Fish tainting in the Alberta oil sands region: a review of current knowledge

Janelle L. Tolton, Rozlyn F. Young, Wendy V. Wismer and Phillip M. Fedorak

ABSTRACT

The Athabasca oil sands in northeastern Alberta, Canada represent the second largest petroleum reserve in the world. The process of extracting bitumen from the oil sands uses huge volumes of water, drawn from sources in the Athabasca River basin, and numerous mining companies operate adjacent to the river. Oil sands process-affected water (OSPW) from open pit mining is placed in large settling basins or tailings ponds that have the potential to leak. The goal is to eventually reclaim the tailings ponds to become functional ecosystems. Natural outcrops of oil sands in contact with surface waters also occur, and there are anecdotal reports in the media that fish caught near the Athabasca oil sands have an unusual flavor or odor. Several analytical and sensory studies have been undertaken to address this issue. Two major questions related to fish tainting arise: (1) Do the current oil sands mining, extraction and upgrading processes cause fish tainting in surrounding waters? (2) What is the tainting potential for fish that become established in reclaimed waters in the future? This review examines the types of compounds in OSPW that might contribute to tainting and the sensory science literature available related to fish tainting and the oil sands.

Key words | Athabasca region, end pit lakes (EPL), fish tainting, oil sands processed waters (OSPW)

BACKGROUND

In the Athabasca River basin in northeastern Alberta, there are vast petroleum deposits in the form of oil sands; naturally occurring mixtures of sand, clay, minerals, water and bitumen. Alberta’s oil sands represent the second largest reserve of petroleum in the world (Government of Alberta 2011). More than 95% of Canada’s oil reserves are in Alberta’s oil sands, which are estimated to contain $1.7 \times 10^{12}$ barrels of crude bitumen (Government of Alberta 2011). Bitumen is a biodegraded, heavy, viscous form of oil that can be upgraded and refined to fuels such as gasoline or diesel.

One process of extracting bitumen from the oil sands uses water drawn from the Athabasca River or nearby sources, requiring between 3 and 4.5 barrels of water to produce one barrel of synthetic crude oil (Government of Alberta 2011). In the surface mining method of oil sands extraction, large volumes of process water are generated and these cannot be released into the river. This oil sands process-affected water (OSPW) is placed in large settling basins or tailings ponds which have the potential to leak. Usually there are interceptor wells around the tailings ponds to collect any seepage and the seepage is returned to the pond. Ferguson et al. (2009) provide a detailed study of the hydrodynamics of a large tailings pond. OSPW contains suspended solids, clays, residual bitumen, low concentrations of dissolved polycyclic aromatic compounds (PACs) and naphthenic acids (NAs), which have been historically suspected to be the primary cause of OSPW toxicity (MacKinnon & Boerger 1986). Structures of chemicals commonly found in OSPW are found in Figure 1. Much of the OSPW is recycled within the extraction process. The chemical contents of OSPW are quite variable, and these differences depend upon their source and the...
specific process used in the oil sands extraction (for examples, see Fedorak et al. 2002; Allen 2008). The chemical compositions of these waters used in fish tainting studies have not been reported in the literature, and we use the general term ‘OSPW’ throughout this review.

Oil sands companies operate under a zero water discharge policy, therefore none of the OSPW can be intentionally released into the environment (Clemente & Fedorak 2005). Currently there are about $840 \times 10^6$ m$^3$ of tailings stored in various settling ponds in the region (Siddique et al. 2011). In addition to bitumen and dissolved organics that are present in OSPW, the water also contains higher concentrations of ammonia, sodium, potassium, chloride, sulfate, sulfide and bicarbonate than the Athabasca River (MacKinnon & Boerger 1999).

The Athabasca River flows from the Columbia icefields in the Rocky Mountains to Lake Athabasca. Along its course, the river passes by pulp and paper mills, several communities (including Fort McMurray), oil sands extraction operations and flows over some naturally exposed oil sands outcrops (Squires et al. 2010). Fish species of importance to aboriginal peoples in the Athabasca River include walleye, northern pike and lake whitefish (Table 1). There are anecdotal comments in the media and on the Internet reporting off-flavor or off-odor in fish caught near the Athabasca oil sands. For example, Köhler (2007) reported that ‘fish pulled from the Athabasca downstream of the oil sands taste of gasoline and smell of burning galoshes in the fry pan’. However, there is no rigorously collected scientific evidence that wild fish taken from natural waters near the Athabasca oil sands operations are tainted.

