Use of Stable Carbon and Nitrogen Isotopes to Trace Natural and Anthropogenic Inputs into Riverine Systems in the Athabasca Oil Sands Region

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Stable isotopes of carbon and nitrogen in fish were examined as a potential tracer of exposure to oil sands constituents in naturally eroded environments and in areas of anthropogenic activity (municipal and industrial effluent discharges; oil sands surface mining) within the Athabasca River drainage basin of northern Alberta, Canada. Longnose sucker (Catostomus catostomus), trout-perch (Percopsis omiscomaycus), and slimy sculpin (Cottus cognatus) showed changes in δ13C values with the river gradient. Site-specific differences in the δ13C values of fish were more pronounced for the small-bodied fish species in the lower reaches of a tributary (slimy sculpin) and immediately downstream of tributary inputs along the Athabasca River (trout-perch), where potential exposure to the oil sands constituents is elevated. There were also species and site-specific trends for δ15N values. Site-specific trends attributed to municipal or industrial effluent discharge or tributary inputs may prove to be a useful tool for defining residency on the oil sands deposit. This study has provided baseline data of isotope values for fish species which are currently used (longnose sucker) or may be used in future environmental effects monitoring programs. Defining residency and exposure to the oil sands deposit is critical to establishing exposure-response relationships, particularly since there are new expansions to oil sands mining operations.

Key words: riverine fish, stable carbon and nitrogen isotopes, oil sands constituents, industrial and municipal discharges

Introduction

Since the early 1930s oil sands have been mined from the Athabasca oil sands (AOS) deposit, the largest of four deposits in northern Alberta, Canada. The AOS deposit encompasses an area of approximately 46,000 km², the majority of which is located within the lower Athabasca River drainage basin (58,000 km²) (AEUB 2001; Conly et al. 2002). Oil sands in this region, found mainly in the McMurray Formation, contain estimated bitumen reserves of 206 x 10⁹ m³ (AEUB 2001; Conly et al. 2002). Oil sands mining has occurred intermittently in the McMurray Formation, and many areas are readily mined using surface mining technology. The Athabasca River and several tributaries flowing through this region are exposed to the McMurray Formation intermittently in the riverbed and/or continuously in the valley walls (Conly et al. 2002).

Recent studies in the lower Athabasca River basin have provided valuable information on the spatial distribution, nature, and concentrations of oil sands constituents (Headley et al. 2001; Conly et al. 2002; Golder Associates 2002), and the effects on fish species (Tetreault et al. 2003a, 2003b; Colavecchia et al. 2004; Colavecchia et al. 2006). Levels of alkylated polycyclic aromatic compounds (PACs) as high as 34.7 μg/g have been found in tributary sediments compared with levels of <2 μg/g parent and alkylated PACs in Athabasca River sediments (Headley et al. 2001). Parent and alkylated PACs, naphthenic acids (NAs), benzothiophenes, and methylcarbazoles have also been identified in material extracted from semipermeable membrane devices deployed in rivers within the oil sands area (Parrott et al. 1996). Naphthenic acids occur naturally at concentrations of 1 to 2 mg/L in the Athabasca River in the region of the oil sands deposit with higher levels (6 to 9 mg/L) in sediment porewater in a region of mining activity (Tar Island Dyke) (FTFC 1995). In addition, nutrient inputs to the Athabasca River from upstream reaches as well as municipal and industrial discharges in the area of Fort McMurray have been examined as part of the Northern River Basins Study (Culp et al. 2000; Scrimgeour and Chambers 2000).

Increased oil sands mining activity and refinery development are recognized areas of environmental concern in this northern river ecosystem (Wrona et al. 2000). Both the oil sands industry and government agencies acknowledge the potential for release of reclamation and operational water from the oil sands facilities to the Athabasca River (OSWRTWG 1996). Currently, the Suncor Incorporated Athabasca Oil Sands Project discharges effluent into the Athabasca River at a rate of approximately 35,000 m³/day (Scrimgeour and Chambers 2000). Due to the natural spatial heterogeneity
of contact of the oil sands formation with the Athabasca River and its tributaries, and the potential for additional oil sands mining discharges, defining residency and levels of exposure to oil sands constituents for fish species is difficult. This work was initiated to examine the use of stable isotopes ($\delta^{13}$C and $\delta^{15}$N) as indicators of exposure of fish to oil sands constituents within the Athabasca River basin.

Stable isotope analysis (SIA) has been used in freshwater ecotoxicological studies to trace sewage, pulp mill effluents, and persistent organic pollutants (Kidd et al. 1994; Kiriluk et al. 1995; Wassenaar and Culp 1996; Farwell 2000; Stapleton et al. 2001; Wayland and Hobson 2001) as well as oil in marine environments (Coffin et al. 1997). Petroleum and its associated hydrocarbons have had $\delta^{13}$C values reported in the range of approximately -25 to -30‰ (Aggarwal and Hinchee 1991; Kelley et al. 1997; Lapham et al. 1999). Oil sands constituents, specifically the toxic constituents, PACs and NAs, have some potential to be degraded (Kropp and Fedorak 1998; Headley and McMartin 2004; Clemente and Fedorak 2005; Quagraine et al. 2005). In addition, PACs are present in invertebrates exposed to oil sands mature fine tailings (Ganshorn 2002). While there is a potential for hydrocarbons from oil sands sources to overlap with the $\delta^{13}$C values of other allochthonous and autochthonous sources of carbon fuelling riverine systems (Rounick and Winterbourn 1986; France 1995), in this preliminary study we were interested in establishing site-specific $\delta^{13}$C trends. Nitrogen stable isotopes ($^{15}$N, $^{14}$N) were used to define trophic levels (DeNiro and Epstein 1981) and to determine the influence of nutrient sources (municipal and industrial effluent discharges) on the $\delta^{15}$N values of fish species.

