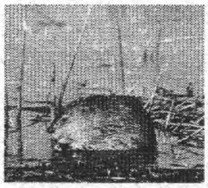
Canada Alberta Northwest Territories

Northern River Basins Study



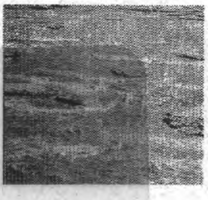




NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 114

WATER ODOUR, ATHABASCA RIVER, 1994 (POST ALPAC)



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by

ra Kenefick[1], Brian Brownlee[2], Elizabeth Hrudey[1],
Gordia MacInnis[2] and Steve Hrudey[1]

ronmental Health Program, University of Alberta[1]
al Water Research Institute, Environment Canada[2]

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PREFACE:

The Northern River Basins Study was initiated through the "Canada-Alberta-Northwest Territories Agreement Respecting the Peace-Athabasca-Slave River Basin Study, Phase II - Technical Studies" which was signed September 27, 1991. The purpose of the Study is to understand and characterize the cumulative effects of development on the water and aquatic environment of the Study Area by coordinating with existing programs and undertaking appropriate new technical studies.

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been reviewed by the Study Science Advisory Committee in regards to scientific content and has been approved by the Study Board of Directors for public release.

It is explicit in the objectives of the Study to report the results of technical work regularly to the public. This objective is served by distributing project reports to an extensive network of libraries, agencies, organizations and interested individuals and by granting universal permission to reproduce the material.

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Whereas the above publication is the result of a project conducted under the Northern River Basins Study and the terms of reference for that project are deemed to be fulfilled,
IT IS THEREFORE REQUESTED BY THE STUDY OFFICE THAT;
this publication be subjected to proper and responsible review and be considered for release to the public.

F J Wrona
(Dr. Fred J. Wrona, Science Director)

14 May 96
(Date)

Whereas it is an explicit term of reference of the Science Advisory Committee "to review, for scientific content, material for publication by the Board",
IT IS HERE ADVISED BY THE SCIENCE ADVISORY COMMITTEE THAT;
this publication has been reviewed for scientific content and that the scientific practices represented in the report are acceptable given the specific purposes of the project and subject to the field conditions encountered.
SUPPLEMENTAL COMMENTARY HAS BEEN ADDED TO THIS PUBLICATION: [ ] Yes [ ] No

P A Larkin
(Dr. P. A. Larkin, Ph.D., Chair)

24 May/96
(Date)

Whereas the Study Board is satisfied that this publication has been reviewed for scientific content and for immediate health implications,
IT IS HERE APPROVED BY THE BOARD OF DIRECTORS THAT;
this publication be released to the public, and that this publication be designated for: **[ ] STANDARD AVAILABILITY [ ] EXPANDED AVAILABILITY**

Lucille Partington
(Lucille Partington, Co-chair)

May 29/96
(Date)

Robert McLeod
(Robert McLeod, Co-chair)

May 21/96
(Date)

WATER ODOUR - ATHABASCA RIVER, 1994 (POST ALPAC)

STUDY PERSPECTIVE

Water is essential to life. It can be an important vector for conveying contaminants into humans. To assist the Board in addressing concerns about the safety of drinking water supplies and their intent to make recommendations concerning drinking water, the Drinking Water component has designed a five-step program of studies. The steps included:

1. Synthesis of existing data on water use and water quality;
2. Investigation of odour in water and tainting in fish;
3. Review of health records for water borne diseases;
4. Assessment of conventionally treated and non-conventional water; and
5. Final synthesis report.

Related Study Questions

2) What is the current state of water quality in the Peace, Athabasca and Slave River basins, including the Peace-Athabasca Delta?

8) Recognizing that people drink water and eat fish from these river systems, what is the current concentration of contaminants in water and edible fish tissue and how are these levels changing through time and by location?

This report deals with step two and is a follow up to "Water Odour, Athabasca River, February and March, 1993" (NRBS Report Number 42). The purpose of these two studies was to evaluate any changes to water odour that may have occurred after the Alberta-Pacific (Alpac) pulp mill near Athabasca came on stream. In NRBS Report 42 it was recommended that a detailed study of the Hinton combined effluent be undertaken to isolate and identify the compounds responsible for the odour and to expand the number of target compounds. During the summer of 1993 the Weldwood mill in Hinton changed to the chlorine dioxide bleaching process and the characteristic "pulp mill odour" identified in the 1993 study was no longer detectable to the odour panel. Consequently the impact of the Hinton combined effluent (HCE) on downstream odours was markedly less than in the 1993 survey. The gas chromatography / mass spectrometry and the olfactory chromatography results suggest that the target compounds contribute very little to the odour of the samples and that the likely contributing compounds have not yet been detected by the methods used in this survey.

In the previous report, the science team had concerns that anisoles and veratroles were not found in the HCE and that the effluent was not tested for guaiacols and other precursors of anisoles and veratroles. The mass spectrometry had non-detects for the three anisoles and veratroles tested for In this report in this report. The olfactory gas chromatography detected 2,4,6-trichloroanisole, but not in the HCE, although it was present in the Whitecourt municipal effluent with a weak intensity. It was also present at various locations in the river, but not immediately downstream of any effluent outfalls.

The information from this report will be combined with information collected in "Water Odour, Athabasca River, February and March, 1993" and "A Review and Annotated Bibliography of Water and Fish Tainting in the Peace, Athabasca and Slave River Basins" (NRBS Report Numbers 42 and 52) to give an overview of the current state of water odour and fish tainting. Together with the other Drinking Water projects, these studies will form the basis for the Drinking Water Synthesis report and will be used in the companion Human Health Monitoring Program that will be examining human health issues in Northern Alberta.

REPORT SUMMARY

The purpose of this study was to determine the potential for off-flavour tainting of water and/or fish in the Athabasca River by compounds discharged from bleached kraft and chemi-thermomechanical pulp mills. This study combined three different analytical methods commonly used in monitoring for the presence of odorous compounds in water supplies. A trained flavour profile panel was used to characterize the odour of the samples, two trained analysts evaluated the samples using olfactory GC and all samples were quantitatively analyzed for the presence of target odour compounds using GC/MS. These three techniques all provide quite different information and all have certain limitations.

The flavour profile panel method is most appropriate when monitoring for the presence of compounds that will lead to public complaints, relies on varying sensitivities to certain odours, and does not easily allow for reporting the presence of specific compounds. Consistency and specificity of the odour profile panel results require rigorous training in the recognition of target compounds and assignment of appropriate intensities.

The olfactory GC technique is useful when there are a number of odorous compounds present in a sample. The GC accomplishes the separation of each of the odour compounds and still allows for olfactory detection. The sensitivity of this method is limited by the dilution of odours by the inert carrier gas as well as the small volumes of sample that can be injected for capillary gas chromatography. The extraction of the samples using CLSA offers a ten thousand fold concentration of the sample so that these sensitivity problems are partially offset.

The analyses by gas chromatography with mass selective detection was the most quantitative analytical method, but also the least sensitive. To increase sensitivity of the instrument a selected ion monitoring program was set up to monitor the abundance of certain ions that are known to be present in the mass spectra of the target compounds. Sensitivity is increased because rather than slowly scanning for all possible ions, the detector scans many more times and much more rapidly for the small group of selected ions. However, the analyses are then limited to monitoring for the chosen target compounds. Any odorous non-target compounds, which may significantly contribute to the odour of a sample, will not be reported.

The flavour profile panel work, shows a decrease in the impact of Hinton combined effluent on the odour of the Athabasca River compared with the 1993 survey. The contribution from the Alberta Pacific discharge was even smaller than the Hinton contribution. The odour contributions to the Athabasca River from tributaries were minor. The odour contributions from other effluent sources (sewage treatment plants and chemi-thermomechanical pulp mills) are less distinctive than the Weldwood and AlPac mills and their role in affecting downstream odour is not as clear. Notwithstanding these observations, the observed impacts on raw water odour could not be identified for the treated drinking water at Ft. McMurray, possibly because of removal of odorous compounds in treatment and / or masking of the raw water odour with chlorinous odours. The raw water supply at Ft. Chipeweyan was not particularly odorous and the finished water also exhibited a strong chlorine odour that would have masked any subtle odours present.

The CLSA-GC/MS and OGC results suggest that there were very limited contributions to the odour of the samples by the target compounds. None of the target odour compounds, by themselves, can explain the odour character that was perceived by the odour panel in the Hinton combined and AlPac effluents and affected downstream samples. There are likely other contributing compounds that have not yet been detected by the methods employed in this survey. This suggests the need for a continued characterization of the compounds that are primarily responsible for creating the current odour of these pulp mill effluents.

ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

1.1 OBJECTIVE

The purpose of this study was to determine the potential for off-flavours in Athabasca River water from compounds discharged by bleached kraft pulp mills. In February and March of 1993, a total of 30 water samples were collected from the mainstem and tributaries of the Athabasca River and were subjected to a battery of chemical and sensory analyses to determine the extent to which odourous compounds associated with pulp mill effluents are transported downstream under ice conditions. The project involved chemical analyses including gas chromatography / mass spectrometry (GC/MS), gas chromatography / flame ionization detection (GC/FID) and olfactory gas chromatography (OGC), as well as flavour profile panel analyses by an experienced sensory panel. Water samples were again collected from the Athabasca River during February and March of 1994 and subjected to the same chemical and sensory analyses. This second synoptic survey was carried out after the Alberta Pacific (AlPac) pulp mill came on stream. Comparison of the results from the two winters will allow for a preliminary determination of the effects of the AlPac mill on water tainting.

1.2 BACKGROUND

Bleached kraft pulp mill effluent and discharges related to other industrial developments are known to contain odorous compounds that have the potential to cause taste and odour problems for downstream users. The significance of off-flavours in water has been reviewed and discussed by a number of researchers (Persson, 1983; Zoeteman, 1980; Mallevialle and Suffet, 1987).