Although reports of fish tainting in the Athabasca River basin are anecdotal, the concerns of aboriginal peoples, oil sands industry stakeholders and the Alberta government require continued investigation into the problem. Oil sands mining operations are expanding and continue to generate large volumes of OSPW that companies must reclaim prior to the closure of their leases. Many different reclamation ponds have been established by oil sands companies to investigate the best strategy for building end pit lakes (EPL), functioning aquatic ecosystems containing

<table>
<thead>
<tr>
<th>Fish species</th>
<th>Characteristics</th>
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<tbody>
<tr>
<td>Lake whitefish (<em>Coregonus clupeaformis</em>)</td>
<td>Primarily bottom feeders that consume crustaceans, snails, insects and other small aquatic organisms. This species is the main fish harvested by the aboriginal food fishery and the commercial fishing industry in Alberta. An individual of this species traveled 388 km from Fort McMurray to the north shore of Lake Athabasca</td>
</tr>
<tr>
<td>Northern pike or jackfish (<em>Esox lucius</em>)</td>
<td>Predators that primarily feed on fish and other vertebrates. They also sparsely consume insects. Northern pike are a popular sport fish in Alberta</td>
</tr>
<tr>
<td>Walleye (<em>Sander vitreus</em>)</td>
<td>Diet consists of yellow perch, lake whitefish, minnows and insects. They also consume snails and frogs if insects are scarce. Walleye are a prized sporting fish in Alberta and have been known to travel up to 400 km in 18 months</td>
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combinations of oil sands process-affected material (Westcott 2007). The resulting landscapes are likely to include wetlands and EPL with viable fish populations that may be susceptible to tainting by OSPW compounds.

There are two major questions related to fish tainting that need to be answered. First, do natural outcrops of oil sands and current oil sands mining, extraction and upgrading processes actually cause fish tainting in the oil sands region? This has not been adequately documented and this issue must be unequivocally resolved in the short term. Second, what is the potential for the fish that eventually become established in the EPL to be tainted? This paper addresses the methodologies of sensory science for assessing fish tainting by OSPW, summarizes some compounds that may play a role in fish tainting with regard to EPL, describes fish species of concern and reviews reports (some of which are not in the public domain) documenting fish tainting studies in the Athabasca region.

## SENSORY TESTING FOR ASSESSING FISH TAINING

Fish taint is a foreign flavor or odor in the organism induced by conditions in the water to which the organism was exposed (Group of Experts on the Scientific Aspect of Marine Pollution (GESAMP) 1982). Using human sensory tests for the analysis of fish taint has proven to be a reliable and sensitive methodology (Davis et al. 2002). Taint can be detected by olfactory (smell) or gustatory (taste) senses. The human nose is 10 to 100 times more sensitive than instrumental analyses such as gas chromatography, which can detect roughly 10^9 molecules per mL air (Meilgaard et al. 1999).

Flavor is described as a sum of perceptions and stimulations of the sense ends of the alimentary and respiratory tracts (Meilgaard et al. 1991). The combination of the gustatory perception (taste, 30–40%) caused by soluble substances in the mouth and olfactory perceptions (smell, 60–70%) of volatile odors creates the flavor of food. It is essential to include human sensory studies as well as analytical analyses when establishing detection thresholds. The detection threshold is the lowest stimulus concentration capable of producing a detected sensation (Meilgaard et al. 1991).

There are discrepancies among researchers for the choice of optimal method to detect thresholds of taint in fish, with either the triangle test or 3-alternative forced choice (3-AFC) test preferred. When performing a triangle test, a total of three blinded samples are presented to panelists: two of the exposed fish and one control or vice versa. A double triangle test is rarely used in modern sensory testing and the purpose of this test and its statistical methods are not well described in the literature. The 3-AFC method is similar to a triangle test but is considered to be directional. Panelists are presented with three blinded samples, one exposed fish and two control samples, and are told to select the sample which is the ‘most intense’, or for the case of fish tainting, told to determine which sample has an off-odor. The 3-AFC method should be used to determine detection thresholds of mixtures of OSPW components in water or fish whereas the triangle test is utilized to determine an overall difference, and could be effectively used to determine if a sample of fish or water is perceived to be tainted relative to a control (Edge et al. 2010).

When panelists are trained and familiar with a stimulus, it helps to decrease the error in judgments and fewer panelists (8–12) are required. Because trained panelists are required to have above average gustatory and olfactory sensitivity, their skills are best used in analytical situations such as to identify and quantify sensory characteristics of food products. The threshold determination of a compound by a group of untrained individuals would reveal its detection level in the general population, whereas a trained panel would be used for a threshold determination where greater sensitivity in detection is desired. When performing general population panels, a larger number of participants (60 or more) are required because of the individual variation in olfactory and gustatory sensitivity. In a preference test, no more than four blinded samples are presented to each of 40 or more panelists who then rank them from ‘most liked’ to ‘least liked’. A limitation of the preference test for fish tainting is that the variability among fish from the wild may be too great to guarantee identical samples for panelists.

In addition to the selection of appropriate sensory technique and type of sensory panel, the choice of statistical method for data analysis is critical for accurate interpretation of the results. In sensory science, a significance level of $p < 0.05$ is usual; however, for probability-based tests
such as the triangle test, it is important to specify the level of significance observed in addition to the cut-off level.

In early fish tainting assessment studies, many participants masticated and ingested spiked or OSPW-exposed fish samples. Because of the increasing knowledge regarding the toxicity of some OSPW chemicals, panelists may no longer taste spiked fish samples but rather must assess taint via odor detection.