The objective of this study was to evaluate the use of stable isotopes of carbon ($^{13}$C,$^{12}$C) and nitrogen ($^{15}$N, $^{14}$N) as a tool to trace exposure of fish to oil sands constituents in naturally eroded environments and in areas of anthropogenic activity (municipal and industrial effluent discharges; oil sands surface mining) along the Athabasca River and its tributaries. In the Athabasca River, a large-bodied species (longnose sucker, *Catostomus catostomus*) and a small-bodied sentinel species (trout-perch, *Percopsis omiscomaycus*) that differ in mobility and feeding habits, were examined. Longnose sucker, a highly mobile benthivorous species, were collected at sites upstream of the AOS deposit and on the AOS deposit. On the AOS deposit, longnose sucker and trout-perch were examined from sites upstream and downstream of municipal and oil sands industrial effluent discharges. Another small-bodied sentinel fish (slimy sculpin, *Cottus cognatus*) was used to examine site-specific isotope trends at upper (upstream of AOS deposit) and lower (on AOS deposit) reaches of the Steepbank River, a tributary of the Athabasca River.

### Materials and Methods

**Description of the Athabasca River Drainage Basin**

The Athabasca River is an unregulated river originating in the Rocky Mountains of western Alberta and flowing northeast through boreal mixed-wood regions to Lake Athabasca (Fig. 1). The Athabasca River drainage basin of 155,000 km² is a subbasin of the Arctic Ocean drainage basin (Chambers et al. 2000). The upper reaches of the Athabasca River and/or its tributaries (upstream of the Town of Athabasca) receive continuous discharge from numerous pulp mills and sewage treatment plants (Chambers et al. 2000; Scrimgeour and Chambers 2000). Further north, in the area of the AOS deposit, the landscape is dominated by boreal forest and muskeg (Conly et al. 2002). Oil sands, in close proximity to the surface, are actively mined by two oil sands companies with an annual production of 21.5 x 10⁶ m³ of bitumen with planned expansions to 66 x 10⁶ m³ by 2010 (AEUB 2001). At the town of Fort McMurray, the Athabasca River received a continuous discharge of 14,000 m³/d from the municipal sewage treatment plant (STP) in 1994, with nutrient inputs of 27 kg/d of total P and 344 kg/d day of total N (Scrimgeour and Chambers 2000). The mean annual flow of the Athabasca River at Fort McMurray is 650 m³·s⁻¹ with mean monthly flows of 180 m³·s⁻¹ in the winter and 1,400 to 1,500 m³·s⁻¹ in July (1994 data; as cited in Conly et al. 2002).
Downstream of Fort McMurray (>30 km) in the region of mining activity, water quality measurements in 2001 indicated low levels of total recoverable hydrocarbons (<0.5 mg/L) and naphthenic acids (NAs) (<1 mg/L) for sites upstream of the Steepbank and Muskeg rivers (Golder Associates 2002). However, historical measurements from upstream of the Steepbank River were as high as 20 mg/L of NAs (west side of the Athabasca River) and 2 mg/L of total recoverable hydrocarbons (Golder Associates 2002). Measurements of sediment quality in 2000 and 2001 showed higher levels of total extractable hydrocarbons (C11 to C30) ranging from 62 to 210 mg/kg upstream of the Steepbank River compared with 28 to 140 mg/kg further downstream at a site upstream of the Muskeg River (Golder Associates 2002). In the area of Tar Island Dyke (west side of the Athabasca River, approximately 35 km downstream of Fort McMurray), sediment porewater had elevated NAs concentrations (6 to 9 mg/L) (FTFC 1995). Effluent from the Suncor Incorporated Athabasca Oil Sands Project discharged into the Athabasca River (west side, approximately 37 km downstream of Fort McMurray) had low total P (7 kg/d) and total N (42 kg/d) compared with effluent from the Fort McMurray STP (Scrimgeour and Chambers 2000). Levels of oil sands constituents (mixtures of PACs, alkylated PACs, and NAs) ranging from 0.1 to 1 μg/L have been measured in oil sands refinery effluents (as cited in Wrona et al. 2000).

The Clearwater River is the largest tributary that discharges into the Athabasca River in the lower basin. The Clearwater valley walls, while flanked by the McMurray Formation, are not exposed to the McMurray Formation due to a layer of colluvium, with the exception of outcrops (Conly et al. 2002). Several small tributaries are exposed to the McMurray Formation, particularly in the lower reaches, in proximity to the discharge into the Athabasca River (Conly et al. 2002). Approximately 53% of the estimated mean annual suspended sediment load of 1.2 Mt in the region of the AOS deposit originates from the tributaries (35% from the Clearwater River, 18% from other tributaries), with the remainder coming from the upper reaches of the Athabasca (Conly et al. 2002).

