measured with hexadecane and phenanthrene, was far superior to that of deeper samples. The presence of bitumen, which does not contain hexadecane or other n-alkanes, was reported to decrease the rate of mineralization of hexadecane and amino acids.

Using gravimetric and colorimetric procedures, Forrester et al. (1983) reported the presence of microbes in Syncrude's mining operations tailings pond which were capable of growing on bitumen. Some isolates grew at the expense of the saturate components and others on the asphaltenes resulting in weight reductions of up to 42% of the added bitumen. Maximum degradation was observed in very rich media which contained (in addition to the bitumen and mineral salts), dodecane, malt extract, peptone and yeast extract.

Several of the chemical and physical parameters that affect biodegradation have been surveyed in a report by Costerton and Geesey (1979). Their results show that nutrient levels in the river fluctuate widely, but on average are quite low, at about 1 mg/L for Kjeldahl nitrogen and about 0.1 mg/L for total phosphorus. These low levels would probably be insufficient to sustain a flourishing hydrocarbon-degrading population, except perhaps in June when levels are higher. Foght et al. (1985) in a study of the microbial activity of Syncrude tailings pond populations reported that the mineralization of phenanthrene required the addition of nitrogen and phosphate. Thus it is possible that the lack of either of these nutrients could control the rate of biodegradation of hydrocarbons in the Athabasca River. However, iron should not be a limiting factor in the river, since levels are quite high (Lutz and Henzel 1976).

Aeration rates should be sufficient for degradation to proceed, since dissolved oxygen readings averaging about 10 ppm have been reported (Costerton and Geesey 1979), with seasonal fluctuations. As well, pH levels, which range from 7.5 to 8.65, are within the acceptable range for degradation. It would appear that any incursion of sour water from the process plant does not significantly affect the pH of the river, except perhaps in a limited area immediately adjacent to the outfall, and therefore will not adversely affect the microbial population.

Seasonal temperature variations monitored by Costerton and Geesey (1979) indicate that temperatures optimal for microbial degradation in the river occur from May to September, as expected.

Total Organic Carbon loads in the river fluctuate with season and sample site, but average about 10 mg/L in river water (Costerton and Geesey 1979) and 480 to 670 mg/kg for upstream and downstream sediments, respectively (Strosher and Peake 1978). This level may be effective in reducing microbial degradation of hydrocarbons by providing alternative carbon sources for growth (diauxie), but this cannot be determined without further information on the nature of the compounds contributing to the organic carbon measurements. In the downstream sediments, much of the organic carbon is represented by asphaltenes and hydrocarbons (Strosher and Peake 1978); long chain n-alkanes have also been identified in sediments (Nix et al. 1979). These compounds would not contribute to the diauxic growth phenomenon.

The presence of toxic materials in the river has not been directly determined. However Strosher and Peake (1978) report that phenol levels (determined by gas chromatography) in river water and sediment samples were low (about 0.01 mg/L and 2.1 to 3.1 mg/kg, respectively). These levels would probably not be toxic to microflora. Similarly, levels of heavy metals were found to be low (Lutz and Hendzel 1976; Allan and Jackson 1978), and should not present problems with toxicity to microflora.

The effects of biosorption and bioemulsification processes in the Athabasca river are unknown. However, with the low numbers of planktonic bacteria observed to be sorbed to inorganic clays in the river, it may be that biosorption and bioemulsification play important roles in microbial degradation by concentrating the insoluble compounds.

Individual substrate concentrations in the river may be below levels required for efficient degradation. For example, Strosher and Peake (1978) report that downstream levels of aliphatic hydrocarbons are in the range of 0.001 to 0.024 mg/L for water and 24.6 to 54.4 mg/kg for sediments. Since this class represents a variety of compounds, only some of which will induce microbial degradation, it can be seen that the concentrations for individual hydrocarbons may be below threshold values for degradation, especially in the water column. This is even more apparent in upstream samples which have a lower concentration of hydrocarbons. Similar values can be found for the aromatic, polar and asphaltenic fractions. In combination with low nutrient levels and cold temperatures for half the year, it is apparent that hydrocarbons could resist microbial degradation in the Athabasca River, despite the high numbers of bacteria present in the system.

4.3 MICROBIAL DEGRADATION PROCESSES

When considering the sources of potential fish tainting compounds, the biotic fate of polluting materials must be addressed. Several parent hydrocarbons found in oils have been implicated in fish tainting (e.g. benzene, naphthalenes) through direct uptake by the fish. In addition, there is the potential for microbial alteration of non-tainting parent compounds to produce metabolites which cause tainting. This microbial alteration may occur outside the fish (in the river water column or in sediments), and the tainting compounds may then be taken up by the fish; or inside the fish, as a result of microbial gut flora acting on ingested compounds, and the tainting compounds may then be disseminated to the flesh. The latter route is probably insignificant. Alternatively, microbes may remove tainting compounds from the environment through their degradative capabilities.

The metabolism of different representative classes of hydrocarbon compounds will be discussed here. As these studies are usually carried out with pure hydrocarbons, the microbial degradation of such compounds in conventional crude oils will be considered. Both prokaryotic (i.e. bacterial and cyanobacterial) and eukaryotic (i.e. fungal and algal) metabolic activities will be discussed, although it is usually bacterial metabolism which will dominate in unstressed environments.

4.3.1 Metabolism of Aliphatics

The aliphatic fraction of petroleum includes the saturated straight-chain alkanes (i.e. n-alkanes), branched chain alkanes (the isoprenoids) and saturated cyclic molecules (alicyclics). Microbial metabolism of these compounds, whether bacterial or fungal, is obligately oxygen-dependent (Singer and Finnerty 1984).

Bacterial degradation of n-alkanes is inducible, and may proceed by one of several pathways. The most common pathway is mono-terminal B-oxidation through the corresponding alcohol, aldehyde and monobasic fatty acid to produce a 2-carbon (acetate) moiety plus the shortened fatty acid carbon chain. The fatty acid may then be directly incorporated into bacterial membranes, or may be further metabolized by additional rounds of oxidation with cleavage of 2-carbon fragments (Singer and Finnerty 1984). In this manner, a hydrocarbon such as n-hexadecane (n-C_{16}) may be reduced to eight acetate molecules, each of which may serve an anabolic role. That is, complete breakdown of the molecule may occur, without production of tainting compounds. Alternatively, diterminal oxidation may occur, producing dicarboxylic acids, or subterminal oxidation may produce secondary alcohols. Although these are usually minor metabolic routes, they may result in the accumulation of oxygenated products with amphipathic properties (i.e. molecules with both lipophilic and hydrophilic properties). Less is known about the pathways of fungal n-alkane metabolism, but many yeasts primarily use the B-oxidation pathway described above. Other oxygen-containing alkanes (such as secondary alcohols, ketones, diols, esters) may be produced by bacteria, algae and fungi through the process of co-metabolism. This route is common in microbes which cannot use the n-alkane as a carbon source; rather, they fortuitously oxidize the n-alkane while growing at the expense of another substrate (Singer and Finnerty 1984). The oxygenated products often are not metabolized further by the original microbe, since it lacks the specific degradative enzymes to utilize the products as sources of cell carbon and energy. Such compounds may be potential tainting compounds.

Branched chain alkanes are more difficult to degrade than n-alkanes, and their metabolism may be repressed by the presence of n-alkanes. Their degradation may result in mono- or dicarboxylic branched fatty acids, which may be incorporated into membranes, may accumulate, or be further metabolized. For example, the isoprenoid pristane may be completely degraded to propionyl- and acetyl-CoA anabolic subunits (Ratledge 1978).

Alicyclic hydrocarbons (molecules containing saturated rings) are common constituents in the environment, being found in plant products and in fossil fuel deposits. While the alicyclic content of oils and tars is variable, North Sea oils and Athabasca bitumen are relatively rich in these compounds (Higgins and Burns 1975). The naphthenic fraction of crude oils also contains substituted alicyclic compounds (e.g., cyclohexanecarboxylic acid). The microbial degradation of these compounds has been the subject of recent reviews (Gibson 1980; Trudgill 1978, 1984a) which conclude that very little is known about the organisms and the processes involved. These compounds have been found to accumulate at the air-sea interface, in spillage areas and in heavy oil and bitumen deposits but are not observed in microbially rich terrestrial environments which suggests that microbial attack does take place. A review of the literature indicates the failure to find pure cultures which are capable of growing on alicyclic hydrocarbons. Degradation of alicyclics however is observed by the action of a consortium of microbes (Gibson 1980).

Trudgill (1978) states that the Athabasca tar oils are rich in alicyclic and polyalicyclic components. In general, these alicyclic hydrocarbons (or, cycloalkanes) are more resistant to microbial degradation than the linear or branched alkanes, and their degradation is often dependent upon a consortium of microbes acting to oxidize the cyclic molecule (Gibson 1980). For example, the compound cyclohexane is degraded almost exclusively by communities of two or more microbes, with the initial oxygenation to cyclohexanol and cyclohexanone being accomplished with broad-specificity mono-oxygenases produced by a variety of organisms (Perry 1984). Further metabolism through the ester and ring cleavage products requires specific enzymes, with the potential for accumulation of n-hexanedioic acid (Figure 5). The alkyl-substituted cycloalkanes are more suited to supporting microbial growth, since the side chains are oxidized relatively easily by B- or w-oxidation. Further metabolism may produce acetate plus naphthenic acids such as cyclohexanoic acid, cyclopentanoic acid (which are relatively easily degraded), methyl-substituted cycloalkanoic acids, or acetate-substituted cycloalkanes (which are more difficult to degrade; Trudgill 1984b; Figure 5). Naphthenic acids have been implicated in fish tainting.