**COMPONDS THAT MAY PLAY A ROLE IN FISH TAINTING**

**Hydrocarbons and heterocyclic compounds**

In 1982, fires and equipment failure at Suncor resulted in a spill of coker distillate fractions into a wastewater pond (Birkholz et al. 1987). For 10 weeks following the incident, more than 50 tons of oil and grease were released into the Athabasca River. Birkholz et al. (1987) analyzed the water soluble fraction of the oil from the surface of the wastewater pond and found alkylated benzenes, benzo thiophenes and dibenzo thiophenes (Figure 1). Following this release of hydrocarbons into the Athabasca River, the downstream commercial fishery was closed and there were reports of walleye and lake whitefish with ‘petroleum-like off-flavors’ (Jardine & Hrudey 1988).

Rogers et al. (2007) exposed rainbow trout (Oncorhyncus mykiss) to dilutions of OSPW and extracted the muscle tissue to search for PACs. They suggested that an analytical approach could help identify the compounds present in exposed fish and would aid in developing a fingerprint for tainted fish. Their method could detect naphthalene in fish tissue as low as 0.05 mg/kg but the authors did not detect any PACs in fish exposed to OSPW. Rogers et al. (2007) reported that fish exposed to model OSPW compounds had distinct odors of naphthalene and benzo thiophene.

**Naphthenic acids or acid-extractable organics**

Grewer et al. (2010) discussed the term ‘NAs’ in detail and demonstrated that 71–89% of the components in this toxic fraction of OSPW, commonly referred to as ‘NAs’, do not fit the chemical formula C_{n}H_{2n+2}O_{2} that is representative of the classical NAs. Thus, Grewer et al. (2010) recommended using the term ‘oil sands tailings water acid-extractable organics’ (OSTWAEO) rather than ‘NAs’ to describe this portion of OSPW. Throughout this paper, we use the term ‘OSTWAEO’, although the cited publications used the older, ambiguous term ‘NAs’, which can also include some phenols (Brient et al. 1995) that are known to cause fish tainting (Figure 1). A few commercial sources of NAs have been used in fish tainting studies. We refer to these preparations as ‘NAs’ with the commercial source provided (e.g. Merchem NAs).

Edge et al. (2010) collected OSTWAEO from Syncrude’s Pond 9 to use for sensory studies. They reported an odor detection threshold in walleye of 12 mg OSTWAEO/kg. This detection threshold can be used to estimate the tainting potential of OSPW and EPL. Given the low bioconcentration factor for Merchem NAs in muscle tissue, approximately 2–4 (Young et al. 2011b), and the odor detection threshold for OSTWAEO of 12 mg/kg (Edge et al. 2010), Young et al. (2011a) estimated that EPL containing OSTWAEO above 3 mg/L would have the potential to taint fish. All OSPW currently stored on site contain OSTWAEO at concentrations exceeding this estimated tainting level.

In a study done by Young et al. (2008), 23 fish, including walleye, northern pike, lake whitefish and white sucker (Catostomus commersoni), were caught from the Athabasca River, Clearwater River or Lake Athabasca and analyzed for ‘NAs’. Four of the fish from the Athabasca River, one from each species, were found to have detectable concentrations of ‘NAs’ at concentrations from 0.2 to 2.8 mg/kg. This concentration range has been estimated to be below the tainting threshold (Young et al. 2011a), suggesting that fish in the Athabasca River are unlikely to be tainted by OSTWAEO.

Commercial NAs or OSTWAEO smell differently in various substances and with increasing concentrations. Edge et al. (2010) used a trained panel to determine the odor detection threshold for Merchem and Acros NAs and OSTWAEO (from Syncrude’s Pond 9) in phosphate buffer and in fish. The odor descriptions given by the trained panelists differed between phosphate buffer and fish for the same source of NAs; Acros NAs were given ‘oil’ and ‘plastic’ descriptions; Merchem was described as ‘gasoline’; and OSPW...
NAs as ‘gasoline’ and ‘tar-like’. Descriptors for the detection threshold concentrations varied compared with higher concentrations, suggesting that the odor of NAs may depend on their concentration.

**FISH TAINTING CONCERNS IN END PIT LAKES (EPL)**

EPL will be constructed from mined-out oil sands pits located north of Fort McMurray, Alberta (Westcott 2007). EPL are man-made reclamation ponds that store different processed oil sands by-products (soft tailings) and are covered with various cap waters. The tailings used to fill the bottom of the pit can include mature fine tailings (MFT), thickened tailings and consolidated or composite tailings (CT). Cap water may be composed of water from the Athabasca River, runoff, process waters, pore water and precipitation. Wayland et al. (2008) analyzed PACs in four sediments from experimental wetlands at an oil sands operation. PACs ranged from ~1.2 to 20 μg/g of sediment (dry wt). Pore water from soft tailings also contains process-related chemicals. Madill et al. (2001) extracted pore water from Mildred Lake settling basin (MLSB) to estimate a total of 2.6 μg PACs/L OSPW. One of the main reasons for the development of EPL is to bioremediate chemicals in the soft tailings. Successful bioremediation should result in clean, non-toxic water which can sustain biological life. Reclaimed sites must meet the Alberta Environment criteria for self-sustaining ecosystems (Government of Alberta 2011).