The Steepbank River is 116 km in length with a gradient of 2.4 m/km in the upper reaches, and a steeper gradient of 5.7 m/km in the lower reaches (<20 km from confluence with the Athabasca River) (Barton and Wallace 1979). The geomorphology of the Steepbank River basin changes dramatically from unconsolidated material (sandy till, sand, and gravel layers and intermittent muskeg) of the North Steepbank River to shale and sandstones of the Clearwater Formation (overlain on the Fort McMurray Formation) upstream on the Steepbank River (Conly et al. 2002). In the lower reaches, the Steepbank River is incised into the oil sands of the McMurray Formation. The Steepbank River has natural sources of oil sands material with sediment PAC concentrations as high as 34.7 μg/g, but is not directly impacted by oil sands surface mining activity (Headley et al. 2001).

**Sampling Sites—Tributaries and Mainstream Athabasca River**

In the fall of 1999 (September 6 to October 4) and 2000 (September 8 to 29), longnose sucker were collected along the Athabasca River at one site upstream of the AOS deposit and two sites within the region of the AOS deposit (Fig. 1). Locations included: **LS upper AR**, upstream of the AOS deposit in the vicinity of Duncan Creek between the confluence of the Calling River and Pelican Portage (210 km upstream of Fort McMurray and 250 km upstream of the Suncor Incorporated discharge); **LS middle AR**, 5 km downstream of Fort McMurray on the oil sands deposit (sampled in 1999 only); **LS lower AR**, downstream of Tar Island Dyke and the Suncor Incorporated discharge (35 to 40 km downstream of Fort McMurray and upstream of the confluence of the Steepbank River).

Trout-perch were collected at three sites along the Athabasca River within the region of the AOS deposit in the fall of 2000 (September 10 to 16). Locations included: **TP upper AR**, upstream of the confluence of the Steepbank River (downstream of Fort McMurray and approximately 12 km upstream of the Suncor Incorporated discharge); **TP middle AR**, immediately downstream of the Suncor Incorporated discharge (approximately 37 km downstream of Fort McMurray and about 2 km upstream of the confluence of Steepbank River); **TP lower AR**, immediately downstream of the confluence of the Muskeg River.

In 2000 (September 10 to 16), slimy sculpin were collected along the Steepbank River at three sites: **SS upper SR**, upstream of the AOS deposit (approximately 21 km from the confluence with the Athabasca River); **SS middle SR**, downstream on the AOS deposit (approximately 16 km from the confluence); **SS-lower SR**, downstream of development on the AOS deposit (approximately 650 m from the confluence).

**Sample Collection and Stable Isotope Analysis (SIA)**

Fish were collected with backpack elctrofishers (trout-perch and slimy sculpin) or an electrofishing boat (longnose sucker). Sex, fork length, and total weight (and carcass weight for small-bodied fish) were determined. Dorsal white muscle samples for SIA were placed in 2-ml cryovials and immediately frozen in liquid nitrogen (-80°C) in the field prior to transport to the University of Waterloo. Longnose sucker tissue collected from 10 mature females and 10 mature males per site for each year were prepared for SIA. A minimum of 10 fish per site were analyzed for trout-perch and slimy sculpin. At the laboratory, samples were placed in a -20°C freezer prior to SIA preparation. Muscle samples were freeze-dried and ground with a ball mill grinder in preparation for SIA.
Prepared samples were analyzed for carbon (\(^{13}\text{C}/^{12}\text{C}\)) and nitrogen (\(^{15}\text{N}/^{14}\text{N}\)) isotope ratios using a Micromass VG Isochrom continuous-flow isotope ratio mass spectrometer at the Environmental Isotope Laboratory, Department of Earth Sciences, University of Waterloo. \(\delta^{13}\text{C}\) and \(\delta^{15}\text{N}\) values were calculated from the difference between the isotope ratio \((R = \text{^{13}C/^{12}C} \text{ or } ^{15}\text{N}/^{14}\text{N})\) of a sample and a reference standard using the following equation, \(\delta X \text{(parts per thousand, or per mille [‰])} = \left[\frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}}\right] \times 10^3\). The reference standards used to calculate the \(\delta^{13}\text{C}\) and \(\delta^{15}\text{N}\) values were Pee Dee Belemnite and atmospheric nitrogen (\(\text{N}_2\)), respectively. International Atomic Energy Agency standards were used to monitor an analytical precision of \(\pm 0.20\text{‰}\) and \(\pm 0.30\text{‰}\) for \(\delta^{13}\text{C}\) and \(\delta^{15}\text{N}\), respectively, within the range of linearity. For comparisons of the \(\delta^{13}\text{C}\) or \(\delta^{15}\text{N}\) values of different samples, a more negative value represented a decrease in the quantity of \(^{13}\text{C}\) or \(^{15}\text{N}\) relative to \(^{12}\text{C}\) or \(^{14}\text{N}\), respectively, and is referred to as \(^{13}\text{C}\) or \(^{15}\text{N}\) depletion. A more positive \(\delta^{13}\text{C}\) or \(\delta^{15}\text{N}\) value represents an increase \(^{13}\text{C}\) or \(^{15}\text{N}\) and is referred to as \(^{13}\text{C}\) or \(^{15}\text{N}\) enrichment.