4.3.2 Metabolism of Aromatics

Although the alkane-degradative pathways are similar in prokayotic and eukaryotic microbes, degradation of aromatic molecules differs significantly in these two kingdoms. In general, the bacteria are more adept at extensive aromatic degradation than are the fungi. Bacterial metabolism of aromatics, which has evolved to produce energy and cell carbon for growth, proceeds by dioxygenase attack, producing cis-dihydrodiols

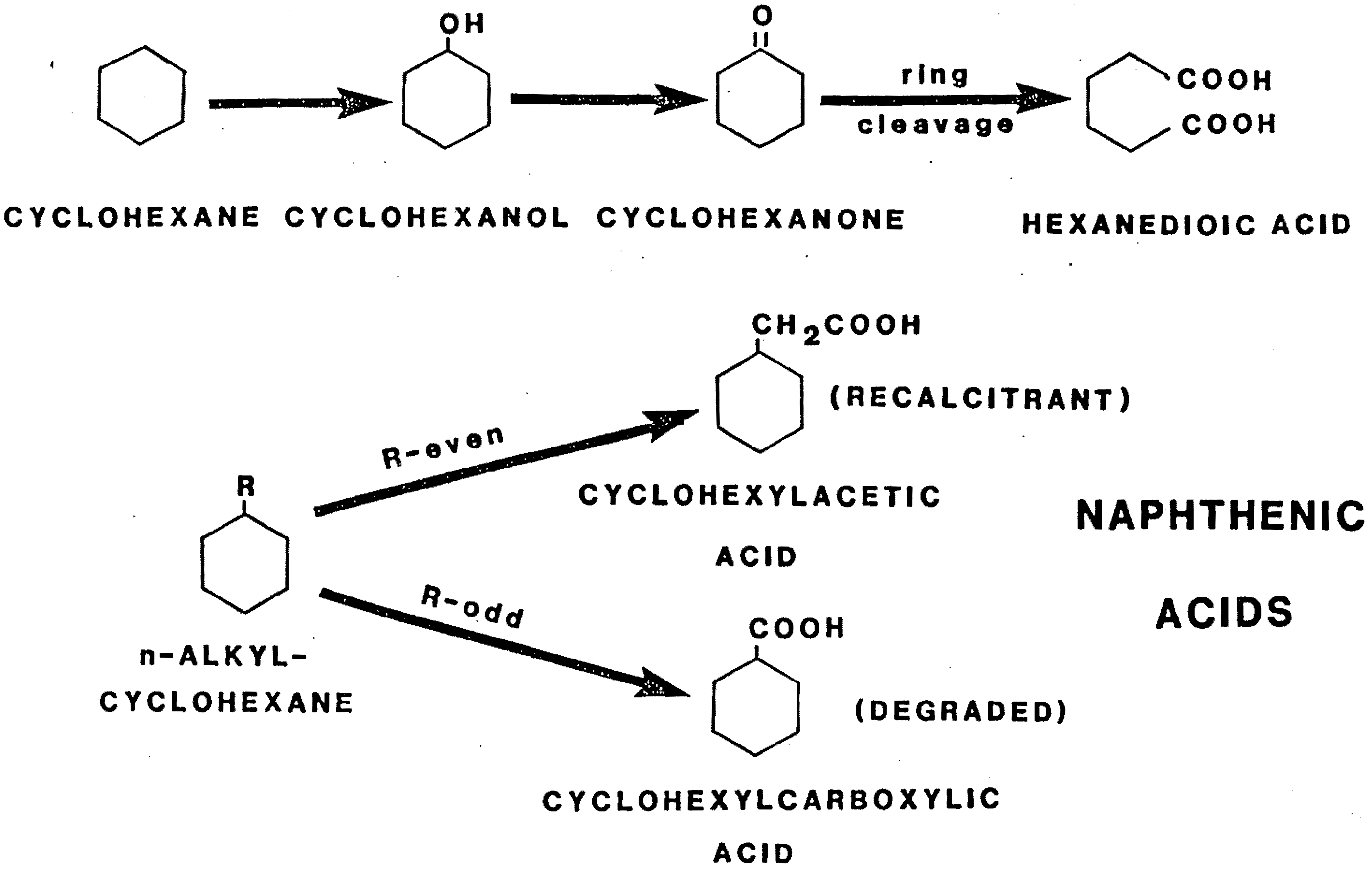

Figure 5. Common microbial pathways for degradation of alicyclic molecules yielding potential tainting compounds. Arrows represent one or more enzymatic steps.

(catechols) which may be further metabolized by ring cleavage (Gibson and Subramanian 1984). These metabolic pathways usually converge on common intermediates such as catechol and salicylate (Figure 6) which are then degraded to compounds like acetate which are used for cell growth. By-products with tainting potential such as phenols, cresols, and dihydroxybenzenes may accumulae under conditions adverse to complete metabolism, such as oxygen or nutrient limitation.

In this way, bacteria can promote removal from the environment of aromatic molecules with potential tainting metabolites. However, it is only the small (i.e., mono-, di-, and tri-cyclic aromatics) which may serve as growth substrates and be completely metabolized by bacteria, whereas alteration of larger aromatics (e.g. polycyclic aromatic hydrocarbons, PAH's) may occur without extensive degradation. For example, tetracyclics like benzo(a)pyrene and benzanthracene may be oxygenated to <u>cis</u>-dihydrodiols without ring cleavage occurring (Gibson and Subramanian 1984). Whether or not these compounds are responsible for tainting is not known, but they are retained in tissues (Fewson 1981).

In contrast to bacterial attack, eukaryotic metabolism (in both fungi and higher animals) employs mono-oxygenases, or "mixed function oxidases" (MFO's) which produce arene oxides (Zander 1980). These arene oxides are unstable and ultimately rearrange to produce phenols, <u>trans</u>-diols, quinones, or glutathione conjugates (Cerniglia 1984). These oxygenated compounds are often not metabolized further (Gibson and Subramanian 1984) in higher eukaryotes and may be conjugated and excreted. These compounds have been associated with fish tainting and carcinogenesis. For example, incomplete metabolism of naphthalene by fungi or algae can lead to accumulation of 1- and 2-naphthols and 1,2-dihydronaphthodiol in the environment (Gibson and Subramanian 1984).

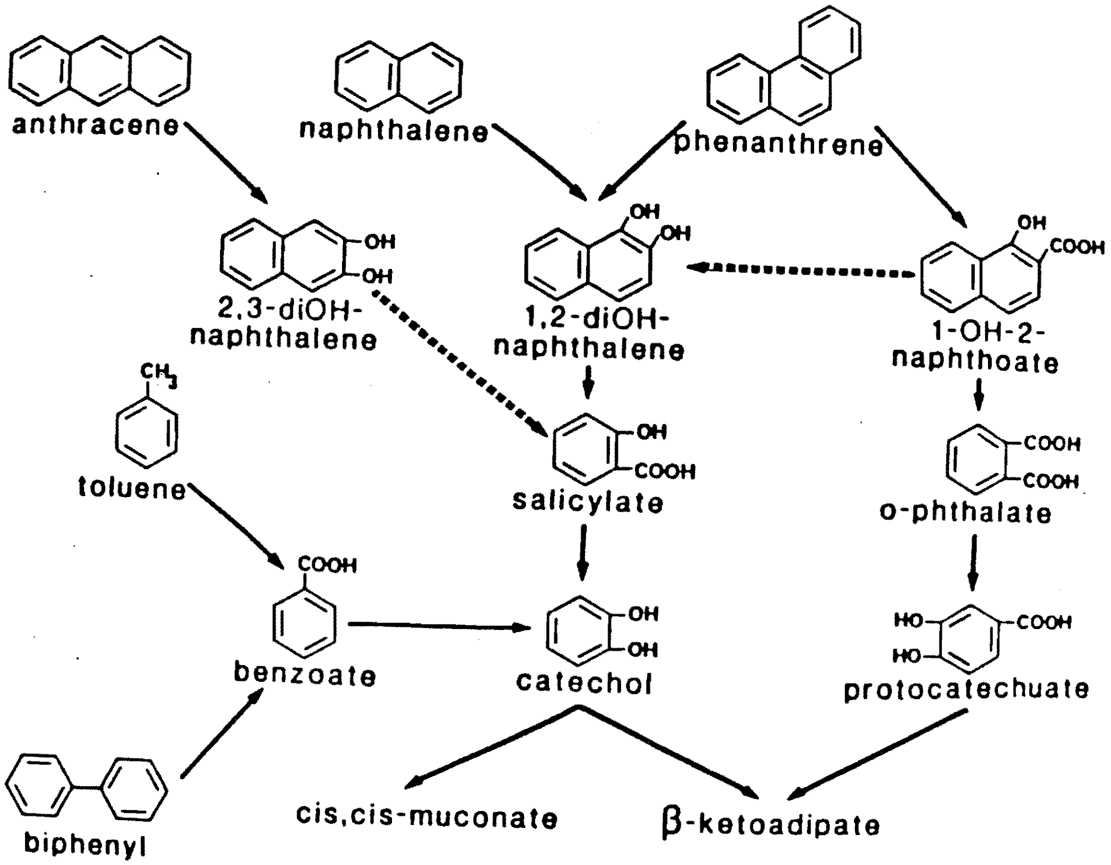

Figure 6. Common microbial pathways for degradation of aromatic molecules. Selected intermediates are illustrated. A broken line indicates that the pathway is used by a limited number of species.