In an early review of odour compounds in water and their sources, Cees and co-workers indicated that there are two basic sources of odour substances: industrial and municipal sewage effluents or algae and heterotrophic micro-organisms (Cees *et al.*, 1974). Lin categorized the two sources of tastes and odours in water as natural or man-made and emphasized that off-flavour events may develop from either one or the other, or a combination of both (Lin, 1976a). The odour sources Lin set forth were categorized as resulting from the presence of gases, salts, minerals, aquatic organisms, wastewater treatment plant effluent, industrial discharges, non-point source run-off, water treatment processes or organisms in water distribution systems. Lin also went on to point out that naturally occurring taste and odour compounds are the most common, but objectionable situations created by man-made sources are often the most troublesome.

Although there has been considerable research into the health effects of chlorinated organics and other compounds that are found in pulp mill effluents (Wigilius *et al.*, 1988), the specific compounds responsible for off-flavours in waters as a result of pulp mill discharges are not well understood. A summary of the organic compounds found in spent liquors from pulp bleaching (Kringstad and Lindström, 1984) lists a number of compounds that are possible contributors to odour problems in water. The compounds present in softwood pulping effluents include; chlorinated phenols, chlorinated guaiacols, dichlorovanillin, and chlorinated catechols. These were also reported to be present in hardwood pulping effluents but chlorinated syringols and chlorinated syringaldehydes were also found. In one study, persistent chlorinated acids, phenols, anisoles and veratroles were suggested as possible tainting compounds downstream of pulp bleaching and chlorodisinfection plants (Paasivirta *et al.*, 1983). In another study, biologically treated effluent samples from 9 Canadian bleached softwood mills were analyzed for chlorinated phenolics (Kovacs *et al.*, 1984). Odour thresholds were determined for selected chlorinated phenolics and for a synthetic mixture of these compounds. Results of this study indicated that chlorinated phenolics present in effluent discharged from bleached kraft mills are not expected to contribute an off-odour to recipient waters. However, microbial metabolism of chlorophenols has been shown to cause the formation of chloroanisoles from chlorinated phenols and these anisoles are much more odorous and more likely to cause tainting (Paasivirta *et al.*, 1983, Griffiths and Fenwick, 1977). Chlorinated anisoles and veratroles have been implicated in other studies of taste and odour problems related to BKME discharges (Brownlee *et al.* 1993).

Although most of the compound-specific work on pulp mill effluent odours has focused on chlorinated compounds, the literature does not provide a reliable basis to attribute odour problems primarily to chlorinated compounds. The work by Domtar Fine Papers (1971) to identify the most odorous process streams did not identify specific compounds but the process streams identified were rich in odorous organosulfur compounds. The production of these compounds is independent of bleaching practices and their control depends on good in-plant spill control and efficient wastewater treatment. Headley (1987) has found sulphones, sulphides and thiophenes in pulp mill effluents. He reported that sulphones and sulphides are present in biologically treated kraft mill effluents and the thiophenes were reported to originate from the cooking process of lignin, in which sodium sulphide and sodium hydroxide are used.

The biogenic compounds that cause taste and odour problems can be 'produced' through the decay of dead organisms, or through the activities of living organisms. The odours caused by decaying vegetation have been characterized as musty, earthy, moldy, swampy, fishy, and grassy (Lin, 1976b). Mallevialle and Suffet (1987) cite a number of references indicating that the odours of decay are due to decomposition of vegetation by bacteria or fungi which produce odorous compounds. The microorganisms that have been reported to produce taste and odour compounds are summarized in Table 1.

The anthropogenic sources of tastes and odours in water have been summarized in a number of reviews (Mallevialle and Suffet, 1987; Lin, 1976a; 1976b; 1977; Cees *et al.*, 1974). Common components of man-made odour contributors include petroleum based hydrocarbons, phenols, pesticides, alkyl benzene sulfonates (ABS), water treatment chemicals and disinfection byproducts. (Lin, 1976). Zoeteman *et al.* (1971) reported a list of crude oil and oil product odour threshold concentration (OTC) values which indicated that the petroleum products could cause odour problems at µg/L levels. Fok *et al.* (1984) reported periodic taste and odour episodes in treated drinking water. They suggested that the organic contaminants responsible for these episodes could have been hydrocarbons and phenolics introduced to the raw water source river as a result of urban street runoff. Combinations of odorous compounds can result in interactions between the odors of each component. The resulting odour is often greater than the sum of all components (Rosen *et al.*, 1963). Such a phenomenon is known as odour synergism.

There are many taste and odour problems associated with drinking water treatment processes. Hrudey and co-workers observed more intense odours in treated water than in the raw water and suggested the likelihood that compounds were formed during oxidative reactions resulting from disinfection processes. Four odorous, low molecular weight aldehydes were found (2-methyl propanal, 2-methyl butanal, 3-methyl butanal, and phenylacetaldehyde) (Hrudey *et al.*, 1988). A summary of a survey conducted to determine practices and problems associated with the use of chlorine dioxide by U.S. water utilities indicates that overall, odour complaints were more numerous and more diverse when chlorine dioxide was used (Dietrich *et al.*, 1992). The negative effect of chlorination in treated water was noted in an early discussion of the taste and odour problems associated with phenol and chlorinated phenols. Chlorine disinfection has long been known to intensify taste and odour problems due to chlorination of the trace levels of phenols which are often present in raw water supplies (Burttschell *et al.*, 1959). There has also been a study into the effect that

Table 1. BIOLOGICAL SOURCES OF TASTE AND ODOUR IN WATER

Organism	Odour Descriptor	Reference
green algae	grassy	Jüttner, 1983
	musty	Mallevialle & Suffet, 1987
	fishy	Mallevialle & Suffet, 1987
blue-green algae	grassy, vegetable	Slater and Blok, 1983
	earthy, musty	Slater and Blok, 1983
	rotten, sulphur	Jenkins *et al.*, 1967
diatoms	spicy	Mallevialle & Suffet, 1987
	geranium	Mallevialle & Suffet, 1987
	grassy	Mallevialle & Suffet, 1987
flagellates	cucumber	Lin, 1977
	fishy	Lin, 1977
	violet	Lin, 1977
	musty, grassy	Lin, 1977
fungi	earthy	Wood *et al.*, 1983
bacteria	sulphur	Whitfield & Freeman, 1983
	rotten egg	Lin, 1976b
actinomycetes	earthy, musty	Gerber, 1983
	potato-bin	Gerber, 1983

materials that come into contact with drinking water (pipes, reservoir linings, tanks, etc.) have on the taste and odour of the water (Rigal, 1992). It was found that rubber, polyurethanes, epoxydic resins and PVC pipes can cause off-flavours in water that was relatively odourless after treatment. Anselme *et al.* (1985) reported severe odour problems caused by defective polyethylene water pipes. They found that 20% of 264 pipes tested were defective. Problems were mainly attributed to defective manufacture resulting in release of polymer additives like alkylphenols and oxidation of pipe surfaces causing the release of polar compounds such as aldehydes and ketones.

Shumway and Palensky (1973) reported that primary, secondary and disinfected secondary effluents from a municipal sewage treatment plant all have the potential to cause tainting in water and fish at levels ranging from 11 to 26 % (v/v). Burlingame *et al.* (1976) reported the presence of a number of chlorinated anisoles (trichloroanisoles, tetrachloroanisoles and pentachloroanisole) which cause intense odours in secondary and tertiary effluent of a wastewater treatment plant. Garrison, Pope and Allen (1976) list many specific compounds that have been found in municipal wastewater treatment plant effluents. Many of these compounds, such as phenols, aromatic hydrocarbons, and chlorinated organics, are capable of tainting water.

Bleached kraft mill effluent was reported to impair the taste and odour of drinking water at effluent concentrations ranging from 0.1 to 0.4% (Kovacs and Voss, 1986). Pulp mill effluent contributions to river water levels of phenols and trichlorophenol are also important because of the recent Swedish reports of bio-methylation of trichlorophenol to 2,4,6-trichloroanisole, an extremely potent source of musty odours in water and fish (Nyström *et al.*, 1992). A preliminary survey (Brownlee *et al.*, 1993) of the Athabasca River from upstream of Hinton to 120 km downstream of Ft. McMurray has found evidence of odour compounds arising immediately downstream of Hinton that persist as far downstream as Ft. McMurray.

This study was to be undertaken in 1994 during the months of February and March. During this sampling period the Athabasca River and the tributaries sampled were ice-covered and were at low flows. Because many odorous compounds are problematic at ng/L concentrations and are often quite volatile, this sampling period was purposely chosen to allow collection of river water when dilution of effluents is usually lowest and odour compound persistence is greatest.

The Northern River Basins Study Board co-chair, Mr Bev Burns, has identified a need "to reconcile science with societal values and concerns". In the case of sensory evaluations, the different values held by the scientific community and the general population were recognized as significant. This study used a trained sensory evaluation panel made up of a cross-section of the general population with appropriate sensory capabilities. This panel was shown to demonstrate good correlation with another established panel during the background study in 1993 (Kenefick *et al.*, 1994)

Given the potential contributions of off-flavour compounds from various industrial and natural sources and the relative contribution of effluents during low winter flow, there is a need to evaluate the occurrence and significance of off-flavour compounds in the northern river systems. In the case of the Athabasca River, it was particularly important to obtain baseline information on the presence of off-flavour compounds before the Alberta-Pacific pulp mill came on stream. Unfortunately, the baseline data was gathered before the pulp mill at Hinton implemented a 100% chlorine dioxide substitution in their bleaching process in the fall of 1993. This process changed the effluent characteristics significantly and rendered the 1993 baseline data to be of historical value only. Under-ice baseline data directly comparable to the 1994 post-AlPac data is not available.

2.0 METHODS

The water and effluent samples were collected by Alberta Environment on behalf of the Northern River Basins Study. A total of 14 Athabasca River water samples were collected between the first sampling point at Highway 40 and the final sampling point at Lake Athabasca near Big Point Channel Mouth. Effluent samples were collected from Hinton (Weldwood pulp mill and municipal sewage treatment plant effluents combined), Alberta Newsprint, Millar Western, Whitecourt Waste Water Treatment Plant, Slave Lake Pulp, Athabasca Waste Water Treatment Plant, Alberta-Pacific, Fort McMurray Waste Water Treatment Plant, and Suncor. Raw and finished water samples were collected from the Fort McMurray and Fort Chipewyan Water Treatment Plants. In addition, 5 samples were collected from tributaries that feed the Athabasca River. All water and effluent samples were collected at the time-of-travel of the Athabasca River at sampling sites shown in Figure 1 and on the sampling dates listed in Table 2.