**Statistics**

Data were presented as the mean ± the standard error of the mean (SEM) for fish parameters and stable isotope signatures. Significant differences in fish length and weight and stable isotopes were determined using a one-way analysis of variance (ANOVA) and Tukey’s post hoc test (pairwise comparisons). Statistical analyses were performed at \(\alpha = 0.05\) using SYSTAT 10.0 (SPSS, Chicago, Ill., U.S.A.).

**Results**

Isotope analyses of dorsal muscle for the three fish species examined in this study showed both species-specific and site-specific trends (Fig. 2). In the Athabasca River, trout-perch were \(^{15}\text{N}\) enriched relative to longnose sucker, which is indicative of different feeding habits between the two species. Site-specific trends included a trend toward \(^{15}\text{N}\) depletion of trout-perch at \(\text{TP middle AR}\) (downstream of Suncor Incorporated discharge) although it was not statistically different \((p \geq 0.135)\). The \(^{15}\text{N}\) enrichment of longnose sucker at \(\text{LS middle AR}\) (downstream of STP discharge) was found to be significantly different from \(\text{LS upper AR}\) \((p = 0.037)\). Slimy sculpin along the Steepbank River were more \(^{15}\text{N}\) depleted than fish from the Athabasca River. At the upstream site \((\text{SS upper SR})\), slimy sculpin were more \(^{15}\text{N}\) enriched compared with downstream sites on the deposit.

All fish species showed changes in \(\delta^{13}\text{C}\) along the river gradient (Fig. 3). The \(\delta^{13}\text{C}\) values of fish on the AOS deposit are more \(^{13}\text{C}\) enriched than bitumen collected from both the Syncrude mine site (-30.3‰) and from the Steepbank River (-30.2‰). Longnose sucker and trout-perch showed trends of \(^{13}\text{C}\) depletion at sites downstream of the Athabasca River on the AOS deposit (Fig. 3a).

![Fig. 2. Doral muscle \(\delta^{13}\text{C}\) and \(\delta^{15}\text{N}\) values (mean ± SEM) from longnose sucker (LS) (1999, 2000), trout-perch (TP), and slimy sculpin (SS) collected from the Athabasca and Steepbank rivers in September of 1999 and 2000.](image)

![Fig. 3. Muscle \(\delta^{13}\text{C}\) values (mean ± SEM) from (a) longnose sucker (LS) and trout-perch (TP) collected at distances along the Athabasca River (AR) upstream and downstream of the confluence of the Steepbank River, and (b) slimy sculpin (SS) collected along the Steepbank River (SR) at distances from the Athabasca River. The dashed lines estimate the boundary of the AOS deposit.](image)
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**Longnose sucker** δ¹³C values were not significantly different between **LS upper AR** located off of the AOS and either of the downstream sites on the AOS deposit (p ≥ 0.070). The ¹³C depletion of trout-perch at **TP lower AR** was significantly different from the upstream sites (p ≤ 0.004). A different isotope trend was evident for slimy sculpin from the Steepbank River with ¹³C depletion upstream of the AOS deposit and progressive ¹³C enrichment downstream (Fig. 3b).

There were no significant differences between sites for length and weight for slimy sculpin or trout-perch (Table 1), although there were differences in the size of longnose sucker between sites and years (Table 2). Of the three sites sampled in 1999, both male and female longnose sucker were generally longer and heavier at **LS middle AR**, however only males had significantly increased length and weight compared with **LS upper AR** (Table 2). Longnose sucker analyzed for SIA showed similar trends of increased length and weight at **LS middle AR** (Fig. 4a). Longnose sucker of similar size, particularly smaller fish (<1,050 g), tended to have ¹⁵N enriched muscle at **LS middle AR** compared with **LS upper AR** (Fig. 4b). Overall, longnose sucker from **LS middle AR** were larger in size and slightly more ¹⁵N enriched compared with the upstream and downstream sites (Fig. 4c).

Differences in longnose sucker size (length and weight) were also evident between the 1999 and 2000 collection years at the **LS lower AR** site (Table 2). Both male and female longnose sucker were significantly longer and heavier at **LS lower AR** in 2000 whereas no

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**TABLE 1.** Mean ± SEM (n) length and weight of mature male and female trout-perch (Athabasca River) and slimy sculpin (Steepbank River) collected in 2000.