Toxicity is a major issue for the success of EPL as functioning ecosystems. If there is a large quantity of soft tailings in an EPL, the water may be initially toxic to aquatic life because of the concentrations of OSTWAEO (MacKinnon & Boerger 1986). OSTWAEO are not biodegraded easily (Scott et al. 2005) and can be taken up by fish (Young et al. 2007, 2011b). Nero et al. (2006) used yellow perch (Perca flavescens) and goldfish (Carassius auratus) for a 3-week exposure to samples from several tailings ponds, including MLSB. Mortality was not observed in any of the pond waters; however gill and liver pathological indices suggested sublethal effects of exposure to high salinity, OSTWAEO or PACs found in Syncrude’s Pond 5 water. In addition, van den Heuvel et al. (1999a, b, 2000) stocked yellow perch into some different experimental ponds and showed that with exposure to PACs, disease increases, though no effect on reproduction and growth was observed. Fish from these exposure studies were not subjected to sensory analyses.

Initial biological concerns regarding EPL are the growth and survival of plants and invertebrates. Aerobic microbial biodegradation occurs in tailings ponds, which should decrease the concentrations of OSTWAEO and other compounds, helping to sustain aquatic life (Han et al. 2008). The EPL will go through stages, over decades, to reach the goal of becoming biologically active, self-sustaining and functional aquatic ecosystems (Westcott 2007). At any stage, the quality of the water in the EPL will influence fish survival and tainting.

**FISH SPECIES OF THE ATHABASCA REGION**

Many species of freshwater fish are found along the Athabasca River and its tributaries, such as arctic grayling (Thymallus arcticus), goldeye (Hiodon alosoides), lake trout (Salvelinus namaycush), lake whitefish, mountain whitefish (Prosopium williamsoni), northern pike, walleye, white sucker and yellow perch. For the purpose of this review, lake whitefish, northern pike and walleye have been described (Table 1) because they are commonly caught and consumed by aboriginal people in the Athabasca region (Brenda Miskimmin, Summit, Environmental Consultants Ltd, personal communication). The fish of the Athabasca River are important to many First Nations groups, as a source of food and income, and to commercial fisheries and sport fisherman along the river.

The fish species found in the Athabasca River basin are not typically used for sensory studies of fish taint. Many species native to the Athabasca River are difficult to rear in the laboratory. Native species used for fish health studies during exposure to OSPW include fathead minnows (Pimephales promelas) (Siwik et al. 2000; Kavanagh et al. 2011) and yellow perch (van den Heuvel et al. 1999a, b; Nero et al. 2006; Peters et al. 2007). Rainbow trout have been most commonly used in sensory studies after live exposure to OSPW or compounds in these waters (Tables 2 and 3; Rogers et al. 2007). Research species that are maintained in the laboratory can have the advantage of known disease...
Table 2 | Early sensory studies with native and non-native fish to the Athabasca River

<table>
<thead>
<tr>
<th>Reference and fish details</th>
<th>Compounds or OSPW tested</th>
<th>Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dromey (1987)</td>
<td>Benzothiophene, dibenzothiophene</td>
<td>Panelists preferred the taste of exposed rainbow trout over spiked fillets. The odor detection threshold of benzothiophene may be ≤0.01 mg/kg. Considerable individual variation was observed</td>
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<tr>
<td>Rainbow trout</td>
<td></td>
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<tr>
<td>Spiked and live exposure</td>
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</tr>
<tr>
<td>Jardine &amp; Hrudey (1988)</td>
<td>Alkylated benzenes, alkylated thiophenes, alkylated naphthalenes, benzothiophene, dibenzothiophene, 2,5-dimethylphenol</td>
<td>Chemicals with higher MW have higher detection thresholds and are less potent. Naphthalene, benzothiophene and 2,5-dimethylphenol had the lowest detection thresholds, and thus had the strongest capability to cause taint in fish</td>
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<tr>
<td>Walleye</td>
<td></td>
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<td>Spiked fillet</td>
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<tr>
<td>Koning &amp; Hrudey (1992)</td>
<td>Fresh tailings pond water, dilute fresh tailings pond water (6%), aged tailings pond water (1 year), catchment basin water</td>
<td>Fresh tailings pond water had the highest detectable taint of the four wastewaters. Phenols, cresols and dimethylphenols were found in fresh tailings pond water and in fillet tissue and bile. All tailings pond-derived water was found to significantly (p ≤ 0.05) taint fish</td>
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<tr>
<td>Rainbow trout</td>
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<td>Live exposure</td>
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<tr>
<td>Diversified Research</td>
<td>Syncrude Pond 1, Mildred Lake, Beaver Creek Reservoir, Syncrude Ponds 3 and 4 (combined), Syncrude Pond 5, Syncrude Pond 6</td>
<td>Fish exposed to Mildred Lake and Ponds 3 and 4 (combined) were significantly different (p ≤ 0.05) from control Pond 1 fish. A preference test compared Mildred Lake, Ponds 3 and 4 (combined) and Pond 1 fish. There was no significant preference (p ≤ 0.05) for the three samples tested. Compounds in Ponds 3 and 4 (combined) have the potential to taint rainbow trout</td>
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<tr>
<td>Laboratories Ltd (1992)</td>
<td></td>
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</tr>
<tr>
<td>Rainbow trout</td>
<td></td>
<td></td>
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<tr>
<td>Live exposure</td>
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</tr>
<tr>
<td>Athabasca River water in the lab, Athabasca River water in the field, 0.5% Suncor refinery effluent water, Control water, 0.5% Tar Island dyke water</td>
<td>Fish exposed to 0.5% Tar Island dyke water were found to taste different from fish exposed to Athabasca River water. Fish exposed to 0.5% refinery effluent water were least preferred in a preference test. Refinery effluent water at 0.5% is believed to cause taint in fish</td>
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<tr>
<td>Golder Associates Ltd (1996)</td>
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<tr>
<td>Rainbow trout</td>
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<td>Live exposure</td>
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*These 0.05 ha experimental ponds were established in 1989. Pond 1 contained no MFT or OSPW, with a water cap of muskeg surface runoff. Ponds 3 and 4 contained MFT with a water cap of muskeg surface runoff. Pond 5 contained MFT and OSPW from MLSB. Pond 6 contained N and P fertilizer, MFT and a water cap of muskeg surface runoff.