Bacterial metabolism of alkyl-substituted aromatics, such as methylnaphthalenes or phenylethanol may proceed via the aromatic ring or the alkyl substituent, depending on the degrading organism (Fewson 1981), thus producing catechols or alcohol-substituted aromatics. Possible by-products such as acetophenone, butylphenol, cresols, methoxyphenol, naphthols and xylenols have been related to fish tainting. When side-chains longer than the ethyl group are present, it is likely that the side chain is oxidized first, due to steric hinderance of the aromatic attack (Gibson and Subramanian 1984). Recent studies (Davies and Westlake 1979; Fedorak et al. 1984) showed that fungi would use the n-alkanes in crude oil but not aromatics like naphthalene or phenanthrene. However, some fungi were found to degrade the aromatic nucleus of alkybenzenes if the alkyl side chain was of sufficient length.

4.3.3 Metabolism of Heterocyclics

Heterocyclic aromatic molecules, where an aromatic carbon atom is replaced by nitrogen, sulfur or oxygen, are more resistant to microbial degradation than are their hydrocarbon analogues. There is some information on the microbial attack of nitrogen heterocycles, in particular the carbazole and quinoline groups. Bacterial cultures have been isolated from freshwater systems which readily use quinoline compounds for growth (Bohonos et al. 1977). Finnerty et al. (1983) also report on bacterial isolates which use carbazoles as sole sources of carbon, nitrogen and energy. Fedorak and Westlake (1984) report on the bacterial utlization of carbazoles and alkyl-carbazoles in Norman Wells crude oil. In contrast to the utilization of nitrogen heterocycles for growth, the information in the literature on the microbial degradation of sulfur heterocycles suggests that their oxidation by bacteria is brought about by co-oxidative processes. The metabolism of dibenzothiophene, which has been used as a model compound for studying bacterial metabolism of sulfur heterocycles, has recently been reviewed by Ensley (1984) who concludes that the heterocyclic ring (i.e., the one containing the sulfur atom) is not broken during the oxidation process. As a group, condensed thiophenes (e.g., DBT) have shown a high potential for biological accumulation and toxicity and are considered as possible mutagens and carcinogens; however, their potential as tainting compounds is still not resolved. The sulfur heterocycles are a major organic group found in the Suncor upgrading plant effluents (Strosher and Peake 1976).

Furans, which contribute to the taste and odour of foods (Trudgill 1984b), are analogous to the thiophenes, having an oxygen substitutent rather than a sulfur atom. They may be found naturally in tar oils, or may be formed in cooked foods by the pyrolytic breakdown of sugars. They also appear as degradation products of lignin polymers (Trudgill 1984b), and are themselves relatively degradable.

4.3.4 Metabolism of Asphaltenes

Asphaltenes, although by definition a solubility class (i.e., they are insoluble in n-pentane), show markedly similar characteristics varying only in the proportion of hetero-elements oxygen and sulfur, with the nitrogen content being relatively constant. The structures are unknown but are considered to consist of condensed polynuclear aromatic ring systems (from 6 to more than 15) bearing alkyl side-chains. The presence of such systems is linked through saturate chains or other rings. As all the evidence concerning the ability of microbes to grow on asphaltenes is based on gravimetric data (i.e., circumstantial) there is no information regarding degradative pathways used (if any) for microbial growth on asphaltenes.

4.3.5 Metabolites From Natural Sources

In addition to these anthropogenic and diagenic compounds and their metabolites, there are naturally produced compounds of microbial origin or of microbial alteration which have tainting potential. These include the volatile fatty acids such as acetic, propionic and butyric acids, and various sulfides and mercaptans. These compounds may be produced by microbial flora during normal growth on natural substrates. As well, phenolics may be produced through microbial (especially fungal) metabolism of lignins. Another compound, produced primarily by actinomyces species and to some extent by cyanobacteria, is geosmin. This compound is a natural by-product of the organisms' growth and has been implicated in off-tastes in fish flesh.

4.4 AQUATIC FATE MODELS

4.4.1. Background Information

Proper management of hydrocarbons with fish tainting potential may require the ability to predict probable river water concentrations. Such predictions must incorporate the key biotic and abiotic river processes defined in sections 4.1 to 4.3, and allow testing of variable wasteload and streamflow conditions. Numerous aquatic fate computer simulation models have and are being developed. This section reviews the general approach to modelling the aquatic fate of compounds, and reviews a range of available model packages. This review is done in the context of modelling hydrocarbons in the Athabasca River.

Models are simplified analogues of ecosystems, in which the important processes relevant to fate of a compound have been represented mathematically. To the extent that the model is accurate, behaviour of elements within the model should mimic behaviour of real ecosystem components. The concentration of an organic compound in the environment depends upon the quantity released to the environment and the processes which influence its fate. The principal processes may be classed under three headings: Transport, transfer and transformation (Mills et al. 1985).

Transport processes include all ways that compounds are carried from one place to another, including precipitation, dissolution, advection (transport by moving water), volatilization and sedimentation. Transformations are those processes which alter the compound in some way, usually (but not always) to more innocuous end products. Included in this class are biodegradation (metabolic breakdown by microbes), photolysis (light-activated degradation), hydrolysis and oxidation-reduction reactions. Between these two classes are transfer processes, which alter the state or availability of the compound without effecting a transformation. Sorption to suspended solids and acid-base equlibria (pH effects) are the most important transfer processes.

In addition to the physical-chemical process, there are strictly biological processes, bio-accumulation and biomagnification which are known to be important for petroleum refining wastes. Bio-accumulation refers to assimilation of substances directly by aquatic biota; accumulation in fish flesh by diffusion across the gills is an example. Biomagnification refers to accumulation through food chains. Importance of each process, and their rates and interactions vary among compounds. Which processes are pivotal to determining ultimate concentrations of a given compound will figure in the decision as to which fate model should be used.

Aquatic fate models are essentially elaborated mass balance equations of the form (O'Connor and St. John 1982):

$$\frac{d\,(\text{Concentration})}{dt} = \text{Transport} - \text{Transformations} - \text{Transfers}$$

Fate models solve this equation by representing the environment as a group of interconnected compartments and deriving mathematical expressions which govern the transfer of the substance from one compartment to another. Usually, separate compartments are delineated for water, sediments, atmosphere and the biota, but depending upon the model and its purpose many more smaller compartments may be defined (Mills et al. 1985). Forcing functions which control the movement of the substance may be theoretical or empirical, or incorporate elements of both (e.g., Park et al. 1982). Perhaps the best models are created by carefully measuring the important (to degradation) properties of the chemical, and the driving forces in the environment, and then merging the two (Burns 1982). In reality, limitations of our understanding of aquatic ecosystems often necessitates a more pragmatic approach. Thus three classes of mathematical models may be identified (Yeh 1982).

Parametric or empirical models are those in which the forcing functions are based on experiment and observation, tempered by judgement, but without a foundation in theory. They are usually small, often site-specific, and designed to answer a particular, well-defined question.

Stochastic models define forcing functions in terms of probabilities of transfer from one model compartment to another, and express results as a probable final distribution of the substance modelled. The mathematics of such models is extremely complex and as such many are still in developmental stages.

The third class of mathematical models is principle based, or mechanistic (Yeh 1982). These models are based upon extrapolations of physical, chemical and biological principles, coupled with reasonable assumptions about the ecosystem under consideration. The forcing functions form a set of simultaneous or differential equations. Mechanistic models may be very complex, but different levels of detail are possible. The fugacity models discussed below (Mackay 1979; Mackay and Paterson 1981, 1982) are examples of mechanistic models.

Mills et al. (1985) have summarized the steps in modelling fate of a given substance:

1. Determine the important processes influencing aquatic fate. The immediate fate is critical: will the substance stay near the surface and volatilize quickly or sink to the sediments? Will it dissolve, or adsorb to suspended particles? Once these questions are answered the persistence and ultimate fate of the substance are more readily predicted.
2. Delineate the important environmental compartments. The fewer compartments the simpler the model, but all compartments likely to experience a significant flux of the substance should be included. Sediments pose a special problem because, while they may be important sinks (and later, sources) for organic compounds, accurate data on their character is difficult to come by. Often, the size of the sediment pool of the modelled substance is neglected, and fluxes to and from the water column are used instead.
3. Mathematically represent hydrologic flow. The usual assumptions, especially for first approximations, are that lakes are uniformly mixed, inflows to rivers mix instantly, and river flow is segregated longitudinally; that is, a slug of

pollutant added at one point remains intact as it moves downstream. More sophisticated models include the effects of dispersion and diffusion (Yeh 1982).