<table>
<thead>
<tr>
<th>Species</th>
<th>Sex</th>
<th>Site</th>
<th>Fork length (cm)</th>
<th>Carcass weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trout-perch</td>
<td>F</td>
<td>TP upper AR</td>
<td>7.2 ± 0.1 (18)</td>
<td>3.19 ± 0.16 (18)</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>TP middle AR</td>
<td>7.3 ± 0.1 (21)</td>
<td>3.43 ± 0.16 (21)</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>TP lower AR</td>
<td>6.9 ± 0.1 (24)</td>
<td>2.82 ± 0.09 (24)</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>TP upper AR</td>
<td>6.7 ± 0.1 (26)</td>
<td>2.61 ± 0.07 (26)</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>TP middle AR</td>
<td>6.6 ± 0.1 (24)</td>
<td>2.64 ± 0.11 (24)</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>TP lower AR</td>
<td>6.3 ± 0.1 (22)</td>
<td>2.21 ± 0.12 (22)</td>
</tr>
<tr>
<td>Slimy sculpin</td>
<td>F</td>
<td>SS upper SR</td>
<td>7.1 ± 0.2 (17)</td>
<td>2.72 ± 0.27 (17)</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>SS middle SR</td>
<td>6.5 ± 0.2 (14)</td>
<td>2.16 ± 0.19 (14)</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>SS lower SR</td>
<td>6.9 ± 0.3 (17)</td>
<td>2.60 ± 0.28 (17)</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>SS upper SR</td>
<td>6.4 ± 0.2 (13)</td>
<td>2.18 ± 0.26 (13)</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>SS middle SR</td>
<td>7.1 ± 0.2 (11)</td>
<td>2.94 ± 0.18 (11)</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>SS lower SR</td>
<td>7.2 ± 0.2 (27)</td>
<td>3.00 ± 0.25 (27)</td>
</tr>
</tbody>
</table>

a Data from: Tetreault et al. 2003b; Tetreault 2002.
b TP = trout-perch; AR = Athabasca River; SS = slimy sculpin; SR = Steepbank River.

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**TABLE 2.** Mean ± SEM (n) fork length and weight of mature male and female longnose sucker collected at sites along the Athabasca River in 1999 and 2000.

<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>Sex</th>
<th>Length (cm)</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS upper AR</td>
<td>1999</td>
<td>F</td>
<td>42.5 ± 0.5 (21)</td>
<td>921 ± 38 (21)</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>F</td>
<td>42.3 ± 0.7 (20)</td>
<td>897 ± 43 (20)</td>
</tr>
<tr>
<td>LS middle AR</td>
<td>1999</td>
<td>F</td>
<td>44.3 ± 0.9 (18)</td>
<td>1,073 ± 77 (18)</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>F</td>
<td>42.4 ± 0.8 (20)</td>
<td>915 ± 39 (20)</td>
</tr>
<tr>
<td>LS lower AR</td>
<td>1999</td>
<td>F</td>
<td>48.3 ± 0.8 (20)</td>
<td>1,341 ± 72 (20)</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>F</td>
<td>43.4 ± 0.8 (20)</td>
<td>953 ± 70 (13)</td>
</tr>
<tr>
<td>LS upper AR</td>
<td>1999</td>
<td>M</td>
<td>37.6 ± 0.8 (19)</td>
<td>636 ± 39 (19)</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>M</td>
<td>38.4 ± 0.7 (19)</td>
<td>692 ± 45 (19)</td>
</tr>
<tr>
<td>LS middle AR</td>
<td>1999</td>
<td>M</td>
<td>42.2 ± 1.6 (13)</td>
<td>953 ± 70 (13)</td>
</tr>
<tr>
<td>LS lower AR</td>
<td>1999</td>
<td>M</td>
<td>40.0 ± 1.0 (14)</td>
<td>769 ± 61 (14)</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>M</td>
<td>45.4 ± 0.7 (20)</td>
<td>1,097 ± 46 (20)</td>
</tr>
</tbody>
</table>

Note: Statistical differences (p < 0.05) were reported for each sex where letters following the mean ± SEM (n) refer to differences between sites for a given year and numbers refer to differences between years for a given site.

²LS = longnose sucker; AR = Athabasca River.
differences were found between years at LS upper AR. Trends of increased longnose sucker length and weight at LS lower AR in 2000 were also evident in the samples analyzed for SIA (Fig. 5a). The population of average-sized longnose sucker collected in 1999 was slightly $^{15}$N enriched compared with the larger longnose sucker collected in 2000 (Figure 5b, c).

**Fig. 4.** Length-to-weight (a) and $\delta^{15}$N-to-weight (b) relationships for longnose sucker collected downstream of Fort McMurray sewage discharge (LS middle AR) relative to upstream of the AOS deposit (LS upper AR), and (c) mean ± SEM $\delta^{15}$N and weight for three sites sampled along the Athabasca River in the fall of 1999.

**Fig. 5.** Length-to-weight (a) and $\delta^{15}$N-to-weight (b) relationships for longnose sucker collected downstream (LS lower AR), and (c) mean ± SEM $\delta^{15}$N and weight for two sites sampled along the Athabasca River in 1999 and 2000.
Discussion

δ15N Trends

The fish species examined in this study had distinct δ15N values related to differences in habitat and feeding habit. Forage fish (trout-perch) were more 15N enriched relative to benthivorous fish (longnose sucker), consistent with the δ15N trends for the same two species collected from a tributary of the Moose River (Ontario, Canada) (Farwell 2000). In the lower reaches of the Athabasca River of this study, longnose sucker were more 15N enriched compared with longnose sucker from the upper reaches (Hinton area) (Hesslein and Ramalal 1992), however direct comparisons between these studies are complicated by factors including pulp mill and sewage effluent discharge at Hinton (Chambers et al. 2000; Culp et al. 2000; Scrimgeour and Chambers 2000). In other studies of the midreaches of the Athabasca River, Dubé et al. (2005) found 15N enrichment of longnose sucker downstream of effluent discharges from pulp and paper mills and municipal sewage treatment.