All samples were collected without preservation and were cooled until delivery to the University of Alberta laboratory. All samples were delivered within 24 hours of collection. A 28L water sample was collected at each sampling point and effluent samples (8L) were collected. At the laboratory the effluents were diluted 20:1 with de-ionized, odour-free water for closed-loop stripping and sensory analysis.

2.1 ODOUR PROFILE ANALYSIS

Subsamples (1L) of each water and diluted effluent were delivered to the sensory panel within 24 hours of arrival at the University of Alberta laboratory.

The panel established at the University of Alberta for this project was selected prior to the 1993 synoptic survey by screening 12 potential panelists for anosmia using the scratch and sniff smell identification test produced by Sensonics Inc. (Haddon Heights, N.J.) Of the screened group, 8 suitable potential panelists were selected and further evaluated for their discrimination of the primary taste categories by means of testing solutions of sucrose (sweet), citric acid (sour), quinine (bitter) and NaCl (salty) together with distilled water. The final panel for any test session consisted of 3 to 5 panelists. Further characterization and intensity training was carried out using a series of 19 common odorants that are now available as a test kit for odour type and strength comparisons. The kits are prepared using polypropylene bottles with flip-top caps, containing the chosen odorant dissolved in virtually odorless mineral oil that is absorbed in polypropylene felt (Amoore, 1992).

A 100mL aliquot of each sample was transferred to an odour-free 250mL Erlenmeyer flask with a ground glass stopper and heated to 45 °C. The heated sample was gently swirled in a circular manner to ensure that volatile compounds were released into the headspace. The flask was brought to the nose, the stopper removed and the odour attributes were determined by sniffing at the flask opening. The odour attributes and intensities were recorded in the order perceived. The intensities were based on a multiple point scale (0=no odour, tr=trace or threshold, 1=weak, 2=moderate, 3=strong). Half units were also used by panelists to further distinguish intensities.

The panel was presented with all samples coded by simple numbers that precluded identification of sample source. Hence the sensory reactions obtained were free of any expectations beyond the general knowledge that the survey was directed towards determining odours in the Athabasca River system.

2.2 LARGE VOLUME DICHLOROMETHANE EXTRACTIONS

A large volume sample (20L) was sequentially extracted with dichloromethane (DCM) (600mL then 300 mL) after the addition of 1.0 µg biphenyl-d10 standard and with pH adjustment to 11-12 by the addition of pre-extracted (isooctane) 10N sodium hydroxide. An acidic extraction of the sample was carried out with DCM (400 mL then 200 mL) after pH adjustment to 2-3 with pre-extracted (dichloromethane) 12N sulfuric acid. All large volume organic extracts were separated from the aqueous layer, dried over pre-combusted sodium sulfate and reduced to approximately 10mL using a rotary evaporator. These extracts were then reduced to approximately 1 mL under a gently nitrogen stream.

Undiluted effluent samples (1 L) were extracted with DCM (4 x 50 mL) in a separatory funnel after pH adjustment to 11-12 by addition of 2 mL of 10N sodium hydroxide (pre-extracted with isooctane). This gave the base/neutral extract. After pH adjustment of the aqueous phase to 2-3 by addition of 3 mL of 12N sulfuric acid (pre-extracted with DCM), the sample was extracted with DCM (4 x 50 mL). This gave the acid extract. The base/neutral and acid extracts were dried (Na_2SO_4) and concentrated in the same manner as the large volume extracts.

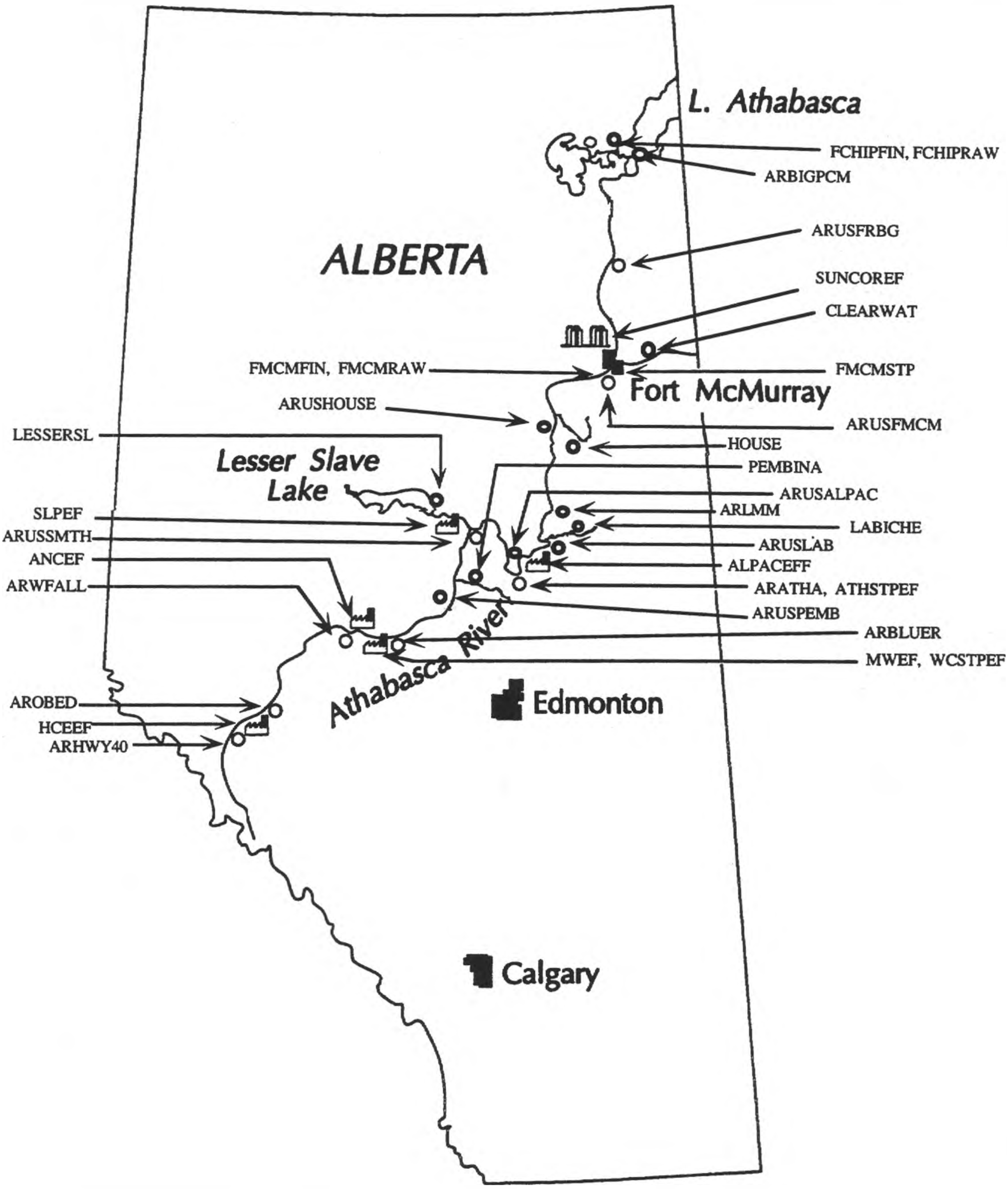

Figure 1. SAMPLING SITE MAP

Table 2.

TASTE AND ODOUR WATER SAMPLING SCHEDULE
Athabasca River 1994

Time-of-travel (days)	Sampling Date	Site	Sample Code
1	Feb. 10	ENTRANCE	ARHWY40
1	10	Hinton Combined Effluent	HCEFF
1	10	OBED	AROBED
5	15	WINDFALL	ARWFALL
5	15	Alberta Newsprint Effluent	ANCEF
6	15	Millar-Western Effluent	MWEF
6	15	Whitecourt STP Effluent	WCSTPEF
6	16	BLUE RIDGE	ARBLUER
12	22	u/s PEMBINA R.	ARUSPEMB
12	22	Pembina R.	PEMBINA
14	23	u/s SMITH @ HWY 2	ARUSSMTH
14	23	Lesser Slave R.near AR confluence	LESSERSL
14	23	Slave Lake Pulp Effluent	SLPEF
18	25	ATHABASCA	ARATHA
18	25	Athabasca STP Effluent	ATHSTPEF
19	Mar. 01	u/s AlPac	ARUSALPAC
19	02	AlPac Effluent	ALPACEFF
22	02	u/s LA BICHE R.	ARUSLAB
22	02	La Biche R.	LABICHE
23	03	u/s Lake McMillan	ARLMM
25	07	u/s HOUSE R.	ARUSHOUSE
25	07	House River	HOUSE
29	10	u/s Horse River (u/s Ft. McMurray)	ARUSFMCM
29	10	Fort McMurray Raw Water	FMCMRAW
29	10	Fort McMurray Finished Water	FMCMFIN
29	10	Fort McMurray STP Effluent	FMCMSTP
30	10	Clearwater R.	CLEARWAT
30	10	Suncor Effluent	SUNCOREF
32	15	u/s FIREBAG R.	ARUSFRBG
38	17	u/s Big Point Channel Mouth	ARBIGPCM
38	15	Fort Chip Raw Water	FCHIPRAW
38	15	Fort Chip Finished Water	FCHIPFIN

2.3 CLOSED-LOOP STRIPPING - GAS CHROMATOGRAPHIC / MASS SPECTROMETRY ANALYSIS

One litre subsamples of each sample collected were analyzed, in duplicate, as received. A known mass of chlorodecane and chlorohexane were added to each 1L sample, as recovery standards, prior to close-loop stripping analysis (CLSA). The samples were closed-loop stripped onto 1.5 mg carbon filters for 2 hours (water bath temperature at 30°C and filter temperature at 50°C) using a Brechbühler AG closed-loop stripping apparatus. The filters were then removed and extracted twice with 10 µL and once with 5 µL of carbon disulfide : acetone (9:1). A known mass of biphenyl-d10 was added to the extract as an injection standard. A 2 µL sample was analyzed by gas chromatography-mass spectrometry (GC/MS) using a cool-on-column injection and 10µL of doubly distilled dichloromethane was added prior to subsequent analyses by OGC and GC/FID. The GC-MS analysis was carried out in the selected ion monitoring (SIM) mode on an HP 5890 GC with an HP 5970 mass-selective detector and an HP 59940 Chemstation® data system. The GC-MS conditions were: 35°C to 90°C at 4°C/min and then 10°C/min to 280°C; HP-5MS column, 30m x 0.25mm ID, 0.25 µm film thickness; column head pressure 70 kPa; injector temp 35°C; detector temp 300° C. Peaks of three characteristic ions for each target compound and internal standards were monitored and the presence of a compound in an extract was confirmed if the peaks of the three ions all maximized at the same retention time and had standard intensity ratios within 20% of those of the calibration standards. Characteristic ions, their typical relative intensities and their retention times are shown in Table 3. Target compounds were chosen on the basis of known odour compounds. Many of the odour compounds in bleached kraft mill effluent were, and still remain, unidentified. This is recognized as a definite weakness in this field of study, but resolution of this problem was certainly beyond the scope and budget of this project.