4. Mathematically represent transport, transfer and tranformation processes. Empirical, stochastic, or principles-based forcing functions may be used, but often the matter is decided by the nature of data available.
5. Determine the load of the compound under consideration, and the mode of entry into the aquatic environment. Possibilities include: continuous input, cessation of input, washoff from land application, leaching, or accidental spills. Immediate fate in terms of volatilization and adsorption (or desorption) will be different for each of these situations.

The final step is to run the model, with the appropriate time-step, and evaluate the results.

4.4.2 Limitations of Models

Models, by definition, are less complex than nature. However, it is axiomatic that a simplified representation cannot imitate nature perfectly, hence, some loss of accuracy is inevitable. This inaccuracy must be weighed against the difficulty, expense, and feasibility of adding more detail. For first approximations, where it is only necessary to predict which compartment of the environment will accumulate most of a given compound, a relatively simple model may suffice. Where the fate of a compound must be predicted more exactly, subtle transformations and minor pathways must be included in the model. But there will always be some loss of detail, and hence some inaccuracy, when a model is built. It is the modeller's task to find the optimal balance between realism and simplicity.

Within the limits of their predictive capabilities, simpler models tend to be more widely used (Slissak and Delos 1982), for a number of reasons. First, simpler models are easier to understand. Sophisticated models may predict more accurately, but over-complication limits their use because each of the many parameters entered must be justified, and in addition nonconformities of results with data are much harder to correct.

Very complex models also tend to compensate for changes in one parameter by changing the others. When one parameter is constrained (for heuristic purposes or to ensure biological reasonableness) a good fit to data may still be obtained by accomodating changes in other parameters. It is important to ensure that a model behaves sensibly even when the fit to the data may be worsened (Bunnell and Tait 1974; Bunnell et al. 1977).

The problem of compensating errors in complex models may be reduced by careful testing of model components against data, independent of the model as a whole. Even this may not entirely eradicate the problem, because complex models may develop emergent properties - that is, the model as a whole may exhibit behaviour not found in any of its component parts. Emergent properties result from the interaction of model components with each other, and in very complex models interactions are so many and diverse that the degree and kind of emergent behaviour can be difficult to predict.

It must be recognized that simulation results can only be as good as the input data. Aquatic fate models commonly require data on such things as intensity and spectral distribution of sunlight, redox potential of sediments, or decomposition activity by benthic bacteria. Much of this information may not be available for a particular site, or if it is, the accuracy and applicability to model use is often unknown. Physical and chemical properties of the compound being assessed are also required. Literature values for these parameters are now available for most organic compounds. Where essential data are estimated or derived from literature values, model results will reflect the accuracy of the data used; the magnitude of error will depend upon the importance of the estimate-based process to the ultimate fate of the compound, and the sensitivity of the model to variations in that datum.

Model implementation should include sensitivity analysis on the primary pathways. Estimates for sensitive parameters should be carefully scrutinized and possibly confirmed with site-specific monitoring, field research or laboratory testing.

4.4.3 Data Requirements

For this discussion, models and their data requirements may each be separated into two congruent classes. Models are (relatively) simple or complex; simple models have relatively few data requirements, compared to those of complex models. Field and laboratory data are the two classes of model information. Virtually all models demand the same laboratory data, which includes a chemical and physical profile of the compound being modelled. Characteristics such as molecular weight, solubility, octanol-water partition coefficient, ionic species, and chemical configuration (e.g., polarity) are all required. This information is readily available for all but the most uncommon organic compounds.

Where models differ is in their requirements for field data. At one extreme are screening models (EXAMS, SRI) which will perform adequately with no site-specific data at all. An overview of the general behaviour of a compound may be had from default parameter values which typify a certain ecosystem type (e.g., river) or region. At the other extreme, complex models such as HSPF or PEST require a detailed site-specific survey of the physical, chemical, climate, and biological environment in order to be implemented successfully.

Most models require estimation of the following parameters: river morphology (depth, width, channel shape), discharge, water chemistry (pH, dissolved oxygen, temperature, hardness), bed load and suspended solids concentration. Atmospheric data, such as weather, or at least season, and intensity of sunlight is usually also required. Where photolysis is an important factor, the spectral distribution, as well as intensity of radiation may be needed.

All models will also require that the ecosystem be well enough understood that sensible compartments may be defined, and the fluxes of water and other material between them specified. This usually entails measuring flow rates and suspended solids concentrations at points all along and across the channel. For a model with many small compartments, a thorough sampling program is required. Of course, the location of the pollutant input, as well as its concentration and nature (e.g., ionic state) must be known.

Requirements in terms of biological data also vary widely. Naturally, all the species present which may substantially influence transformation or transport or which may be sinks for the modelled compound must be known. In addition, models require estimates of rates of respiration and biotransformation by aquatic bacteria. In some models populations must be estimated as well. Some of these data may safely be extrapolated from laboratory culture studies, but the inherent variability of organisms suggests that field sampling would provide better estimates. PEST, a model designed to stress the biological aspects of fate, requires that the physiology and ecology of fish and other organisms be thoroughly understood. Again, much of this information may be derived from the literature, but field sampling would be worthwhile to verify parameter estimates.

Some screening models, such as FUGACITY require few field data, but compensate by demanding much more physical and chemical information about the compound. Such things as melting point, vapour pressure and a number of partition coefficients are required for calculation of fugacity. However, an attractive feature of this model is its formulation at three levels of resolution. This permits the user to quickly determine, with a level 1 analysis, which processes are critical. Effort may then be focused on deriving (from literature or experimentation) better estimates of parameters relevant to those processes, and ignoring all others.

4.4.4 Modelling Aquatic Fate in the Athabasca River

When evaluating the applicability of the modelling approach, or specific models, to the Athabasca River, several special problems need to be considered. Foremost among these is the problem of mixed effluent. Aquatic fate models typically have been designed to deal with one compound at a time. But petroleum wastes can comprise a variety of organic compounds of widely varying physical and chemical properties. The problem is thus not to simply predict the fate of a given compound, but to determine which of many compounds are likely to be a problem because of their ultimate fate, and as well to anticipate interactions between them.

The problem of kinetic interactions among chemicals dramatically complicates fate models because the number of potential interactions increases very rapidly as more chemicals are considered (Bergmen and Meyer 1982). Such interactions are usually ignored in fate models, but they may be important, especially in the biological component of the model. Reinert et al. (1979; cited in Bergman and Meyer 1982) report an antagonistic effect of DDT on bioaccumulation of dieldrin by fathead minnows; accumulation of dieldrin was less when DDT was present although accumulation of DDT was not affected. Such effects have not been specifically demonstrated for petroleum effluents, but the complex composition of these effluents makes interactions (both antagonisms and synergisms) possible.

Of greater consequence, and certainly of more general occurrence, is preferential metabolism by bacteria. When presented with two carbon sources of different structure, bacteria generally will preferentially degrade the compound which supports the faster growth rate; the decay rate of the more recalcitrant compound may be much less when in mixtures than when alone (Bergmen and Meyer 1982). Preferential metabolism is common even when ordinary substrates are considered: decomposer organisms in soil and sediments degrade simple sugars before cellulose, and cellulose before lignin (Swift et al. 1979). On the other hand, addition of nutrients, especially nitrogen and phosphorus, may accelerate decay of otherwise recalcitrant compounds. Nix et al. (1981), studying natural bacterial populations in the Athabasca River, found that amino acids and starch were degraded more quickly than hydrocarbons, and that significant degradation of hydrocarbons occurred only after supplementary nutrients were added. Clearly, some degree of preferential metabolism is virtually certain where complex petroleum effluents are concerned, and that, along with other synergistic and antagonistic interactions, will bring another level of complication to the problem of modelling aquatic fate.

Three approaches are available for modelling complex effluents (Bergmen and Meyer 1982):

1. Model general properties of the effluent, and ignore the actual chemicals involved. This is the approach used when modelling biochemical oxygen demand from sewage effluent (an organic complex effluent) or total dissolved solids from irrigation return-flow. BOD or TDS are general properties of mixtures of compounds, the composition of which remains largely unknown. Problems arising from individual compounds cannot be identified with such models.
2. Model chemical classes by choosing one representative chemical from each class. This provides a first approximation of fate of broad classes of compounds, reliable to the extent that members of each class behave similarly. It improves on the general-properties model because different fates of different classes may be followed, and thus compounds which may need more detailed modelling may be separated from those that pose no problem. Bergmen and Meyer (1982) cite several examples of chemical-class models being developed by USEPA, but none are presently in general use.
3. Model each compound separately. This is the opposite extreme from general-properties models, and would require an extensive cost and effort if applied to a very complex effluent like petroleum. Also, single-compound models neglect the problems of interactions discussed earlier. However, this approach may be feasible if a relatively small number of compounds are chosen (by a chemical-class model or by independent information) to receive

closer scrutiny. For example, individually modelling the compounds which are known both to taint fish, and to be present in petroleum effluent may be feasible. The actual modelling approach used will depend upon the intent of the study. Moving from generalproperties to single-compound models, predictions for a given compound become increasingly accurate, but data needs also rise dramatically.