background, and less stress is involved in their culture and transport. It is important to keep in mind that various fish species may take up chemicals from the environment differently, often depending on their relative lipid contents (Heras et al. 1993).

**EARLY FISH TAINTING STUDIES IN THE ATHABASCA OIL SANDS REGION**

The earliest report of ‘off flavors’ in fish near oil sands operations was in 1982, after discharged hydrocarbons leaked into the Athabasca River from Suncor’s oil sands plant (Birkholz et al. 1987; Jardine & Hrudey 1988; Lockhart et al. 2002; The Royal Society of Canada Expert Panel 2010). This spill into the Athabasca River was investigated using laboratory experiments with lake whitefish exposed to oil sands plant effluent (Lockhart et al. 2002). Whitefish fillets were confirmed to be tainted by sensory panel taste and odor analysis. Research to identify compounds that could play a role in fish tainting has continued since this initial episode.

The first human sensory studies pertaining to fish tainting in the Athabasca oil sands region used sensory science methodologies that are less common or currently out of favor with sensory scientists. The reports highlighted in this review include works that are unpublished and do not meet modern sensory science standards, but are included...
because they did give insight into the potential for some OSPW to cause fish tainting.

Early sensory science studies with fish native and non-native to the Athabasca Region are outlined in Table 2. Very few of these studies used fish species native to the Athabasca River, which may impact the level of chemical uptake by the fish.

Initial sensory research involving potential fish tainting compounds and detection thresholds was conducted at the University of Alberta in the 1980s following the Suncor oil spill. Dromey (1987) studied the ability of benzothiophene and dibenzothiophene to taint rainbow trout. An 11-member trained panel assessed benzothiophene in both exposed and spiked fish. Eight directional paired comparison tests, in ascending concentration order, were completed to identify detection thresholds of benzothiophene. Panelists were asked to taste and smell the fish to identify the intensity of the tainted sample.

The benzothiophene detection threshold in exposed fish was determined to be 0.04 mg/kg. However, many panelists could detect taint in the lowest concentration presented to panelists (0.01 mg/kg), thus further sensory testing would be required at concentrations below 0.01 mg benzothiophene/kg to accurately determine the detection threshold of benzothiophene in rainbow trout. Dromey (1987) observed a considerable amount of individual variability in olfactory acuity among trained panelists for benzothiophene. The results of Dromey (1987) indicate that the actual detection threshold of benzothiophene in fish may be less than 0.01 mg/kg and that potential variability among panelists should be considered during the screening process.

Jardine & Hrudey (1988) used the Consistent Series Threshold Method for detecting oil sands wastewater chemicals in walleye by sensory evaluation (Table 2). Eight compounds (naphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, p-xylene, benzothiophene, dibenzothiophene and 2,5-dimethylphenol) were presented in spiked walleye to at least nine trained panelists for screening odor and taste detection. Because thiophene, 2-methylthiophene, toluene and mesitylene were difficult for panelists to detect, these chemicals were not pursued for the detection threshold evaluation.