The quantitation of each compound was based on the peak areas of specific quantitation ions. The internal standards 1-chlorodecane and 1-chlorohexane were used to calculate a response factor for each target compound from the CLSA of a series of concentrations of calibration standard mixtures. The response factors and the relevant standard are listed in Table 4. This method of quantitation results in reporting a final value which has been adjusted for recovery and therefore represents the quantity in the water sample. The biphenyl-d10 standard was used to calculate the recovery of 1-chlorodecane and 1-chlorohexane in each CLSA extraction. The detection limits for the CLSA extraction combined with GC/MS analysis for the target compounds are also listed in Table 4. The CLSA-GC/MS detection limits are affected by stripping efficiencies and the condition of the GC/MS. Method blanks, filter blanks and controls with known standard concentrations were also extracted using the CLSA and analyzed using GC/MS during the course of the project.

2.4 OFACTORY GAS CHROMATOGRAPHIC ANALYSIS OF CLOSED-LOOP STRIPPING EXTRACTS

The CLSA extracts were also analyzed by olfactory gas chromatography (OGC) using a Hewlett Packard 5890 Gas Chromatograph where the GC conditions were: 35°C to 90°C at 4°C/min and then 10°C/min to 280°C; DB-5 column, 30m x 0.32mm ID, 0.25 µm film thickness; column head pressure 70 kPa; cool-on-column injector temp 35°C. For OGC, the column was raised through a heated transfer unit from the GC oven to a glass detection cone (Olfactory detection outlet kit, SGE International). Air drawn by a venturi from the GC oven is used to heat the transfer zone and the glass cone is purged with nitrogen that has been humidified by passing it through a reservoir containing Milli-Q water. After a 2µL sample was injected and the solvent peak had eluted, the effluent was continually monitored by time. Elution time, intensity and odour descriptor were recorded. A six point intensity scale was used (*=very weak, to ******=very strong). Control samples of known standard concentrations were used to help establish consistency of descriptors and intensity values. Method blanks and filter blanks were also checked using the OGC analytical method. The CLSA extracts were also analyzed using the GC and column described above, but with the column connected to a flame ionization detector (FID) at a detector temperature of 280°C.

2.5 OLFACTORY GAS CHROMATOGRAPHIC ANALYSIS OF DICHLOROMETHANE EXTRACTS

OGC analysis of the DCM extracts was carried out with the same instrument used for OGC of the CLSA extracts. An HP-5 column, 30 m x 0.25 mm ID, 0.25 µm film thickness was used. The column head pressure was 70 kPa. The initial column temperature was 30°C, programmed to 90°C at 4°C/min and then at 10°C/min to 280°C. Splitless injection with 1 µL sample volume and 0.5 min delay was used. The injector temperature was 250°C.

Table 3.
GC/MS DATA FOR TARGET ODOUR COMPOUNDS AND INTERNAL STANDARDS

Compound	Retention Time (min)	Quantification Mass (amu)	Confirmatory Ions (with relative intensities)
thiophene	3.1	84	84(100), 58(67), 45(60)
dimethyldisulfide	4.0	94	94(100), 45(65), 79(60)
2-methylthiophene	4.4	97	97(100), 98(60), 45(24)
3-methylthiophene	4.5	97	97(100), 98(57), 45(29)
1-chlorohexane	6.2	91	91(100), 43(80), 93(33)
2-ethylthiophene	6.5	97	97(100), 112(42), 45(25)
2,5-dimethylthiophene	6.6	111	111(100), 97(62), 59(23)
thioanisole	14.0	124	124(100), 109(47), 78(30)
2-isopropyl-3-methoxy pyrazine	14.3	137	137(100), 152(28), 24(24)
2-isobutyl-3-methoxy pyrazine	16.7	124	124(100), 95(27), 151(19)
2-methylisoborneol	16.8	95	95(100), 135(9), 168(3)
1-chlorodecane	18.5	91	43(100),91(87), 93(27)
2,4,6-trichloroanisole	19.8	195	195(100), 212(88), 210(85)
2,3,6-trichloroanisole	20.6	210	210(100), 212(99), 195(43)
biphenyl-d10	20.7	164	164(100), 162(38), 160(23)
geosmin	21.1	112	112(100), 125(15), 182(4)
3,4,5-trichloroveratrole	24.4	240	240(100), 242(97), 225(92)

Table 4.
GC/MS RESPONSE FACTORS FOR TARGET ODOUR COMPOUNDS RELATIVE TO INTERNAL STANDARDS

Compound	*Recovery Factor Relative to internal standard	**Response Factor Relative to Biphenyl-d10	Detection Limit (ng/L)
1-chlorodecane	-	1.41	-
1-chlorohexane	-	1.05	-
thiophene	0.67 (chlorohexane)	1.99	1.3
dimethyldisulfide	0.14 (chlorohexane)	1.90	1.0
2-methylthiophene	0.72 (chlorohexane)	3.54	2.5
3-methylthiophene	0.83 (chlorohexane)	3.75	2.5
2,5-dimethylthiophene	0.92 (chlorohexane)	1.50	1.2
2-ethylthiophene	0.78 (chlorohexane)	2.46	1.2
thioanisole	0.67 (chlorohexane)	1.42	2.6
2-isopropyl-3-methoxy pyrazine	0.07 (chlorodecane)	1.84	2.4
2-isobutyl-3-methoxy pyrazine	0.06 (chlorodecane)	2.28	2.4
2-methylisoborneol	0.07 (chlorodecane)	2.11	10
2,4,6-trichloroanisole	0.22 (chlorodecane)	0.86	1.2
2,3,6-trichloroanisole	0.24 (chlorodecane)	0.78	1.2
geosmin	0.11 (chlorodecane)	2.05	1.2
3,4,5-trichloroveratrole	0.03 (chlorodecane)	0.61	2.7

* based on 24 CLSA standard extractions
** based on 12 GC/MS injections

3.0 RESULTS and DISCUSSION

3.1 CLOSED-LOOP STRIPPING / GAS CHROMATOGRAPHY

The results of the analyses of the CLSA extracts and the corresponding internal standard recoveries are shown in 5. All CLSA extractions were carried out in duplicate. The recovery of the chlorodecane or chlorohexane in each extraction can be used as an indicator of overall recoveries and highlights the extracts that are questionable. Any extracts with internal standard recoveries less than 10% were not reported. The results given in Table 5 for the effluent samples are those obtained for 20:1 dilutions. The effluent concentrations would be 20 times greater.

The CLSA analytical results demonstrate a number of basic trends. The mainstem Athabasca River sample upstream of Hinton (ARHWY40) did not contain detectable levels of any of the target odour compounds other than geosmin (a biogenic compound). Both the Hinton combined effluent and the Alberta Pacific effluent did not contain detectable levels of any target compounds. Downstream of Hinton the mainstem river sample extracts did not show detectable levels of the target compounds which were found in the 1993 study. Low levels of thiophene and/or dimethyl disulfide, however, were found as far downstream as Lake McMillan. This may be due to the sewage treatment plant effluent present in the Hinton combined effluent as the other three sewage treatment plant effluents (Whitecourt, Athabasca and Ft McMurray) all contained thiophene or dimethyl disulfide. However, three other diluted effluent samples (Alberta Newsprint, Millar Western, and Slave Lake Pulp) also contained low levels of these sulfur compounds. Four of the tributary samples (Pembina, Lesser Slave, House, and Clearwater) did not contain detectable levels of any of the target odour compounds. In the LaBiche River sample only geosmin was detected.

Non-target, total ion chromatographs (TIC) were also obtained for each CLSA extract. TICs for all samples indicated that levels of the non target compounds were also very low. The levels of non-target compounds have diminished significantly since the synoptic survey carried out in 1993 and very little useful information was obtained from these chromatograms. The same trends were apparent in the FID chromatograms.

3.2 OLFACTORY GAS CHROMATOGRAPHY OF CLOSED-LOOP STRIPPING EXTRACTS

Results of the OGC analyses are summarized in Table 6. All effluent samples were diluted 20:1 with odour-free Milli-Q water prior to extraction. There were a variety of miscellaneous odour peaks at trace to weak intensity in many of the samples. These are not reported nor discussed at present because they occurred at low frequency and showed no consistent pattern. The AlPac effluent sample (ALPACEFF) showed weak levels of sulfurous, and musty pyrazine (IPMP) odours and moderate levels of the camphorous odour of MIB. All of the other effluents collected (HCEFF, ANCEF, MWEF, WCSTPEF, SLPEF, ATHSTPEF, FMCMSTP, SUNCOREF) had weak odour peaks or no odour peaks at all. The results for the Hinton combined effluent (HCEFF) differ sharply with those obtained for the same effluent in the 1993 study. It would appear that the change to chlorine dioxide substitution bleaching in the Weldwood process has led to a significant reduction in odour peaks detectable with olfactory GC.