There are several special features of the Athabasca River which should be considered in any modelling program:

1. Temperature. Rates of microbially mediated reactions are temperature dependent, usually with a Q_{10} near 2 (Mills et al. 1985). However, cold-adapted bacteria in the Athabasca River may have compensated so that reaction rates there at low temperatures are greater than predicted by models based on warmer regions. Depending upon the model, this might require only an empirical adjustment of a rate constant, or a major modification of that part of the programme.
2. Low concentrations. As discussed elsewhere, fish-tainting substances may have measurable effects at concentrations near the limit of detection. To be useful, a model of fate of these compounds would need to accurately predict extremely low concentrations. Although models have been developed to handle trace amounts of (e.g.) pesticides, the small quantities considered here may still limit model accuracy because (a)

assumptions regarding speed of reaction and mechanisms of processes which are based on (relatively) concentrated solutions may not apply to very dilute solutions and (b) some effects of scale, or minor reactions which are trivial at higher concentrations (and hence excluded from the model) may be comparatively important at very low concentrations. As a contrived example, suppose a sediment composed of numerous, large particles with a modest affinity for the modelled compound, and a few small particles with a strong affinity for the compound. At high concentrations, where the model is likely to be tested, the fine particles are always saturated with the compound and the behaviour of the more numerous large particles dominates. At very low concentrations, only the small particles are adsorbing the compound, and adsorption affinities extrapolated from higher concentrations will be wrong.

3. Latitude effects. Models developed at low latitudes may assume levels of solar radiation or other latitude-dependent parameters inappropriate for the Athabasca river. For example, the comprehensive model PEST (Park et al. 1982) assumes radiation intensity, for prediction of photolysis, for a latitude of 40°N, a full 15° south of the Athabasca River. These parameters should be easy to correct, as long as the user is aware of them.
4. Background petroleum levels. Unlike a pristine stream receiving point-source effluent, the Athabasca River already contains low levels of petroleum compounds from natural seepage (Strosher

and Peake 1979). This could complicate modelling of fates of anthropogenic additions. For instance, models may include a time lag before decomposition by bacteria is assumed to begin, to allow for adaptation (induction of enzyme systems) to a novel carbon source. In the Athabasca there appears to be no such lag (Nix et al. 1981); bacteria are already fully adapted to petroleum loading.

5. Ice-cover. Most water quality models are not set up to simulate winter conditions and ice. Ice cover creates unique hydraulic conditions which alter the lateral mixing and travel times. In turn, volatilization is restricted, but emulsification may be enhanced.
6. Mixing Zones. Any aquatic fate modelling of hydrocarbons in the Athabasca river will have to account for mixing zone conditions. This factor will preclude the use of many available model packages.
7. Sediment Regime. The suspended sediment regime in the lower Athabasca River is extremely variable and complex. This regime may have to be more carefully characterized.

4.4.5 Aquatic Fate Models - Examples

There are a number of models available for predicting aquatic fate of petroleum compounds. These vary in their underlying structure, data requirements, and complexity.

4.4.5.1. HSPF. Although designed as a comprehensive model of watershed hydrology and flow routing, the Hydrocomp Simulation Program in Fortran may also be used to simulate fates of trace organics. HSPF can model single events or continuous effluent addition. The model actually consists of a network of submodels, only some of which would be used in a particular situation. Submodels relevant to the Athabasca River include those simulating land-use changes, pesticides (or other trace organics), nutrients, and stream modification. The model will consider point or non-point inflows as well as transformations in the channel and releases from sediments. The program requires a great deal of data on watershed land use (if applicable), soils, weather, channel flow, channel geometry, and instream processes, and also demands considerable skill and experience from the user. In order to avoid overwhelming complexity, it is essential that only critical elements of HSPF be used in a modelling exercise.

4.4.5.2. EXAMS. The Exposure Analysis Modelling System is an evaluative model developed by USEPA to predict aquatic fates, persistence and exposures (to biota) of new organic chemicals. EXAMS is a predictive, deterministic, systems model designed to facilitate rapid, general evaluations of the behaviour and hazards of pollutants in the environment. The model is mechanistic (principles-based) but allows for modifications and simplifications based on empirical correlations. The model predicts equilibrium concentrations for each user-defined compartment of the ecosystem, assuming a continuous, low-level inflow. Event loads, such as oil spills, cannot be simulated.

EXAMS was not intended for site-specific use; since its original purpose was to screen manufactured chemicals before they were released, it requires no field monitoring data, and has no explicit calibration procedures. However, the model is flexible enough that site-specific application in the usual manner is possible. As outputs EXAMS predicts the proportion of original load in each ecosystem compartment at equilibrium, the half-life of the compound, and the relative importance of each process to the fate of the modelled compound.

The model incorporates impressive detail and flexibility. Each of the central processes (photolysis, biotransformation, volatilization etc.) is described by a set of differential equations based on standard theory (e.g., the two-phase theory for volatilization) or accepted empirical relationships. Empirical "shortcut" relations, such as the octanol-water partition coefficient may be used if specified by the user. Ionization and sorption are defined as local constraints on other processes, since some transformations, such as volatilization, act only on one form of the molecule. Up to five chemical species (ions) may be modelled.

Transformations are handled at two levels of complexity: as second-order functions of concentration and temperature, or as two separate first-order equations, one each for low and high temperatures. Similarly, there are two subroutines for photolysis, a simple, general one and a more detailed one requiring absorption spectra as input data. The user may specify which routine to use.

Hydrology is modelled in detail (including evaporation, ground water seepage etc.) and pollution may enter the system five different ways: point source, non-point source, fallout, seepage or drift (as from herbicide spraying). The model has 10, 50 and 100 compartment versions. Biota may be specified as one or more compartments, but food chains and biomagnification are not explicitly included. The model does not explicitly consider mixing zones. However, mixing could be approximated by careful delineation of small compartments and their connections.

The model has been tested for theoretical and utilitarian soundness and found adequate, and field validations and sensitivity analyses have been performed. The model is very well documented, with a complete description of theory and design, a user's manual, programmer's guide and catalogue of variables and subroutines (Burns et al. 1981).

Data requirements are large; however, default values built into the model allow approximations to be used, a satisfactory condition for preliminary runs at least. A complete chemical and physical profile of the compound being modelled, and all its species, must be specified. There are roughly 50 parameters for each ionic form. In addition, hydrologic data and compartments of the ecosystem under study must be specified. For each compartment (there may be many) 12 parameters specify geometry (depth, volume, inflow and outflow rates etc.) and another 17 delimit physical-chemical conditions and biota. The user must also describe global parameters such as latitude and cloud cover, and which compartments are connected.

4.4.5.3. PEST. PEST is an EPA evaluative model, similar to EXAMS, except that it is far more detailed, especially with respect to bioaccumulation and biomagnification. The model was designed to predict fate of (toxic) organics in natural aquatic environments and to fulfill the need for detail and biological realism not found in other models. The model is process-oriented, and comprehensive, covering behaviour of the whole ecosystem. Up to 16 compartments may be specified, with concentration changes driven by sets of ordinary differential equations. Most equations are mechanistic, but many are modified empirically. The model assumes uniform mixing within each of the (relatively) small number of compartments, so mixing zones cannot be simulated. Model output consists of (1) concentration of compound in each ecosystem compartment; (including invertebrates and fish); (2) per cent distribution; (3) half-lives of compounds in each compartment.

Transport, transformation, and transfer processes, (hydrolysis, redox, volatilization, sedimentation, sorption, solution, photolysis, microbial degradation and cometabolism, consumption by fish) are all modelled, often in impressive detail. The uptake of compounds by fish both in food and by gill transport is modelled in detail not found in other models. For example, the equations for food consumption vary according to feeding mode, from filterfeeder to carnivore. Physical factors (e.g., temperature), prey densities, and even feeding preferences are all explicitly included. A separate bio-accumulation subroutine describes transport across the gill membrane into blood and from there into body fat. Similarly, the equations controlling microbial degradation allow for changes in microbial biomass (usually treated as a constant) and differences in metabolic rate when metabolizing different compounds. However, the user must supply a great deal of data, such as oxygen re-aeration rates and microbial respiration in the field which is not routinely available. A thorough literature search and laboratory work would have to preceed use of this model.

The model is recent (1982) so it has not been widely used. The authors (Park et al. 1982) tested the model in ponds and reservoirs in the USA, and found that it tends to be conservative i.e., compounds disappear slower than they should. Testing in rivers or northern environments has not been reported. Each of the sub-models (governing one process) was independently tested against field data.

Data requirements are immense. The full model contains 86 parameters, and if one group of organisms (e.g. fish) is seen as important, then their ecology and metabolism must be well known. However some parameters may be ignored or set to zero if a process is known to be unimportant. PEST is written in Fortran IV, and was designed to be easily modified. Documentation includes a user's manual and a programmer's guide (Park et al. 1982).

4.4.5.4. SRI Model. Smith et al. (1977) have developed a model system (here called SRI) which is similar to EXAMS in that it was designed to rapidly predict fates of novel organic compounds in aquatic systems. All SRI routines are based on extrapolation from laboratory work (since field data would not be available for a new compound) integrated with hydrologic data for a given waterbody.

SRI assumes steady state (continuous input) and low concentrations, less than the solubility limit of the compound. The model omits non-bacterial degradation or transformation, transformations within the sediments, and bio-accumulation. All but the first are minor pathways.