<table>
<thead>
<tr>
<th>Reference and fish details</th>
<th>OSPW or commercial chemicals tested</th>
<th>Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>LeBlanc et al. (2000)</td>
<td>Fresh CT waters at concentrations of 10, 1, 0.1 and 0.01% v/v from Suncor, Syncrude and Albian Sands</td>
<td>All samples were significantly different ($p \leq 0.05$) in aroma and flavor within sets of samples of the same concentration. Suncor, Syncrude and Albian CT waters at dilutions of 0.01% v/v were found to taint fish. Potential fish tainting chemicals may smell different at increasing concentrations</td>
</tr>
<tr>
<td>Edge et al. (2010)</td>
<td>0.05–1.7 mg Merichem NAs/kg 3–21 mg Acros NAs/kg 6–22 mg OSTWAEO/kg</td>
<td>Thresholds of Acros NAs (&gt;21 mg/kg), Merichem NAs (0.6 mg/kg) and OSTWAEO* (12 mg/kg) in fish were all significantly different ($p \leq 0.05$) from each other, revealing that odor detection thresholds vary with the source of organic acids used to spike the fish</td>
</tr>
<tr>
<td>Barona et al. (2011)</td>
<td>Athabasca River near oil sands mining operations, McGregor Lake, Buck Lake</td>
<td>Lake whitefish from Buck Lake were preferred significantly more ($p \leq 0.05$) than lake whitefish from McGregor Lake. There was no significant difference in preference among walleye or northern pike from any of the three basins. Negative comments such as ‘oil/tar flavor’ were provided for all three fish species caught in the Athabasca River. There was no evidence that fish from the Athabasca River were tainted</td>
</tr>
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</table>

*From a 1 ha pond (designated as Pond 9) that was established in 1993 by Syncrude. It contained 50,000 m$^3$ OSPW from MLSB with no MFT.
Odor detection thresholds varied greatly among the compounds tested by Jardine & Hrudey (1988). In general, chemicals with a higher molecular weight (MW) had a higher detection threshold and were perceived to be less intense. Naphthalene had a detection threshold of 0.33 mg/kg, whereas 1-methylnaphthalene, 2,6-dimethylnaphthalene, dibenzothiophene and benzothiophene were detected at 1.38, 12.2, 4.67 and 0.12 mg/kg, respectively. Compounds which have intermediate vapor pressures (like naphthalene and benzothiophene) do not dissipate quickly and were detected by panelists more easily than some of the other oil sands chemicals tested. Of the compounds tested, naphthalene, benzothiophene and 2,5-dimethylenol had the lowest detection thresholds and may cause fish tainting if they are present in OSPW at significant concentrations.

Koning & Hrudey (1992) used sensory and analytical methods to compare rainbow trout that were exposed for 24 h to one of four test conditions: (1) fresh tailings pond water treated to reduce the acute toxicity to fish; (2) fresh tailings pond water diluted to 6%; (3) tailings pond water aged for 1 year; and (4) catchment basin water – water that had seeped through the tailings pond dykes and was diluted with water from precipitation runoffs (Table 2). A paired comparison test was completed by a 10-person trained panel to evaluate the degree of taint in fish tainting threshold range of 70–400 μg/L (Koning & Hrudey 1992). The concentration of dimethylphenols detected in the fish tissue was 210 μg/kg fish. Alkylphenols and thiophenols (phenylmercaptan) originating from pulp and paper mills have been reported to taint fish (Lindsay & Heil 1992). Other petroleum compounds, including alkylated benzenes and benzothiophene, were present in the exposure water which suggests that there may be other chemicals involved in causing the taint observed (Koning & Hrudey 1992).

Following research directed at identifying individual tainting compounds and their detection thresholds, some investigators began to study the fish taint potential of different OSPW or tailings-contacted waters. In a study for Syncrude, Diversified Research Laboratories Ltd (1992) assessed if there were perceivable differences among rainbow trout exposed to Syncrude’s Pond 1 water or five other waters listed in Table 2. A double triangle test, with the sequential serving of two triads, was used to compare fish exposed to control Pond 1 with fish exposed to the other waters. Twelve participants, whose level of training was not described, were given three blinded samples (two control fish samples from Pond 1 and one sample of fish exposed to another water, or vice versa) and told to taste each sample and choose the ‘odd’ sample. After choosing the ‘odd’ sample, panelists indicated the degree of difference between the two samples and were asked to indicate if they preferred the ‘odd’ or ‘duplicate’ sample. This process was repeated for each of the five water sources. Based on the number of panelists who correctly identified the ‘odd’ sample in both successive tests, with \( p = 1 / 9 \), a Z score was calculated to determine if there was a statistically significant difference between samples.

Fish exposed to water from Ponds 3 and 4 (combined) or Mildred Lake water were found to be significantly different \( (p \leq 0.05) \) from control Pond 1; each had six out of 12 panelists correctly identifying the ‘odd’ sample in both tests. However, the statistical chart for triangle tests (Roessler et al. 1978) indicates that eight out of 12 panelists must correctly identify the ‘odd’ sample for the difference to be considered statistically significant \( (p \leq 0.05) \). The statistical analysis of the double triangle test was not clearly stated in the Diversified report (Diversified Research Laboratories Ltd 1992). Although panelists identified the odd sample, there was no significant difference in preference between fish exposed to control Pond 1 water and fish exposed to any of the other waters. There was no significant difference \( (p \leq 0.05) \) between fish from Pond 5 and control Pond 1; however, individuals who correctly identified the ‘odd’ sample in the double triangle test described Pond 5 fish as ‘inedible fishy/solvent/rancid oil flavor’ and ‘very strong chemical/crude oil flavor’. This indicates that some panelists may have identified taint in the fish held in
Pond 5 OSPW, despite the lack of significant difference between the OSPW-exposed fish and the control. As indicated by Dromey (1987) in early studies of fish tainting by oil sands chemicals, individual differences in olfactory perception of potential tainted chemicals may occur. Diversified Research Laboratories Ltd (1992) showed that there may be chemicals in Syncrude’s MFT, OSPW, and Mildred Lake water that can cause taint in rainbow trout.