The mainstem Athabasca samples, including the site upstream from Hinton at Highway 40, showed weak to moderate levels of the musty pyrazine (IPMP or IBMP) odours all the way to the Firebag River. The musty, camphorous odour of MIB was detected in mainstem samples downstream of AlPac and as far downstream as the Horse River (immediately upstream of Fort McMurray). The finished water sample collected at Fort McMurray had no detectable odour peaks and the Fort Chip treated water had only one odour peak (2,4,6-TCA). It should be noted that, overall, the 1994 odour profiles had fewer odour peaks and intensities were generally lower than for those obtained in 1993.

Table 5. CLOSED-LOOP STRIPPING - GC/MS RESULTS

Sample ID	Thiophene ng/L	DMDS ng/L	2-MT ng/L	3-MT ng/L	2-ET ng/L	2,5-DMT ng/L	Thioanisole ng/L	IPMP ng/L	IBMP ng/L	MIB ng/L	246TCA ng/L	236TCA ng/L	Geosmin ng/L	345TCV ng/L	Chlorodecane Recovered	Chlorohexane Recovered
ARHWY401	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15.4	ND	48.80%	20.00%
ARHWY402	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.9	ND	42.80%	24.00%
HCEEF1*	ND	ND	ND	ND	ND	ND	ND	8.5	ND	ND	ND	ND	ND	ND	19.20%	23.30%
HCEEF2*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	24.50%	25.80%
AROBED1	ND	24.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	32.40%	25.60%
AROBED2	ND	31.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	27.90%	25.90%
ARWFALL1	ND	15.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	46.20%	42.40%
ANCEF1*	1.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	33.00%	30.60%
ANCEF2*	2	3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	21.00%	18.50%
MWEF1*	ND	3.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	26.80%	24.60%
MWEF2*	1.2	5.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	25.10%	22.90%
WCSTPEF1*	1.1	2.8	ND	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	26.80%	29.70%
WCSTPEF2*	1	5.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	21.10%	22.60%
ARBLUER1	1.7	9.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	29.30%	25.80%
ARBLUER2	1.5	9.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16.40%	16.80%
ARUSPEMB1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10.4	ND	28.10%	27.20%
ARUSPEMB2	1.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.0	ND	18.30%	21.70%
PEMBINA1†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	32.90%	27.80%
PEMBINA2†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	26.40%	28.40%
ARUSSMTH1	ND	9.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10.60%	10.70%
ARUSSMTH2	ND	15.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	21.50%	20.60%
LESSERSL2†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20.90%	18.20%
SLPEF1*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15.80%	13.30%
SLPEF2*	1.9	2.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16.90%	13.60%
ARATHA1	1.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30.00%	26.70%
ARATHA2	2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	28.20%	24.40%
ATHSTPEF1*	ND	142	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30.30%	26.30%
ATHSTPEF2*	ND	92.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	28.70%	24.90%

DMDS - dimethyldisulfide
2-MT - 2-methylthiophene
3-MT - 3-methylthiophene
2-ET - 2-ethylthiophene
2,5-DMT - 2,5-dimethylthiophene

IPMP - 2-isopropyl-3-methoxy pyrazine
IBMP - 2-isobutylyl-3-methoxy pyrazine
246TCA - 2,4,6-trichloroanisole
236TCA - 2,3,6-trichloroanisole
345TCV - 3,4,5-trichloroveratrole

* Effluent sample diluted 20:1 (actual concentrations are 20 times greater)
† Tributary sample

continued ....

Table 5. Concluded.

Sample ID	Thiophene ng/L	DMDS ng/L	2-MT ng/L	3-MT ng/L	2-ET ng/L	2,5-DMT ng/L	Thioanisole ng/L	IPMP ng/L	IBMP ng/L	MIB ng/L	246TCA ng/L	236TCA ng/L	Geosmin ng/L	345TCV ng/L	Chlorodecane Recovered	Chlorohexane Recovered
ARUSALPAC1	2.7	10.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	38.40%	13.80%
ARUSALPAC2	2.1	7.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	84.00%	33.10%
ALPACEFF1*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16.10%	17.40%
ALPACEFF2*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	22.00%	21.10%
ARUSLAB2	ND	9.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	28.90%	40.80%
LABICHE1†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	109	ND	31.30%	25.60%
LABICHE2†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	57.1	ND	14.00%	18.60%
ARLMM1	2.9	12.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	27.10%	27.10%
ARUSHOUSE1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	44.60%	48.10%
ARUSHOUSE2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	24.20%	27.30%
ARHOUSE1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	36.40%	35.70%
ARHOUSE2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	23.50%	21.90%
ARUSFMCM1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	25.60%	27.00%
ARUSFMCM2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	23.50%	21.90%
FMCMRAW1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	46.90%	30.10%
FMCMRAW2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	42.10%	29.80%
FMCMFIN1‡	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20.80%	11.40%
FMCMFIN2‡	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	26.80%	19.80%
FMCMSTP1*	ND	111	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	34.20%	31.70%
FMCMSTP2*	ND	94.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	23.50%	20.60%
CLEARWAT1†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	23.90%	30.20%
CLEARWAT2†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20.60%	25.70%
SUNCOREF1*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	23.90%	30.20%
SUNCOREF2*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20.60%	25.70%
ARUSFBG1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	18.50%	24.70%
ARUSFBG2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	25.60%	31.50%
ARBIGPCM1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20.70%	23.50%
ARBIGPCM2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	21.00%	31.90%
FCHIPRAW1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	13.50%	15.30%
FCHIPRAW2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20.70%	28.90%
FCHIPFIN1‡	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	12.30%	26.70%
FCHIPFIN2‡	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	24.00%	29.60%

DMDS - dimethyldisulfide
2-MT - 2-methylthiophene
3-MT - 3-methylthiophene
2-ET - 2-ethylthiophene
2,5-DMT - 2,5-dimethylthiophene

IPMP - 2-isopropyl-3-methoxy pyrazine
IBMP - 2-isobutylyl-3-methoxy pyrazine
246TCA - 2,4,6-trichloroanisole
236TCA - 2,3,6-trichloroanisole
345TCV - 3,4,5-trichloroveratrole

* Effluent sample diluted 20:1 (actual concentrations are 20 times greater)
† Tributary sample
‡ Treated drinking water sample

Table 6. OLFACTORY GAS CHROMATOGRAPHY FOR CLSA EXTRACTS

Site	Odour Peak and Retention Time in Decimal Minutes									
	SULF	garlic	CROIL	SULF	SULF	IPMP	IBMP	MIB	246TCA	Geosmin
	3.0	5.1	9.0	9.7	10.2	14.	16.6	16.7	20.0	20.90
ARHWY40						++	++			
HCEFF#		+			+		+			
AROBED		+		++	+++	++	+++		++	
ARWFALL	++		+		+					
ANCEF#										
MWEF#			+		+	+	+			
WCSTPEF#						++	+		++	
ARBLUER						+++	++++			
ARUSPEMB							++			
PEMBINA†							++			
ARUSSMTH						+++	+++			
LESSERSL†							++	++		
SLPEF*				+						
ARATHA			+			++				
ATHSTPEF#				++		++				

IPMP - isopropylmethoxypyrazine
IBMP - isobutylmethoxypyrazine
SULF is a sulfury/septic odour
CROIL is a sulfury/mercaptan/crude oil odour
246TCA - 2,4,6-trichloroanisole

\# Effluent sample
† Tributary sample
‡ Water Supply sample

Intensities are on a six-point scale from + (very weak) to ++++++ (very strong)

continued ....

Table 6 Concluded.

Site	Odour Peak and Retention Time in Decimal Minutes									
	SULF 3.0	garlic 5.1	CROIL 9.0	SULF 9.7	SULF 10.2	IPMP 14.5	IBMP 16.6	MIB 16.7	246TCA 20.0	Geosmin 20.90
ARUSALPAC						++	+++		++	++
ALPACEFF#				++		++		++++		
ARUSLAB								++++		
LABICHE†						+		++++		+
ARLMM										
ARUSHOUSE									+	
HOUSE†								++		
ARUSFMCM							+++	++		++
FMCMRAW										
FMCMFIN‡										
FMCMSTP#										
CLEARWAT†							+++	+++	++	
SUNCOREF#							+			
ARUSFRBG						++	+++		+	
ARBIGPCM									+	
FCHIPRAW									+	
FCHIPFIN‡							+		+++	

IPMP - isopropylmethoxypyrazine
IBMP - isobutylmethoxypyrazine
SULF is a sulfury/septic odour
CROIL is a sulfury/mercaptan/crude oil odour
246TCA-2,4,6-trichloroanisole

\# Effluent sample
† Tributary sample
‡ Water Supply sample

Intensities are on a six-point scale from + (very weak) to ++++++ (very strong)

3.3 OLFACTORY GAS CHROMATOGRAPHY -- DICHLOROMETHANE EXTRACTS

The base/neutral extracts of the complete sample series were analyzed by OGC. In all, more than 80 distinct odour peaks were detected in this set of extracts. Retention times and intensities for the most common odour peaks are presented in Table 7. One notable difference with the 1993 results is the absence of 246TCA (musty cork odour) from the bleached kraft mill effluents (BKME), HCEFF and ALPACEFF in 1994.

In 1994, chromatographic conditions were selected to better resolve the more volatile sulfury odour peaks in the early part of the chromatograms. The SULF2 peak at 8.1 minutes was strong in both HCEFF and ALPACEFF and persisted downstream as far as the river mouth (ARBIGCPM). This compound has a sulfury/alkyl sulfide odour and appears to be specific to bleached kraft mill effluent. The SULF5 peak at 14.4 minutes has a skunky odour. It occurred in HCEFF and ALPACEFF, but was also found in chemithermomechanical (CTMP) mill effluents, municipal effluents, and some tributaries. SULF1 also occurred widely and was not specific to BKME. Neither SULF3 nor SULF4 was detected in HCEFF. They were detected in CTMP and municipal effluents as well as tributaries. SULF6 was included because the main source appears to be HCEFF (although a weak response was observed for ATHSTPEF and the Pembina River). It did not persist as far downstream as the SULF2 odour.

The only source of the CROIL odour at 23.2 minutes was HCEFF. This odour persisted as far downstream as ARBIGPCM. It has a sulfury/crude oil character.