SRI is actually two models, a simple one-compartment model and a more sophisticated nine-compartment model. The simple model treats the system as a single, homogeneous, instantaneously mixed reactor, uniform with respect to external forces, water flow and physical properties. The organic compound enters the system as a pulse at time zero; all the process equations describing fate of the compound are collapsed into first-order equations in which concentration is the only variable. This model produces an overall half-life estimate for the compound, and demonstrates which fate processes are important enough to warrant further attention.

The nine-compartment model is run after more detailed information regarding key processes for that compound has been obtained from the literature or through laboratory experimentation. This complex model includes all the usual transport, and transformation processes, except bio-accumulation. The nine compartments can vary in size and composition, and in each the compound may exist dissolved, sorbed to sediments, or within the biota. Transfer between compartments is determined by simple algebraic expressions governing movement of water and sediments. Process equations are still first-order, except biodegradation which is patterned after enzyme kinetics.

Unlike the simple model, the nine-compartment model assumes a continuous supply of pollutant, not an event load. It can simulate rivers or lakes, but compartments are assumed to be uniform, so mixing zones - an important element in the Athabasca River - cannot be modelled.

The SRI model is conceptually simple, but the research upon which it is based is sound and thorough. The model has been tested on a river, a pond and lakes using 13 different compounds - nine of them aromatics associated with petroleum refinery effluent. The model performed well once sufficient physical and chemical data about the compound were provided.

Data required for the model includes sufficient information about the geometry and hydrology of the system to define appropriate compartments, and a thorough profile of the modelled compound's properties, including solubility, volatilization rate, octanol-water partition coefficient, photolysis rate etc. The authors (Smith et al. 1977) realize that extrapolation from laboratory to field involves a risk of error. They developed laboratory procedures to reproduce field conditions as closely as possible. These methods are described and assessed in the model's manual.

4.4.5.5. FUGACITY. Fugacity is a thermodynamic property which describes the chemical potential or activity resulting in a tendency of a chemical to escape from one phase to another. Phases may be water, air, sediments, suspensoids, and biota. Fugacity is to mass diffusion as temperature is to heat diffusion: mass (of a chemical) always flows from high to low fugacity; when the fugacities of two phases for a particular chemical are equal, they are in equilibrium. Fugacity has units of pressure, and varies linearly with concentration; it also depends on temperature, pressure, the nature of the chemical (molecular weight, solubility, structure) and the phase it is in.

The fugacity concept forms the basis for a family of relatively simple fate models (Mackay 1979; Mackay and Paterson 1981, 1982). These models simulate transport and fate of organic compounds in rivers, assuming complete mixing. Within each phase (compartment) of the ecosystem, processes of photolysis, hydrolysis, oxidation and biodegradation are treated by first-order reaction equations, while fugacity controls movement of molecules between phases. Transport is treated simply, depending on discharge divided by volume. The models predict the ultimate concentrations of the modelled substance in the air, water, sediment and biota compartments. No finer resolution is possible. Data requirements are relatively modest, mostly basic morphometric and hydraulic parameters, but many attributes of the modelled compound (specific gravity, melting point, boiling point, etc.) must be provided. An attractive feature of this model system is that it has been defined for four levels of complexity, ranging from an equilibrium, steady-state no-flow system to a non-equilibrium, dynamic, flow system. The user may use the level of complexity appropriate to his needs. However, even the most complex level of Fugacity is considerably simpler than PEST, EXAMS or HSPF. Another variation of the model is discussed by Neely and Mackay (1982).

4.4.5.6. Other Models. In addition to these models, a number of others have been developed for specific purposes. These include SERATRA (Onishi & Wise 1979; cited in Park et al. 1982) and an unnamed model developed by Schnoor et al. (1979). Both resemble

PEST, although their biological resolution is less. Weininger (1978) and Thomann (1978) have developed models of bioaccumulation. Thomann's model is unique in that it is continuous, instead of compartment-based, and it predicts ultimate concentrations of a compound at all levels (based on size) of a food chain. Unfortunately it has not yet been computerized. Di Toro et al. (1982) present an elegant model which describes partitioning of compounds among components of a lake or river based on analytic solutions to a system of differential equations. It is similar to SRI and EXAMS except that it is simpler (and hence more thoroughly understood) and deals with sediment fluxes more extensively.

5.0 MANAGEMENT IMPLICATIONS AND APPROACHES

Water quality management normally involves (1) setting of appropriate ambient receiving water objectives which protect the defined water use; (2) consideration of the chemical, physical and biological properties of the receiving water system; (3) definition of appropriate wastewater effluent standards which will maintain river water concentrations below the receiving water objectives.

Here, the defined water use under consideration is to prevent flesh tainting in commercial fish species (walleye and whitefish) of the Athabasca River system. A review of potential tainting compounds and their probable sources related to oil sands mining and extraction activities are presented in Sections 2 and 3, while Section 4 describes the aquatic fate mechanisms for these compounds and existing computer simulation models of instream assimilation.

Section 5 considers how the existing information can be integrated into effluent standards for overall management of fish tainting compounds discharged to the Athabasca River Basin. The existing Alberta petroleum effluent standards are reviewed, as is the "upset" which occurred at the Suncor oil sands plant in 1982 which resulted in significant hydrocarbon effluents and tainting of the Athabasca River fishery. Two alternative approaches for regulating effluent quality are discussed and an integrated approach is recommended.

5.1 PRESENT PETROLEUM EFFLUENT GUIDELINES

The existing Alberta effluent standards for petroleum refineries are based upon best practical technology for the industry as a whole (Alberta Environment 1976). The license parameters and average effluent concentrations are listed in Table 9, along with the required frequency of monitoring. The actual

TABLE 9. Wastewater effluent guidelines for Alberta petroleum refineries

PARAMETER	EFFLUENT CONCENTRATION (mg/L)	MONITORING FREQUENCY
<u>CHEMICAL</u>		
COD	200	WEEKLY
OIL & GREASE	10	WEEKLY
TSS	25	WEEKLY
PHENOLS	1	WEEKLY
SULPHIDE	0.35	WEEKLY
NH_3-H	12.5	WEEKLY
TON	450 TOU	WEEKLY
pH	6.0-9.5	DAILY
<u>BIOLOGICAL</u>		
24 HOUR STATIC FISH BIOASSAY		MONTHLY
CHROMIUM (HEX)	0.30	POSITIVE MORTALITY
CYANIDE	0.025	POSITIVE MORTALITY
LEAD	0.10	POSITIVE MORTALITY
MERCURY	0.0005	POSITIVE MORTALITY
ZINC	1.0	POSITIVE MORTALITY
NICKEL	1.0	POSITIVE MORTALITY

license for each facility is based upon an allowable effluent loading to the receiving water for each unit of production (reference crude rate). This in turn should produce the concentrations defined in Table 9. The license defines total allowable loadings for the month and a daily maximum.

The eight chemical parameters defined in the Alberta standards are consistent with those recommended by Environment Canada (1974) and the United States Environmental Protection Agency (Federal Register, 1985). In addition to chemical quality the effluent is not to be toxic to fish, as measured by a 24 hour static bio-assay of whole effluent. This latter test is to be done once per month. If trout mortality does occur, toxic metal concentrations are to be evaluated and results related to the critical concentrations defined in Table 9.

When applying for a license to operate, the industry is to assess the general impact on the receiving watershed. Although some form of low flow (7Q10) analysis is usually performed, Alberta has no defined protocol for doing a detailed wasteload allocation, as has been defined by the USEPA for the United States (Delos et al. 1984). Variable standards based upon the size of the receiving water or season are generally not set.

The chemical parameters used in the existing standards are not specifically designed for prevention of fish tainting. Nor do any of the parameters allow for direct estimation of the tainting hazard. The rationale for the parameter concentrations is generally not based upon rigidly controlled laboratory or field studies on tainting potential to species indigenous to the Athabasca River Basin, nor do they specifically account for site specific dilution and instream chemical and biologic processing.

5.2 SUNCOR MISHAP

A series of fires and major process upsets at the Suncor oil sands plant during the winter of 1981-1982 resulted in a substantial discharge of hydrocarbons to the Athabasca River under winter ice conditions. The results of this incident are summarized from the extensive trial transcripts (Justice Dumos) from the subsequent court case arising under the Canada Fisheries Act. This incident can be used to set in perspective the magnitude of loadings which may be required to cause substantial tainting of natural populations in the Athabasca River although exact measures and predictions of these loadings must presently be viewed as speculation.

Suncor's allowable daily average discharge of oil and grease is 210 kg, with a daily maximum not to exceed 520 kg. On 22 February, 1982 the discharge was estimated to be 21913 kg. On many other occasions during February and March 1982 loadings exceeded 1000 kg/day. At a river flow of 100 m^3/sec a conservative estimate of the river's oil and grease concentration at the point of complete mixing is 2.5 mg/L (S. Hrudey, Pers. Comm.). Concentrations in the mixing zone (i.e. the zone extending 40 km downstream from the outfall) would have been considerably higher. Assuming the same river conditions, a licensed loading rate of 210 kg oil and grease would result in a river concentration of approximately 0.024 mg/L. During the height of the mishap oil was visually observed in the water for a distance of at least 50 km downstream of the plant.