There are many factors that contribute to the δ15N of consumers including site-specific natural and/or anthropogenic sources of N. Changes in the δ15N values of longnose sucker with a shift to 15N enrichment at LS middle AR relative to LS upper AR may be a function of isotope fractionation associated with differences in nutrient status (N, P, or N + P limitation) between sites. Previous studies along the Athabasca River have shown N + P limitation in the region of LS upper AR to upstream of Fort McMurray (Scrimgeour and Chambers 2000). At Fort McMurray, the Athabasca River is nutrient saturated due to nitrate inputs from the Clearwater River (non-nutrient limited) as well as ammonium (344 kg/d total N) and P inputs (27 kg/d total P) from STP discharge, resulting in increased epilithic biomass up to 3 km downstream of the sewage discharge (Scrimgeour and Chambers 2000). If N + P are limited, as is the case upstream (LS upper AR), the preferential use of the lighter N isotope (14N) by periphyton may result in depleted 15N periphyton. However, if nutrients are saturated (LS middle AR), a higher rate of productivity may lead to less discrimination in the use of 15N and 14N, thus the potential for 15N enriched periphyton and longnose sucker. Peterson and Fry (1987) found that the δ15N values of phytoplankton in lake ecosystems varied depending on nutrient limitation. Other studies have shown 15N enriched particulate organic matter in eutrophic lakes relative to oligotrophic lakes (Gu et al. 1996), and 15N enriched white sucker muscle from a river with elevated P (Farwell 2000).

The shift to 15N enrichment of longnose sucker at LS middle AR may also be a function of the availability of different quantities and qualities of N influencing the δ15N at the base of the food web. Sources of N in the form of nitrate and ammonia have been found to influence the δ15N of primary and secondary consumers (Wayland and Hobson 2001). Generally, animal and human wastes are more 15N enriched compared with natural and fertilized soils, ammonia, and nitrate sources from fertilizers or the atmosphere (Kendall 1998). Sources of N downstream of Fort McMurray include nitrate from the Clearwater River and ammonia from sewage discharge. Given the increase in periphyton biomass downstream of the sewage discharge at Fort McMurray (Chambers et al. 2000) and the enriched 15N of sewage wastewater (Jordan et al. 1997; Wayland and Hobson 2001), it is possible that N from a sewage source was an important contributor to the 15N enrichment of longnose sucker at LS middle AR. Nutrient enrichment, as indicated by the 15N enrichment of longnose sucker at LS middle AR, would explain the larger fish size at this site compared with the upstream site (LS upper AR) in 1999. In the Moose River basin, 15N enriched white sucker (Catostomus commersoni) also showed trends of increased body weight and condition factor which were attributed to nutrient status (elevated P) (Farwell 2000). A shift to 15N depletion farther downstream (LS lower AR) relative to the LS middle AR site, similar to LS upper AR, suggests that the Fort McMurray STP discharge either does not contribute a significant or detectable source of N utilized by the benthic food web at a distance of 35 to 40 km downstream and thus δ15N values return to reference levels, or that there are competing 15N depleted sources available at this downstream site.

The observed increase in size of longnose sucker at LS lower AR from 1999 to 2000, which is greater than the variability between years at LS upper AR and between sites in 1999, may be a function of fish residency. In 2000, the population sampled at LS lower AR was larger in size and had slightly more 15N depleted muscle. In this area, there are inputs of total P (7 kg/d) and total N (42 kg/d) from Suncor Inc. effluent discharged at a rate of 35,000 m3/day (upstream of LS lower AR), and the area is classified as nutrient nonlimited (Scrimgeour and Chambers 2000). Although information on the characteristics of the effluent (sources/concentrations of N, effluent δ15N) and discharge rates are limited, the increased size and 15N depletion of longnose sucker (LS lower AR, 2000) may be due to the source of N in the Suncor Inc. effluent. Trout-perch collected in the same area, immediately downstream of Suncor Inc. discharge (TP middle AR), were also slightly more 15N depleted and slightly heavier compared with those from the other sites. Also, in this area longnose sucker have access to the Steepbank River where 15N depleted dietary items are available based on the 15N depletion of slimy sculpin from this tributary. If the 2000 population of longnose sucker was predominantly resident, as suggested by SIA, then it is probable that the 1999 population was mainly from farther downstream where there are no industrial or municipal discharges. This finding emphasizes the importance of multiple sampling periods and the use of SIA as a tool to assist in defining residency for environmental assessments.