Geosmin and 246TCA were not detected in HCEFF or ALPACEFF but were detected in several of the CTMP and municipal effluents, and in the mainstem and tributaries. Geosmin is a natural product, and 246TCA is known to be widely distributed.

A broad odour peak was found at 29-30 minutes with a phenolic/pulp mill character. Because it was not a sharp, distinct peak it is likely due to more than one compound. This odour was detected in HCEFF and several mainstem samples downstream from Hinton, but not in ALPACEFF, CTMP and municipal effluents, or in tributaries. It also appears to be specific to HCEFF.

Sulfury odours dominate the base/neutral fraction of the bleached kraft mill effluents currently discharged to the Athabasca River. Two of these: SULF2 and CROIL are candidates as tracers for monitoring odour-related compounds in BKME. The former was observed in both HCEFF and ALPACEFF; the latter appears to be specific to HCEFF.

A few of the acid extracts were analyzed (ARHWY40, HCEFF, ALPACEFF and ARUSFMCM). Sulfury, phenolic, pulp mill, woody and vanilla odours were detected in HCEFF, ALPACEFF and ARUSFMCM samples. These odours may also contribute to the characteristic pulp mill odours observed by the flavour panel in this study.

Table 7. OLFACTORY GAS CHROMATOGRAPHY RESULTS FOR DICHLOROMETHANE EXTRACTS

Site	Odour Peak and Retention Time in Decimal Minutes									
	SULF1	SULF2	SULF3	SULF4	SULF5	SULF6	CROIL	246TCA	Geosmin	PH/PM
	4.9	8.1	10.8	12.9	14.4	14. 9	23.2	24.2	25.6	29-30
ARHWY40			+					+		
HCEFF#	++++	++++			++	++	+++			++++
AROBED	++++	++++	+++		+++	+++	+++			
ARWFALL	++	++++	+		++	+++	++	+	+++	
ANCEF#	+			++				++		
MWEF#	+++		++	+	++			+	+++	
WCSTPEF#	+			++	++			++	+	
ARBLUER	++	+++	+++	+	++	++	++		++	+++
ARUSPEMB		+++	+				+	+	+	++
PEMBINA†				+	+	+		+	+++	
ARUSSMTH	++++	+++	++	++	+++		++		+	++
LESSERSL†					++			++	+	
SLPEF*					++			+	+	
ARATHA							+++	++	+	+++
ATHSTPEF#	+++		+++	+++		+			+	
ARUSALPAC	+	+++					++	+		++

SULF1 - sulfury
SULF2 - sulfury/alkyl sulfide
SULF3 - oatmeal
SULF4 - sweaty socks
SULF5 - skunky
SULF6 - sulfury/onion
CROIL is a sulfury/mercaptan/crude oil odour
246TCA - 2,4,6-trichloroanisole
PH/PM - phenolic/pulp mill

Effluent sample
† Tributary sample
‡ Water Supply sample

Intensities are on a six-point scale from + (very weak) to ++++++ (very strong)

continued ....

Table 7. Concluded.

Site	Odour Peak and Retention Time in Decimal Minutes									
	SULF1	SULF2	SULF3	SULF4	SULF5	SULF6	CROIL	246TCA	Geosmin	PH/PM
	4.9	8.1	10.8	12.9	14.4	14. 9	23.2	24.2	25.6	29-30
ALPACEFF#	+++	+++++	++		++					
ARUSLAB	+	++			+++		+	+	+	++
LABICHE†	++			++	++			+	+++	
ARLMM	+	++++	+		++			+	+	++
ARUSHOUSE	++	++++	++		+++		+++	+	+	+
HOUSE†				++	+			+	+++	
ARUSFMCM	+++	+++			+		+	+	+	+
FMCMRAW		++					++		+	
FMCMFIN‡		++		+	+		+	+	++	
FMCMSTP#	+		++		+				+	
CLEARWAT†	+				+++			+	+	
SUNCOREF#	+		++	+++	+++					
ARUSFRBG	+	++	++		+++		+	+	++	+
ARBIGPCM	++	+			+++				+	
FCHIPRAW				+						
FCHIPFIN‡					+					

SULF1 - sulfury
SULF2 - sulfury/alkyl sulfide
SULF3 - oatmeal
SULF4 - sweaty socks
SULF5 - skunky
SULF6 - sulfury/onion
CROIL is a sulfury/mercaptan/crude oil odour
246TCA - 2,4,6-trichloroanisole
PH/PM - phenolic/pulp mill

Effluent sample
† Tributary sample
‡ Water Supply sample

Intensities are on a six-point scale from + (very weak) to ++++++ (very strong)

3.4 FLAVOUR PROFILE ANALYSES

The flavour profile panel results are presented in Table 8 and are summarized in Figures 2 to 4, which show the average intensity ratings of the panel members, along with the descriptors they used.

The panel was able to detect a moderate increase in odour for the Athabasca River sample collected downstream of Hinton, and mainstem odour levels remained relatively constant downstream to the Firebag River. The effluent samples from Alberta Newsprint, Millar Western, Whitecourt sewage treatment plant, Slave Lake Pulp, Athabasca sewage treatment plant and Ft McMurray sewage treatment plant had lower odour levels and the flavour profile panel used unique descriptors that were not applicable for any of the Athabasca River samples. The odour of the Alberta-Pacific effluent had a characteristic septic, woody, resinous odour that was similar to the Hinton combined effluent odour but less offensive. However, Athabasca River samples collected upstream and downstream of the AlPac discharge had very similar odour intensities. The Suncor effluent was recognized as very distinctive and relatively strong, but it was difficult to recognize any impact of the Suncor effluent on the Athabasca River sample upstream of the Firebag River. The odours of the Pembina River, Lesser Slave River, House River and Clearwater River were minor and likely contributed little to the odour of the mainstem Athabasca River. The LaBiche River was the only tributary with a significant odour but the grassy, musty odour was not noticeable in Athabasca mainstem samples collected downstream of this river. Treated water samples collected from Ft McMurray and Fort Chipewyan both had distinct chlorine odour and any odour contribution from the pulp mill effluents was masked.

The odour panel results indicate that the Hinton combined effluent has a noticeable impact because the upstream sample (Highway 40) has a low odour. In the case of the Alberta-Pacific effluent, the Athabasca River upstream from it already has a bleached kraft mill effluent background. As a result, the impact of the Alberta-Pacific effluent is difficult to discern over this background. For this survey of the Athabasca River, the Hinton combined effluent likely remains to be the most distinct source of odour in the mainstem river although odour intensities are much lower than for samples collected in 1993.

Table 8. UNIVERSITY OF ALBERTA FLAVOUR PROFILE PANEL RESULTS

Sample Site	Panelist 1 Descriptor	Intensity	Panelist 2 Descriptor	Intensity	Panelist 3 Descriptor	Intensity
ARHWY40	veg	0.5	-	-	earthy	0.5
HCEFF	septic	1	-	-	septic/swampy/p&p	2
AROBED	septic	1	-	-	septic/swampy/p&p	2.5
ARWFALL	musty/septic	1.75	-	-	septic/sulfurous	2
ANCEF	musty	0.75	-	-	grassy/musty	0.5
MWEF	seaweed	1.5	turnip	1.25	septic/earthy	1.5
WCSTPEF	musty/dusty	1	-	-	flowery/dusty	0.5
ARBLUER	sewage/muddy	0.5	septic/musty	1.5	earthy/septic	1.5
ARUSPEMB	septic/sewage	1.25	septic/dusty	1.25	woody/septic	1.5
PEMBINA	veg	0.5	septic	1	earthy	1
ARUSSMTH	septic	1	septic/musty	1.75	earthy/grassy	1
LESSERSL	veg	tr	dusty	0.5	earthy/woody	tr
SLPEF	cardboard	tr	fresh	0.5	sharp/chem	1.5
ARATHA	septic	1	earthy/musty	1.25	septic/woody	1.5
ATHSTPEF	sweet/veg	0.5	sweet/veg	0.5	flowery	0.5
ARUSALPAC	septic/cardboard	0.75	swampy/grassy	1	septic/woody	1.5
ALPACEFF	muddy/musty	1	nutty	1	earthy/chem	1
ARUSLAB	septic/muddy	0.75	septic/resin	1.25	septic/woody	2
LABICHE	grassy/veg	1.5	septic/musty	2	musty/rotten veg	2
ARLMM	wood/skunky	1	dusty/swampy	1.25	septic/woody	1.5
ARUSHOUSE	septic/sewage	1.5	musty/septic	2.5	septic	1
HOUSE	veg	1	marshy	0.5	grassy	0.5
ARUSFMCM	septic/sewage	1	resin/septic	1.75	septic	2
FMCMRAW	sewage/cardboard	1	resin/septic	1.75	septic	1.5
FMCMFIN	chlorine	2	chlorine	1.75	chlorine	2
FMCMSTP	soapy	0.75	nutty	0.5	odorless	0
CLEARWAT	veg/grass	0.5	resin	1.5	marshy	1
SUNCOREF	chem	2	chem	2.25	cardboard	2
ARUSFRBG	septic	0.75	septic	1	septic	1.5
ARBIGPCM	chem	1	musty/septic	1.5	septic/grassy	1
FCHIPRAW	veg	0.5	veg	0.5	veg	tr
FCHIPFIN	chlorine	1.5	chlorine	1.5	chlorine	2

p&p - pulp & paper
chem - chemical
veg - vegetation
org - organic
hydro - hydrocarbon
med - medicinal
chlor - chlorine

continued ...

Table 8. Concluded.