Although conclusive evidence is not available there is a strong possibility that the Suncor mishap resulted in tainting of commercial whitefish and walleye in the Athabasca River and its delta. The 1982 fishery was closed because of off-flavours, and experimental tainting studies at the Freshwater Institute (Dept. of Fisheries and Oceans) confirmed that the material discharged from Suncor could taint fish after only a few hours exposure. Tissue analyses on fish caught from the Athabasca River in May

1982 showed elevated levels of aromatic and aliphatic hydrocarbons that could have been petroleum derived (Wellington Consultants Inc, 1983).

Assuming the Suncor mishap did taint natural fish species, this reconstruction of the incident implies that an approximate hundred-fold increase in oil and grease levels in the Athabasca River, at flows near 100 m^3/sec, will result in the occurrence of tainting.

The analysis must be considered approximate and is by no means exhaustive. It does imply that wasteloading related to oil sands mining and extraction has the potential to taint fish at extreme loading rates. It remains to be answered as to where the safe loading limit falls within that 100-fold range. Defining the critical allowable river loading is necessary for effective water quality management of the Athabasca River in the tar sands area and the setting of effluent standards.

5.3 MANAGEMENT APPROACHES

There is a strong probability that the existing petroleum effluent standards may not protect against tainting should they continue to be applied to the Athabasca River Basin.

Two alternative approaches for the setting of effluent standards for prevention of tainting can be considered: 1) whole effluent approach, or 2) chemical-specific technique. The general rationale for each approach, as applied to the discharge of toxic compounds, has been defined by the USEPA (1985). In this report we have adapted these protocols to deal specifically with management of fish tainting potential arising from wastewater discharges.

The whole effluent approach involves the direct measurement of effluent tainting with test organisms under laboratory or controlled field experiments. It would be analogous to LC_{50}

measurements for toxicity, but instead the test fish would be evaluated for off flavour rather than mortality. Once the threshold concentration of the effluent for tainting was defined from dilution experiments with river water (i.e. 100%, 30%, 10%, 3%, 1%) this information can be utilized to calculate the required river dilution which would permit appropriate protection of the fishery. Once an effluent's tainting threshold is defined by experimentation it is necessary to apply uncertainty factors in the permitting procedure. For example if experiments show the effluent will not taint fish at dilution rates of 10% (10:1) or greater, uncertainty factors of 10X for experimental error and 10X for effluent variability may be applied during the wasteload allocation calculations. This would mean the effluent would have to be diluted 1000:1 in the receiving water to ensure protection of the fishery. The questions of where the dilution is achieved must also be considered. The location of desired dilution can be at the end of effluent pipe, the point of complete mixing or some distance in between.

The chemical-specific approach to setting of receiving water objectives and effluent standards is the classical method, and involves managing the specific chemical attributes of the wastewater. The chemical characteristics of the wastewater are evaluated and screened for parameters of concern. Desired concentrations of each parameter are defined for the receiving water (receiving water objective) based upon published criteria or site-specific field or laboratory experiments. In the case of tainting, few existing criteria are established. Once the receiving water objectives are set, the effluent standards can be defined based upon probable future streamflow conditions (most often the 7Q10), upstream quality, other point and non-point source loadings and instream assimilation. Separate objectives may be established for the mixing zone. Numerical models can be

Table 10. Comparative advantages and disadvantages to whole effluent versus chemical-specific methods for setting wastewater standards.

WHOLE EFFLUENT APPROACH

ADVANTAGES	DISADVANTAGES
- relative ease of implementation - development time and cost	- effluent treatability data are lacking making design of wastewater treatment systems difficult.
- accounts for the combined tainting potential of all constituents in a complex effluent.	- ongoing routine monitoring and compliance of the effluents and receiving water is not possible with existing technology.
	- cannot be used to assess food chain biomagnification in the receiving water system.
	- will be process specific therefore the analysis must be repeated when new plants are added, or when process or wastewater treatment methods are altered.
	- is best applied where zero tainting potential is to be achieved at end-of-pipe.

CHEMICAL-SPECIFIC APPROACH

ADVANTAGES	DISADVANTAGES
- treatment systems are more easily designed and monitored for compliance.	- all fish tainting compounds may not be readily characterized and accounted for in the standards.
- the receiving water fate of a pollutant can be measured through modelling	- hydrocarbon chemistry is complex and analysis is expensive.
- changes in plant operation and standards for new plants will be more easily accounted for.	- bioavailability of compounds is not measured directly nor are possible synergistic interactions.
- allows for river water monitoring to test for ongoing compliance and problem identification, i.e. management of accidental spills.	- extensive time and cost committment to develop.
- permits use of receiving water assimilative capacity.	

used to forecast probable instream concentrations for the mixing zone and the river as a whole assuming conservation of mass, physical transport and chemical transformation due to physical, chemical and biological processes.

In the case of managing the discharge of tar sands related effluents with tainting potential the relative advantages and disadvantages of each approach are outlined in Table 10.

The whole effluent approach is appealing due to its simplicity. The research and development costs are probably less than for the chemical-specific method. It measures the direct bio-availability of tainting compounds and accounts for possible synergism. The primary disadvantage to this approach lies in the quantification of tainting. At the moment the only viable method involves the use of a taste panel, which is cumbersome, relatively expensive, and not amenable to handling of large sample numbers on a continuing basis. This means that the day to day measurement of 'tainting', necessary for design and monitoring of wastewater treatment systems, cannot be practically accomplished. There is no readily available test for tainting analogous to the LC_{50} test for acute toxicity.

Because the whole effluent approach would be based upon controlled exposure experiments with indigenous species it would account for exposure due to direct uptake from the water. Although the literature review indicates direct uptake is probably the most significant pathway, the risk of biomagnification through the food chain has not been eliminated. This might occur in the Athabasca River, and if it does can only be accounted for on a chemical-specific basis since each group of organic chemicals is subject to unique degradation pathways. Unlike BOD, which has been successfully managed on a wasteload allocation basis, tainting substances may reconcentrate in the environment. Also, effluent variability resulting from changes in process or wastewater treatment procedures may cause variability in the waste water's tainting potential. The whole effluent approach cannot readily accommodate these changes.

The chemical-specific approach would allow ready monitoring for effluent and receiving water compliance. Wastewater treatability data would be easily derived, allowing rapid assessment of process modifications or receiving water evaluation of potential new plant discharges. Its main disadvantage is that significant chemical-specific criteria on tainting compounds are lacking, necessitating considerable research and development. In turn, bio-availability and synergism in complex effluents are not easily accounted for chemically. If effluent standards are established for specific hydrocarbons or hydrocarbon groups, the existing analytical procedures are often complex and expensive.

In summary, the whole effluent approach is most practical if the overall tainting threshold of the effluent is very low and remains stable throughout time, thereby allowing end of pipe compliance at all times. Conversely, if it is necessary to utilize the natural assimilative capacity of the receiving water for effective wasteload allocation on a short- or long-term basis the chemical-specific approach is more effective. In this context long-term refers to maintaining end-of-pipe levels below the threshold level for receiving water impact on a continuous basis, short-term refers to attaining end-of-pipe control except during periods of extreme receiving water conditions or process upset. Assigning assimilative capacity on a whole-effluent basis when chemical composition is poorly defined and components are not characterized for their stability and fate in the receiving stream is very risky.

With reference to potential discharge to the Athabasca River of effluents with tainting potential there are certain factors which must be accounted for regardless of the wasteload allocation method adopted. These include:

- Testing for tainting potential of all major sport and commercial species across a spectrum of life-history conditions;
- Management of the mixing zone, which is extensive in the Athabasca River downstream from Ft. McMurray;
- Management of both open-water and ice-cover conditions. During winter, metabolism is reduced by cold temperatures and hydrocarbon volatilization is restricted;
- Accounting for effluent variability; the wastewater characteristics of the Syncrude tailings pond can potentially change drastically due to process alterations or upset.
- Effective monitoring for compliance in both the effluent and wastewater; this will undoubtedly require development of novel techniques.
- Potential biomagnification of fish tainting compounds in the Athabasca River;
- Assessment of tainting caused by natural hydrocarbon loadings to the Athabasca River.

At this time it is difficult to decide whether the whole effluent approach, chemical-specific approach, or some unique combination of the two is appropriate for management of petroleum discharges to the Athabasca River. Figure 7 outlines a management protocol that includes collection of the information necessary to make the decision. Each component of this management protocol is detailed in the following sections.