The δ15N values for slimy sculpin from the Steepbank
River were lower than the δ13N values of both fish species collected along the Athabasca River. Comparisons of 15N in slimy sculpin between different watersheds indicated that the Steepbank River slimy sculpin were more 15N depleted. However, the differences seen here between sites were similar to differences seen in slimy sculpin from a forested catchment of the Little River (New Brunswick, Canada) (Gray et al. 2004). The shift from 15N enrichment of slimy sculpin upstream (SS upper SR) to 15N depletion at downstream sites on the deposit may be a function of the change in physical habitat (increased gradient, increased flow) influencing the δ15N values of periphyton. Also, the sources and δ15N of N available for primary productivity may be different due to the dramatic changes in geology since the Steepbank River flows downstream through the oil sands deposit. However, the change may also be a function of a shift in the trophic position of slimy sculpin feeding downstream on the AOS deposit where the diversity of the benthic invertebrate community is lower relative to upstream (Barton and Wallace 1979).

δ13C Trends

The fish species showed varying δ13C trends along the river gradient with 13C depletion of longnose sucker and trout-perch and 13C enrichment of slimy sculpin at distances downstream on the AOS deposit. Slimy sculpin from the Steepbank River showed the most noticeable change in δ13C values (~2‰) with a shift from 13C depletion upstream to 13C enrichment downstream on the AOS deposit. Determinations of the spatial distribution of PACs showed increased levels of PACs (34.7 μg/g) in the lower reaches of the Steepbank River (Headley et al. 2001). Total PACs in the sediments were found to be elevated in the tributaries compared with the Athabasca River (<2 μg/g) (as cited in Headley et al. 2001), which may explain the more pronounced changes in the δ13C values of this sentinel fish species collected from the tributary.

The influence of tributary inputs along the Athabasca River was evident with the small sentinel fish species. The 13C depletion of trout-perch downstream of the discharge from the Muskeg River (TP lower AR) suggests that C sources from the Muskeg River may contribute to the δ13C values of trout-perch. Although suspended sediment loads from tributaries (not including the Clearwater River) only account for 18% of the inputs to the Athabasca River (Conly et al. 2002), these inputs may be a significant source of organic oil sands material as reflected in the δ13C values of fish. The Muskeg River basin is considered to be directly impacted by the oil sands surface mining operation (Headley et al. 2001).

The contribution of C from industrial effluent sources (Suncor Inc.) could not be differentiated from C sources in the receiving environment by the trout-perch isotope data. The similarity of the δ13C values for trout-perch upstream and downstream of the Suncor Inc. discharge (TP upper AR; TP middle AR) suggests that the δ13C values of C sources from oil sands industrial effluent are similar to background C sources and/or the discharge is not of significant quality or quantity to alter the δ13C values of organisms at this trophic level. Low levels of oil sands constituents (mixtures of PACs, alkylated PACs, and NAs) ranging from 0.1 to 1 μg/L have been measured in oil sands refinery effluents (as cited in Wrona et al. 2000).

Although there were different δ13C trends with a shift to 13C enrichment of slimy sculpin along the Steepbank River (mean δ13C downstream, -27.0‰) and 13C depletion of trout-perch (mean δ13C downstream, -26.8‰) along the Athabasca River, the mean δ13C values converge at -27‰ at the farthest downstream site on the oil sands deposit for these small-bodied fish species. The similarity of the δ13C values at downstream sites for fish species that differ in feeding habits may indicate the contribution of energy sources derived from oil sands constituents. The δ13C values for slimy sculpin and trout-perch are approximately 3.0‰ more 13C enriched than bitumen (δ13C, -30.3‰ ± 0.1), which is consistent with a 1‰ enrichment per trophic level from source to consumer (DeNiro and Epstein 1978). However, determining the contribution of C sources from oil sands is complicated as little is known about the isotope fractionation associated with the degradation of bitumen and its associated hydrocarbons. Isotope studies have shown that under certain conditions there is no C isotope fractionation associated with aerobic bacterial degradation of some PACs (Mazeas et al. 2002); however, PACs represent only one group of compounds within the complex mixture of oil sands constituents.

Longnose sucker, a more mobile fish species, showed the least change in δ13C values for sites on and off of the AOS deposit, although there was a progressive 13C depletion from upstream to downstream on the AOS deposit. Longnose sucker were more 13C depleted at all three sites compared with a previous isotope study of longnose sucker from the upper reaches of the Athabasca River (Hesslein and Ramlal 1992); however, comparisons between these studies are complicated by anthropogenic inputs in both studies. Given the morphology of the Athabasca River basin, and the level of natural and anthropogenic influences along the Athabasca River, it is difficult to assess whether the 13C depletion observed in this study is associated with the oil sands or whether it is due to the natural gradient. Studies of white sucker in northern Ontario showed a similar trend with 13C depletion along a river gradient (Farwell 2000). It is possible that the δ13C values of longnose sucker in this study may be influenced by the δ13C values of organic sources originating from the oil sands (δ13C of bitumen; -30.3‰ ± 0.1) and from competing uncharacterized C sources in effluent discharged from the Fort McMurray STP (LS middle AR). However, Wayland and Hobson (2001) found that effluent derived C was not detected in suspended sediments or algae downstream of the
discharge, although the $\delta^{13}C$ values for material in municipal sewage were distinct from background conditions in the receiving environment.