Sample Site	Panelist 4 Descriptor	Intensity	Panelist 5 Descriptor	Intensity	MEAN	Standard Deviation
ARHWY40	odourless	0	swampy	0.5	0.38	{0.25}
HCEEF	septic/resin	1.5	woody	0.5	1.25	{0.65}
AROBED	sour/resin	1.5	septic	1	1.50	{0.71}
ARWFALL	septic/woody	1	septic	2	1.69	{0.47}
ANCEF	musty	1	smoky	1	0.81	{0.24}
MWEF	veg/foul	1.5	-	-	1.44	{0.13}
WCSTPEF	septic/marshy	0.5	earthy	1.25	0.81	{0.38}
ARBLUER	resin/woody	1.5	-	-	1.25	{0.50}
ARUSPEMB	resin/woody	1	-	-	1.25	{0.20}
PEMBINA	musty/sharp	tr	-	-	0.65	{0.44}
ARUSSMTH	woody	0.5	-	-	1.06	{0.52}
LESSERSL	musty/sharp	tr	-	-	0.20	{0.20}
SLPEF	musty/chalky	1	-	-	0.78	{0.61}
ARATHA	woody/septic	1	swampy/septic	1.75	1.30	{0.33}
ATHSTPEF	musty/foul	0.5	earthy/sweet	0.75	0.55	{0.11}
ARUSALPAC	resin/septic	2	earthy/swampy	1.25	1.30	{0.48}
ALPACEFF	burnt rubber	2	rubber/chem	2	1.40	{0.55}
ARUSLAB	woody	1	septic/resin	2	1.40	{0.58}
LABICHE	veg/flowery	1.5	musty	1.75	1.75	{0.25}
ARLMM	resin/woody	1.5	septic/woody	2	1.45	{0.37}
ARUSHOUSE	resin/septic	1	septic	1.5	1.50	{0.61}
HOUSE	veg/musty	1	earthy/grassy	0.75	0.75	{0.25}
ARUSFMCM	woody/resin	1	septic	2	1.55	{0.70}
FMCMRAW	woody/resin	1	septic	1	1.25	{0.45}
FMCMFIN	chlorine	2	chlorine	1.25	1.80	{0.38}
FMCMSTP	septic/sewage	1	soap	0.25	0.50	{0.51}
CLEARWAT	veg	0.5	earthy	1	0.90	{0.42}
SUNCOREF	hydrocarbon	2.5	hydrocarbon	2.25	2.20	{0.54}
ARUSFRBG	resin/septic	0.5	swampy/septic	1	0.95	{0.23}
ARBIGPCM	wet cardboard	1	woody	1	1.10	{0.22}
FCHIPRAW	odorless	0	chalky	0.5	0.32	{0.25}
FCHIPFIN	chlorine	1.5	chlorine	1.5	1.60	{0.65}

p&p - pulp & paper
chem - chemical
veg - vegetation
org - organic
hydro - hydrocarbon
med - medicinal
chlor - chlorine