5.3.1 Wastewater Characterization and Tainting Potential

Initial studies should involve the chemical characterization of the potential effluent waters. Similarly, the direct tainting potential of these wastewaters should be evaluated. The

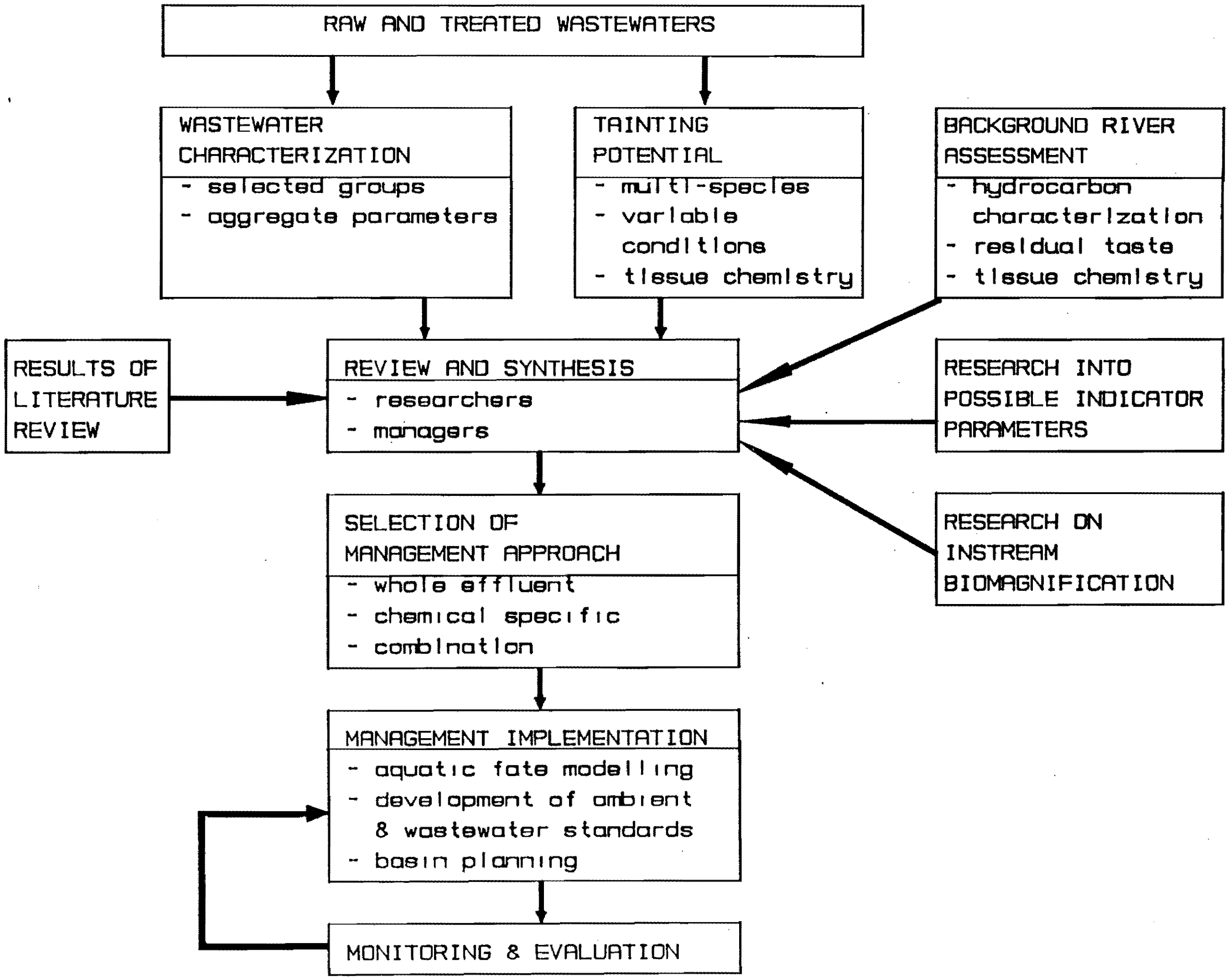

Figure 7. Management Protocol - Fish Tainting Compounds.

wastewater characterization should emphasize the chemical groupings defined in Table 8. This list is developed largely from information on the refined products, and a small amount of data on the Suncor effluent. Special emphasis should be placed on obtaining hydrocarbon characterization of the raw tailings pond water at Syncrude, plus the detoxified or treated tailings water. This should include definition of seasonal and spatial variability in wastewater quality, and all analytical analyses should be quantitative. In addition to the tailings water, the precipitates and sediments in the tailings pond should also be characterized. The characterization should also include assessment of conventional parameters like oil and grease, phenols, and organic carbon. This may be applicable to later cross-correlation between hydrocarbon concentrations and tainting thresholds. Alternatively, these measurements may serve to confirm that conventional measures cannot be reliably used to control tainting.

The same wastewaters tested for chemical characterization should be evaluated for tainting potential via direct uptake. This would include fish exposure to river water dilutions of raw and treated wastewaters followed by assessment for tainting. Factors to be considered include: open-water and ice-cover conditions; water temperature; period of exposure; and fish species and life-stage.

Flesh tainting should be evaluated with a trained taste panel using the methods recently defined by Environment Canada. These results should be cross-referenced with appropriate tissue chemistry, corresponding to the parameters or parameter groups included in the wastewater characterization.

5.3.2 Background River Assessment

In any wasteload allocation analysis background levels must be established. This should include measurement of possible tainting compounds in the water, sediments and biota of the Athabasca River. As for the wastewaters the analytical work should be specific to the groups defined in Table 8. It should also include seasonal analyses, especially during low flow summer and winter conditions.

The river should be sampled: (1) upstream of Suncor, (2) downstream of Suncor and Syncrude, and (3) in the Athabasca delta. In addition, adult whitefish and walleye should also be analysed for off-flavour and background levels of tainting compounds. Because of the natural hydrocarbon load received by the Athabasca River, it would also be beneficial to have comparative data from a nearby tributary system which is not exposed to natural bitumen contamination. The taste panel results should be complemented with the same tissue chemistry evaluation included in 5.3.1.

5.3.3 Research into Possible Indicator Parameters

To overcome the problem of using a taste panel to evaluate tainting, active investigation and research into "indicator parameters" should be initiated. An attempt should be made to define parameters that correlate with tainting but are readily measurable in tissues or the effluent and receiving waters. Once "calibrated" this parameter, or parameters, could be used for setting of effluent or possibly ambient water standards.

There is currently no proven "indicator parameter" which could be used to represent tainting potential. Krishnaswami and Kupchanko (1969) demonstrated a relationship between threshold odour number of petroleum refinery effluents and fish tainting. Krahn et al. (1984) have demonstrated that HPLC-fluorescence analysis of fish bile is a very sensitive method for detecting fish exposure to petroleum. These approaches warrant further evaluation.

5.3.4 Research on Instream Biomagnification

The exposure studies outlined in 5.3.1 will define fish tainting due to direct uptake of hydrocarbons from the water through the skin or across the gills. It will not identify uptake and biomagnification pathways via the sediments or lower trophic levels. Our analysis implies direct uptake may be the primary pathway, however, the risk of biomagnification needs to be addressed through further research and study.

It may be necessary to evaluate microbial activity in the river downstream of the outflow, under different seasonal conditions. For instance, rapid microbial uptake of tainting compounds may indicate a potential for biomagnification; similarly rapid, but incomplete microbial oxidation of hydrocarbons may indicate that tainting metabolites are being produced.

5.3.5 Literature Review on Tainting

The scientific literature on fish tainting is reviewed in Section 2 of this report. In other than general terms, it is difficult to relate this information to the oil sands situation because of inconsistency in experimental approach and analytical variability. Much of the historical literature suffers from inadequate chemical confirmation of tissue and water concentrations. Analytical methods for organic chemistry have improved tremendously in recent years, with the advent of GC-MS and more recently high pressure liquid chromotography (HPLC). The literature also suffers from a lack of information for the fish and benthic species indigenous to the Athabasca River.

Once the more detailed chemical characterization of the wastewaters and background river levels is complete one more attempt to correlate these data with the literature should be attempted.

5.3.6 Review and Synthesis

Once the data from the previous four tasks are available a panel of researchers and water management officials, and possibly industry representatives, should critically review and synthesize the results. At that time a decision on the appropriate management approach can be made, i.e. whole effluent or chemical-specific method, or some combination of the two. Careful correlation of the results may indicate one or two parameters are the main tainting factors and only these compounds need to managed on a chemical-specific basis. Alternatively a refined method for direct measurement of tainting may emerge which makes the whole effluent approach feasible.

5.3.7 Management Implementation

Based upon the outcome of task 5.3.5, the selected management approach can be implemented. This might include: development of ambient river water objectives; aquatic fate modelling of specific hydrocarbons or hydrocarbon groups; simple dilution analysis, assuming the whole effluent approach is adopted; or mixing zone assessment.

The outcome of this component will be a wasteload allocation and setting of wastewater standards. The wasteload allocation will have to be integrated within the overall basin planning program.

5.3.8 Monitoring and Evaluation

A monitoring program will have to be designed to evaluate the assumptions and forecasts made in the wasteload allocation. This will provide feedback to future wastewater effluent management and standards setting.

6.0 IMMEDIATE RECOMMENDATIONS

Section 5.3 defines a protocol for management of fish tainting compounds in the Athabasca River and makes general recommendations for the entire process. Specific research and monitoring activities which should be undertaken as the next step in this process include:

1. Chemical characterization of the raw and treated tailings water at Syncrude, plus the process effluent at Suncor, for the groups of potential fish tainting hydrocarbons defined in Table 8.

2. Screening for background levels of potential fish tainting compounds in the Athabasca River, and a major tributary which does not receive natural or anthropogenic hydrocarbon loadings. This should include water, suspended sediment, and bottom sediment.

3. Initial evaluation of the tainting potential of raw and detoxified tailings pond decant for adult walleye and whitefish.

4. Definition of background taste and tissue residues of tainting compounds in resident commercial fish populations of the Athabasca River and delta and a nearby watershed that does not receive natural hydrocarbon loadings.

5. Initiation of studies into the uptake and biomagnification of tainting hydrocarbons through lower trophic levels or sediments.

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