In a report to Suncor, Golder Associates Ltd (1996) used both a double triangle test and a double overall preference test to evaluate taint in rainbow trout (Table 2). Fish were exposed to five different water samples for 10 days: Athabasca River water in the laboratory; Athabasca River water in the field; 0.5% refinery effluent water; 0.5% Tar Island dyke water; or control laboratory water. The sampling location of the Athabasca River was not reported.

The double triangle test indicated that fish exposed to 0.5% Tar Island dyke water or 0.5% refinery effluent water tasted different than fish exposed to Athabasca River water in the laboratory or field. Control fish were also found to taste different than Athabasca River water-exposed fish. The control exposed fish were significantly (p < 0.05) preferred by panelists to the other fish samples. It was concluded that fish exposed to 0.5% refinery effluent waters were significantly (p < 0.05) rejected by panelists; we would interpret the term ‘rejected’ as ‘least preferred by panelists’ which is the proper sensory terminology.

**RECENT SENSORY RESEARCH ON FISH TAINTING AND THE OIL SANDS**

LeBlanc et al. (2000) exposed live rainbow trout for 10 days to different concentrations of fresh CT waters to evaluate the aroma and flavor tainting potential of waters which originated from three major oil sands companies: Syncrude, Suncor and Albian Sands. Eleven trained panelists participated in the sensory panel and evaluated the aroma and flavor of each sample using a 10-point Difference-from-Control test. Panelists were also encouraged to write descriptors for the control and unknown samples.

Fish exposed to all concentrations of CT waters were significantly (p < 0.05) different from each other and the control (Table 3). Syncrude samples were described by panelists as ‘strong’, ‘fishy’ and ‘oily with sweet notes’ whereas Suncor CT water samples were described as ‘fishy’, ‘metallic’, ‘oily’ and ‘sweet with bitter, musty and sour notes’. ‘Sour’, ‘oily’, ‘strong’ and ‘fishy with sweet, bitter and musty notes’ were used to describe Albian CT water-exposed fish aroma and flavor. LeBlanc et al. (2000) concluded that dilutions of the CT waters from each of the three oil sands companies had the potential to taint fish at 0.01% v/v. Additionally, CT waters from each company induced different sensory descriptors that varied with concentration.

The results of the preceding studies indicate that OSPW, CT waters, and some experimental pond waters (that mimic EPL) have the potential to taint fish. Interestingly, panelists can distinguish between fish exposed to Athabasca River water compared with laboratory control water (Golder Associates Ltd 1996). This result does not confirm anecdotal reports that fish of the Athabasca River are tainted and taste or smell different than they used to; it does suggest that people are sensitive tools for the analysis of fish tainting. Athabasca River water may also contain compounds other than OSPW constituents that can influence the sensory properties of fish.

More recent research on fish tainting in the oil sands region focused on the potential for OSTWAEO (extracted using the method described by Edge et al. 2010) and commercial NAs to taint fish (Table 3). It has been estimated that waters containing OSTWAEO above 3 mg/L would have the potential to taint fish (Young et al. 2010). Aboriginal people in the Athabasca region rely on fish for food and income, therefore the possibility of tainted fish is a great concern.

Edge et al. (2010) determined odor detection thresholds of commercial NAs (Acros and Merichem) and OSTWAEO (from Syncrude Pond 9) in walleye fillets using the 3-AFC method. Buffer solutions of each of these three preparations were first used to familiarize panelists with their odors and to obtain an odor detection threshold in phosphate buffer for both the general population (n = 306) as well as a trained panel (n = 10). Additionally, the trained panel evaluated the odor of spiked fish. The geometric mean was used to calculate mean detection thresholds from individual thresholds for each group of participants. An ANOVA followed by a Tukey’s test was used to determine any significant (p < 0.05) differences among the mean threshold values for each preparation.
The trained panel detected Merichem NAs at a significantly \((p \leq 0.05)\) lower odor threshold \((0.04 \text{ mg/L})\) than OSTWAEO (Pond 9) and Acros NAs in buffer \((1 \text{ and } 1.5 \text{ mg/L}, \text{ respectively})\) \((\text{Edge et al. 2010})\). The general population detection threshold followed the same trend; Merichem NAs had the lowest detection threshold \((0.2 \text{ mg/L})\) followed by Pond 9 OSTWAEO \((2.5 \text{ mg/L})\) and then Acros NAs \((4.8 \text{ mg/L})\). There was a significant difference \((p \leq 0.05)\) among all odor detection thresholds measured in fish. Merichem NAs had the lowest detection threshold \((0.6 \text{ mg/kg})\) whereas Pond 9 OSTWAEO had a detection threshold of \(12 \text{ mg/kg}\). Acros NAs were undetectable by panelists at \(21 \text{ mg/kg}\); the highest concentration tested.