**Conclusions**

This study has provided baseline data of isotope values for fish species (longnose sucker) which are currently used in environmental effects monitoring programs. Similar to the Dubé et al. (2005) study, the $\delta^{15}N$ values of longnose sucker in this study provided the most information in terms of residency even with subtle changes in the $\delta^{13}N$ values. The potential use of $\delta^{13}N$ values to reflect N from anthropogenic sources originating from municipal and industrial effluents is important in establishing residency of highly mobile fish in areas of oil sands mining activity and thus is a valuable tool for assessing exposure to oil sands areas. However, additional isotope information on N sources from tributaries and point-source discharges as well as dietary items from these areas would be beneficial for defining residency. All the fish species showed changes in the $\delta^{13}C$ values along the river gradient, however no trends associated with exposure to oil sands constituents could be established for longnose sucker. Similar $\delta^{13}C$ values (-27%) for the smaller sentinel species were associated with elevated exposure to oil sands constituents along the Steepbank River (slimy sculpin) and inputs from a tributary (Muskeg River) (trout-perch) impacted by oil sands activity. Additional C isotope information on sources and dietary items in the tributaries would contribute to the understanding of carbon dynamics in this riverine system. Dual analyses of C and S isotopes may provide further information on residency within oil sands exposed tributaries versus the main stream for more mobile fish species such as longnose sucker.

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**References**


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Temperature Impact of the Industrial Cooling Water Discharges in a Long Boat Slip of Hamilton Harbour

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The thermal structure of industrial cooling water discharged into a long, narrow and shallow, straight open boat slip (Ottawa Street Slip, [OSS]) was investigated by field measurements during the hottest summer month in 2006. Three-dimensional hydrodynamic and thermal transport models were established and verified with measurements. The main purposes of this study were to understand the mechanism of the thermal structure in the OSS during the hot summer season under the present cooling water discharge conditions, to investigate the influence of harbour water on the thermal structure in the slip, and to establish a means for scientific predictions of the impact of cooling water discharges in a future study. Toward this end, the water temperature at multiple locations along the OSS and meteorological data near the study site were collected during the summer period of 2006. The collected data reveal: (1) during the measured summer period, the water temperature in the slip can be higher than 30°C during a period of high air temperatures; (2) water temperature variations within short periods of 15, 30, 60, and 120 minutes were no more than 4°C during the entire measurement period; (3) water temperature in the slip is controlled by both air and cooling discharge temperatures, and the cooling water temperature's increase due to industrial cooling processing seems to be relatively independent of the intake water temperature; therefore, the water temperature in the slip varied mainly with the air temperature; (4) since water temperature in the slip seemed to closely follow the intake water temperature, the intake channel may need to be optimized to maximize the possibility of getting the coolest water available from Hamilton Harbour; and (5) the cooler harbour water could not penetrate deeply into the slip. The collected water temperature data were also used for verification of three-dimensional hydrodynamic and transport models. The simulation results showed that the established model could reasonably well reproduce general thermal structures in the entire slip. This achieved the ultimate goal of the study for establishing a model to assess the impacts of further increase of cooling water discharge into the OSS.

Key words: thermal plume, numerical modelling, computational fluid dynamics, narrow slip, temperature structure

Introduction

Stream water temperature is one of the most important parameters in ecosystem studies. It is not only very important in many chemical processes present in river systems, but also influences many biological conditions and behaviours. Disruption to the thermal regime of a watercourse can significantly impact the utilization of fish habitat. Understanding natural variations in stream water temperatures is also very important in limnological studies. For instance, temperature greatly influences the rate of decomposition of organic material and the saturation concentration of dissolved oxygen (Nemerow 1985). Stream water temperature can also be one of the factors in determining the habitat potential of a stream (Bovee 1982). The most obvious effects on aquatic organisms are on their survival rate and their growth. For example, high stream water temperatures between 23 and 25°C can affect the mortality of salmonids (Bjornn and Reiser 1991). High stream water temperature can occur naturally or as a result of human impact. An example of the latter is thermal pollution and deforestation, which have been identified as having a negative impact on the thermal regime of a watercourse (Gras 1969; Brown and Krygier 1970; Hartman et al. 1987).

Knowledge and the ability to predict stream water temperature are therefore essential to solve thermal discharge problems and in conducting ecosystem environmental impact assessment studies. A better understanding of the natural thermal regime of a small stream is also very important in the management of fisheries and aquatic resources. The first step in the overall understanding of the thermal structure in streams is the ability to study and predict variation in stream water temperatures.

In general, most of the variation in stream water temperatures occurs in open-water conditions during the summer months. During winter in cold regions, the mass of water is less affected by meteorological conditions as a result of the ice cover, although small temperature changes have been monitored (Marsh 1990). Following ice breakup in the spring, heat-exchange processes between the atmosphere and the body of water take place in attempt to reach equilibrium, resulting in changes of stream water temperature (Triboulet et al. 1977).

To predict stream water temperatures, many models have been developed and used (e.g., Raphael 1962; Cluis 1972; Morin and Couillard 1990; Stefan and Preudhomme 1993). These models can be classified into