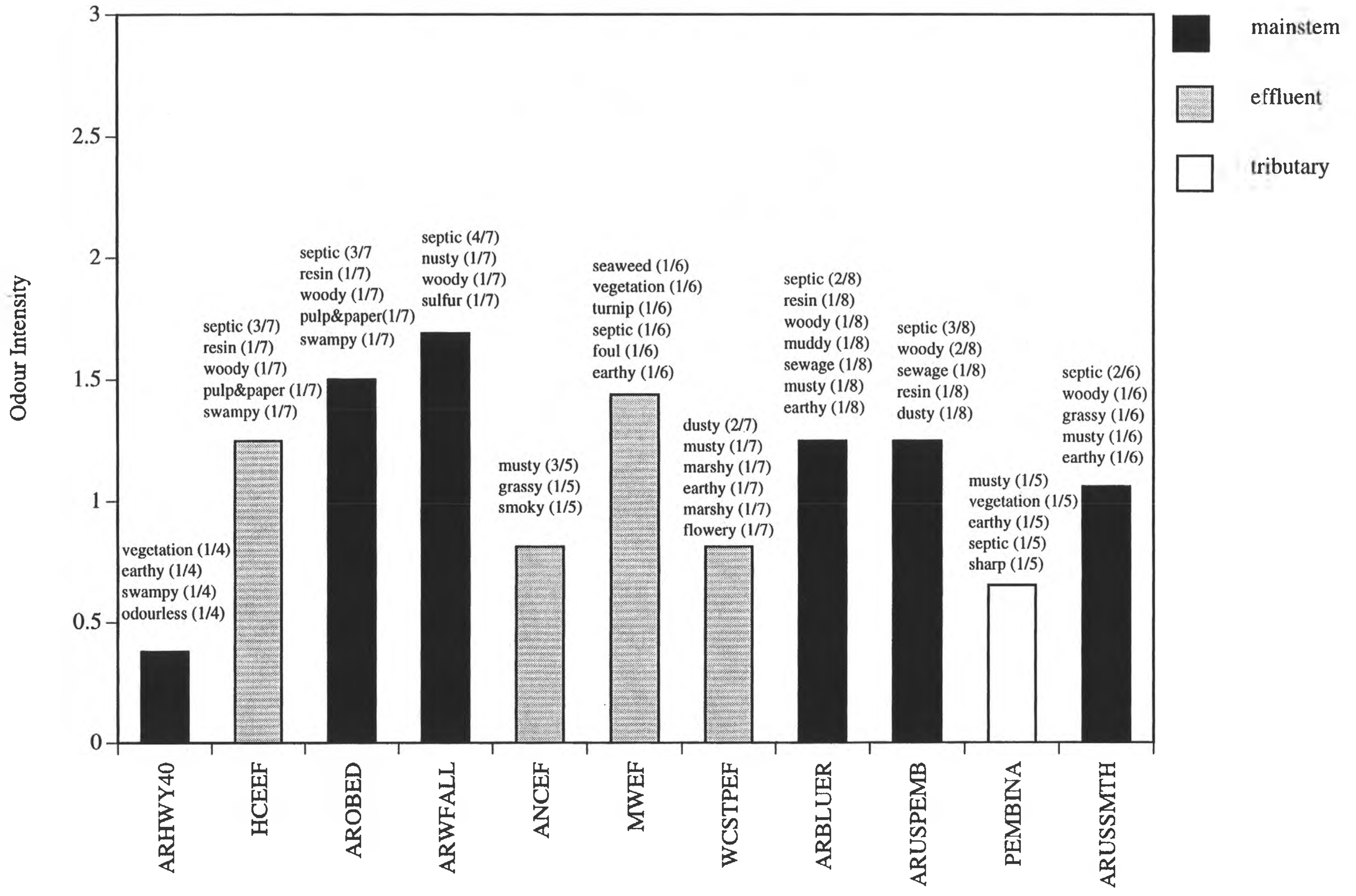

Figure 2. FLAVOUR PROFILE ANALYSES SUMMARY FOR FIRST 11 SAMPLING SITES

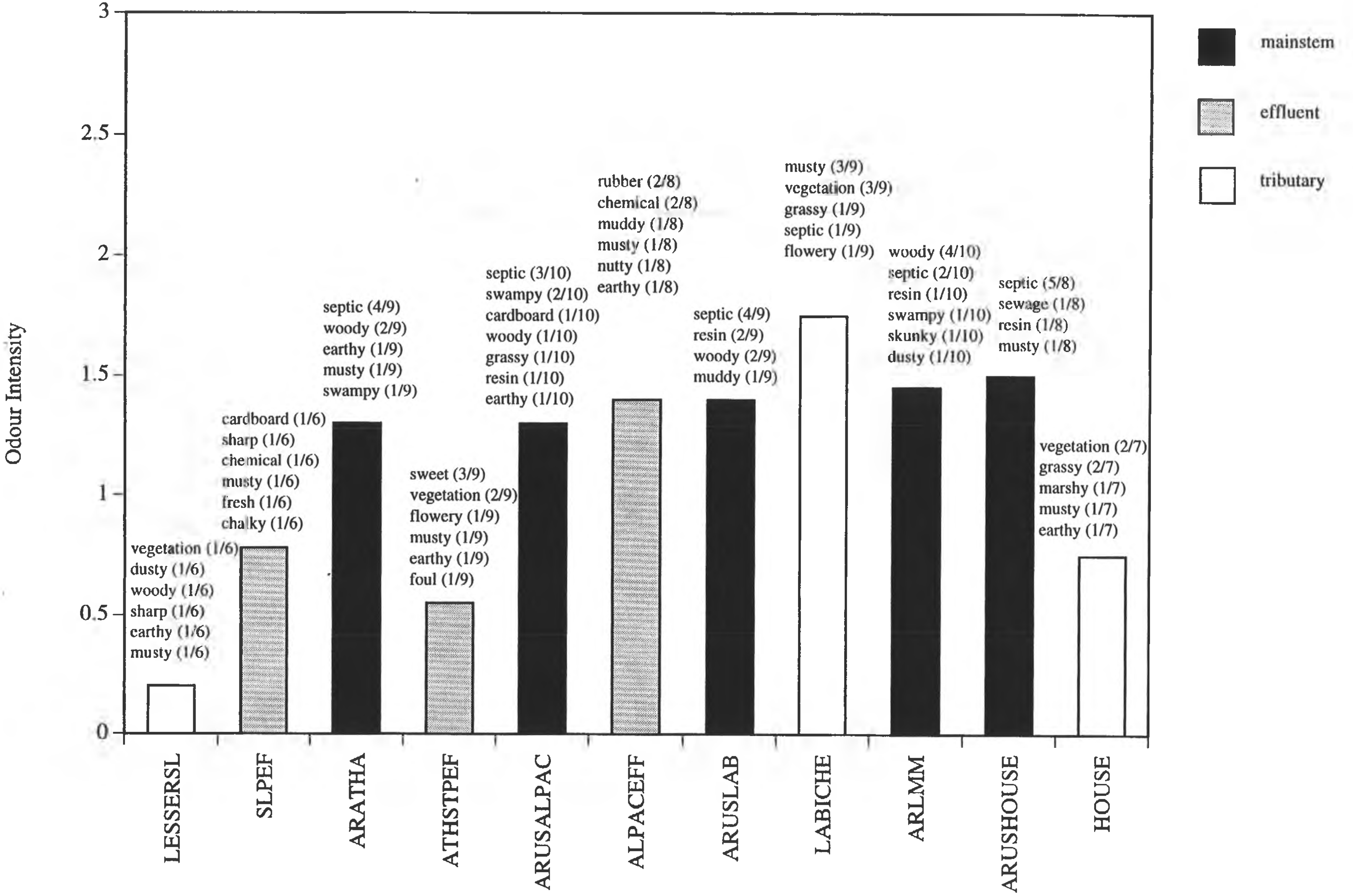

Figure 3. FLAVOUR PROFILE ANALYSES SUMMARY FOR SECOND 11 SAMPLING SITES

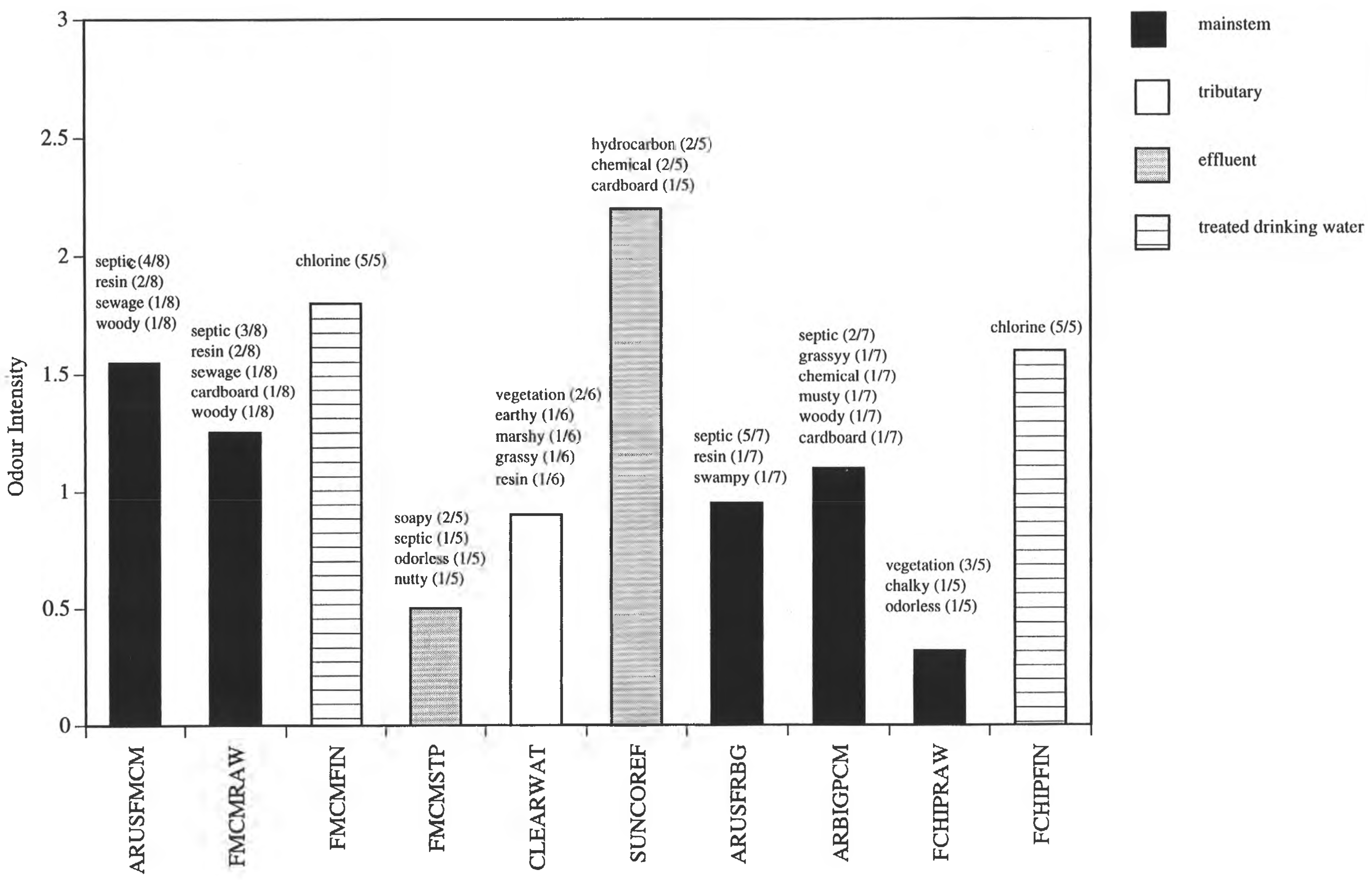

Figure 4. FLAVOUR PROFILE ANALYSES SUMMARY FOR LAST 10 SAMPLING SITES

4.0 CONCLUSIONS

This study combined three different analytical methods commonly used in monitoring for the presence of odorous compounds in water supplies. A trained flavour profile panel characterized the odour of the samples, a trained analyst was used to evaluate the samples using olfactory GC and all samples were quantitatively analyzed for the presence of target odour compounds using GC/MS. These three techniques all provide quite different information and all have certain limitations.

The flavour profile panel method is most appropriate when monitoring for the presence of compounds that will lead to public complaints, relies on varying sensitivities to certain odours, and does not easily allow for reporting the presence of specific compounds. Consistency and specificity of the flavour profile panel results require rigorous training in the recognition of target compounds and assignment of appropriate intensities.

The olfactory GC technique is useful when there are a number of odorous compounds present in a sample. The GC accomplishes the separation of each of the odour compounds and still allows for olfactory detection. The sensitivity of this method is limited by the dilution of odours by the inert carrier gas as well as the small volumes of sample that can be injected for capillary gas chromatography. The extraction of the samples using CLSA offers a ten thousand fold concentration of the sample so that these sensitivity problems are partially offset.

The analyses by gas chromatography with mass selective detection was the most quantitative analytical method, but also the least sensitive. In order to increase sensitivity of the instrument a selected ion monitoring program was set up to monitor the abundance of certain ions that are known to be present in the mass spectra of the target compounds. Sensitivity is increased because rather than slowly scanning for all possible ions, the detector scans many more times and much more rapidly for the small group of selected ions. However, the analyses are then limited to monitoring for the chosen target compounds. Any odorous non-target compounds, which may significantly contribute to the odour of a sample, will not be reported.

The flavour profile panel work, shows a decrease in the impact of Hinton combined effluent on the odour of the Athabasca River compared with the 1993 survey. The contribution from the Alberta Pacific discharge was even smaller than the Hinton contribution. The odour contributions to the Athabasca River from tributaries were minor. The odour contributions from other effluent sources (sewage treatment plants and chemi-thermomechanical pulp mills) are less distinctive than the Weldwood and AlPac mills and their role in affecting downstream odour is not as clear. Notwithstanding these observations, the observed impacts on raw water odour could not be identified for the treated drinking water at Ft. McMurray, possibly because of removal of odorous compounds in treatment and / or masking of the raw water odour with chlorinous odours. The raw water supply at Ft. Chipeweyan was not particularly odorous and the finished water also exhibited a strong chlorine odour that would have masked any subtle odours present.

The CLSA-GC/MS and OGC results suggest that there were very limited contributions to the odour of the samples by the target compounds. None of the target odour compounds, by themselves, can explain the odour character that was perceived by the odour panel in the Hinton combined and AlPac effluents and affected downstream samples. There are likely other contributing compounds that have not yet been detected by the methods employed in this survey. This suggests the need for a continued characterization of the compounds that are primarily responsible for creating the current odour of these pulp mill effluents.

This report summarizes olfactory GC, CLSA/GC/MS and FPA results, but the three methods are difficult to correlate because:

a) CLSA/SIM is somewhat selective and determines target compound presence only. Unfortunately the current literature base was not sufficient tc develop a complete list of compounds responsible for the characteristic "pulp mill" odour.
b) CLSA/OGC detects non-target odour compounds but does not give the overall odour of a sample. However, the variety and intensities of odour peaks give a semi-quantitative statement about spatial distribution of odours.
c) Flavour panel results give an overall odour intensity for each sample and probably yield the most useful information, but these FPA results can not be compared with chromatographic results.

Unless the target compound list is thoroughly researched and adequately expanded, the three methods are difficult to link and they will remain difficult to correlate.

5.0 RECOMMENDATIONS

In our report of the 1993 water tainting study we recommended that a detailed study of the Hinton combined effluent be undertaken, to isolate and identify the compounds responsible for this odour, so that the set of target odour compounds can be expanded. This was initiated in the summer of 1993, but early results were rendered useless when the Weldwood mill changed to the chorine dioxide bleaching process. It was readily apparent that the characteristic "pulp mill odour" was no longer present and the general odour was more woody or resinous and generally less offensive. The large volume extracts from 1994 will be useful for continued study of these resinous effluents.

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7.0 APPENDIX A: TERMS OF REFERENCE

NORTHERN RIVER BASINS STUDY

SCHEDULE A - TERMS OF REFERENCE

Project 4413-C1: Water Taste and Odour Study, Athabasca River 1993/94 (Post-AlPac)

I. Introduction

In February and March 1993, a total of 30 water samples were collected from the mainstem and tributaries of the Athabasca River and were subjected to a battery of chemical and sensory methods to determine the extent to which odorous compounds associated with pulp mill effluents are transported downstream under ice conditions. Large volume (20L) extracts from the Hinton Combined Effluent were prepared and under this project these extracts will be subjected to fractionation/separation/analysis to identify compounds that contribute to the characteristic "pulp mill" odour. After these compounds have been identified, other large volume extracts collected in February and March 1993 will be qualitatively and quantitatively analyzed. In addition, water samples will again be collected from the Athabasca River during the winter of 1993/94 and subjected to the same battery of chemical and sensory analyses as water samples collected this past winter. Comparison of the results from the two winters will allow for a preliminary determination of the effects of the AlPac mill on water tainting.

II. Requirements

1. The large volume extract from the Hinton Combined Effluent collected in February 1993 will be subjected to fractionation/separation/analysis to identify compounds which contribute to the tainting of water. After these compounds have been identified, large volume extracts from other sites sampled in February and March 1993 will be qualitatively and quantitatively analyzed.

2. River mainstem, tributary, effluent and water supply samples will be collected by Alberta Environment/NRBS from the Athabasca River during the winter of 1993/94 and supplied to the contractor. The sampling design for the 1993/94 synoptic survey will be modified from the 1993 winter design to include more sites downstream from the AlPac mill. The contractor will apply the same battery of chemical and sensory analyses on these samples as was used on the February and March 1993 samples. Chemical methods to be used will include closed-loop stripping extraction followed by gas chromatography-mass spectrometry analysis for a suite of target odour compounds. Sensory analysis is to include olfactory gas chromatography (sniff-GC) of the closed-loop stripping extracts and flavour panel analysis of water and effluents by a flavour panel.