\textit{Edge et al. (2010)} also exposed live rainbow trout to \(3 \text{ mg Merichem NAs/L}\) for \(10 \text{ days}\). A triangle test was performed by \(16 \text{ trained panelists}\) to determine if the odor of the exposed rainbow trout was different from the control fish. When steamed samples were evaluated, a statistically significant nine out of \(16 \text{ panelists}\) could select the Merichem NAs-exposed sample. The authors concluded that fish exposed to Merichem NAs can be tainted under these exposure conditions.

\textit{Barona et al. (2011)} performed a sensory preference panel using three species of fish from three river basins in Alberta (Table 3). Walleye, lake whitefish and northern pike were caught in the Athabasca River (near oil sands mining operations), Buck Lake (in the North Saskatchewan River basin) and McGregor Lake (in the South Saskatchewan River basin). The purpose of this study was to determine if fish caught in the Athabasca River are preferred less than the same species of fish caught in other parts of Alberta. It was hypothesized that if fish from the Athabasca River near the oil sands were tainted, they would be the least preferred of the fish from all three sampling locations.

Fish were collected in September and stored at \(-20 \text{ °C}\) for \(4 \text{ months}\) prior to sensory tests \((\text{Barona et al. 2011})\). Forty to \(44 \text{ panelists}\) participated in each of the sensory panels. Three panels were conducted, one for each type of fish. Panelists were asked to rank the three samples as (1) being the most liked and (3) being the least liked. In addition to the ranking of samples, participants were also asked to write what in particular they liked or disliked about each sample. Friedman’s Test for Ranked Data was used to determine if there was a significant difference \((p \leq 0.05)\) in the liking of fish from the three different river basins.

Lake whitefish from Buck Lake were preferred significantly more \((p \leq 0.05)\) than lake whitefish from McGregor Lake. Panelists described the lake whitefish from McGregor Lake as very ‘mushy’ in texture, which made it unappealing. Lake whitefish from the Athabasca River were not significantly different \((p \leq 0.05)\) than lake whitefish from Buck Lake or McGregor Lake. The results from the ranking indicated that there was also no significant difference \((p \leq 0.05)\) in preference for walleye or northern pike from the Athabasca River, Buck Lake or McGregor Lake. Based on the preference ranking results and descriptions of the fish from the three basins, it could not be concluded that fish from the Athabasca River sampled for the preference test were tainted.

\section*{CONCLUSIONS, LIMITATIONS AND RECOMMENDATIONS}

The oil sands are an important resource in Alberta, and their extraction and processing are part of the increasing development along the Athabasca River. The extraction of bitumen from the oil sands ore, primarily through mining operations north of Fort McMurray, produces large volumes of OSPW that can contain many compounds with fish tainting potential. However, to date, the reports of tainted fish in the Athabasca region are anecdotal. There appear to be no analyses of wild fish that were considered to be tainted. It is vital to determine if current oil sands operations cause tainting. This will require fish, that are deemed to be tainted, to be analyzed to determine which compounds cause taint. Fish caught and tasted by local fisherman should be the source of these fish for analyses. Thus, we suggest that fish tainting be included in oil sands monitoring programs. A questionnaire could be distributed to fishermen who perceive they have caught a tainted fish. The tainted fish could be quickly frozen and sent with the completed questionnaire to a recognized laboratory to determine which compounds might be causing the taint. Having these samples and analyses will provide a foundation on which to base continuing studies of fish tainting in the region.

Many of the early studies of fish tainting by OSPW lack modern sensory science rigor. Often, the techniques
employed are improper and the statistical analyses, when described, are lacking. Future studies of fish tainting in the oil sands region should include updated sensory methods and, given the groundwork developed by previous records, will address some of the challenges identified. For example, studying individual OSPW compounds may not reflect the tainting potential of the waters as a whole, and there appears to be considerable variability among panelists detecting the taste and odors of OSPW-exposed fish. In addition, better descriptions and detailed chemical analyses of OSPW samples used in fish exposure studies should be reported.

Although acid-extractable organics in the river do not appear to cause taint, other components of OSPW, phenols and other volatiles (such as those studied by Koning & Hrudey 1992), or mixtures of these compounds, may play a role in fish tainting. Future work should assess the potential for other OSPW components, S and N heterocycles, and two- and three-ring PACs, to contribute to fish tainting in rivers or EPL. Research to develop methods with lower analytical detection limits will help determine if OSPW compounds can be detected in exposed fish. Clearly, further human sensory research is required to investigate fish tainting in the Athabasca region near oil sands operations. In the future, standard sensory science procedures will be required to perform experiments to assess the potential for EPL water to taint fish.

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