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The Use of Stable Isotopes ($^{13}C/^{12}C$ and $^{15}N/^{14}N$) to Trace Exposure to Oil Sands Processed Material in the Alberta Oil Sands Region

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Various oil sands reclamation strategies incorporate oil sands processed material (OSPM) such as mature fine tailings (MFT), engineered tailings (consolidated tailings, CT), and tailings pond water (TPW) into reclamation components that need to develop into viable aquatic ecosystems. The OSPM will contain elevated salinity and organics such as naphthenic acids (NA) and polycyclic aromatic compounds (PAC) that can be chronically toxic to aquatic organisms depending upon levels and age. Due to the complexity of the chemical mixtures, analysis of these compounds in exposed organisms can be challenging. In this study, the stable carbon and nitrogen isotope signatures of selected invertebrates from various types of oil sands reclamation sites were analyzed to determine whether stable isotopes can be used to trace the exposure of aquatic organisms to organic constituents of OSPM. In a series of experimental reclamation ponds of similar age and size, there were trends of ^{13}C depletion and ^{15}N enrichment for benthic invertebrates along a gradient of increased levels of MFT and/or TPW. A survey of 16 sites revealed high $\delta^{15}N$ values for invertebrates in aquatic systems containing MFT and CT (gypsum-treated mixes of MFT and tailings sand), which was attributed to the presence of NH_4^+, a process by-product in OSPM. Findings of this study indicate a potential for the use of stable nitrogen isotopes to define exposure of biota to OSPM during environmental effects monitoring programs both in surface waters and in cases where groundwater seepage containing oil sands processed water enters surface receiving environments in the region.

Large-scale surface mining of oil sands in the Athabasca deposit in Alberta, Canada, began in 1967 and is currently seeing rapid development. Extraction and upgrading of the bitumen from the oil sands produce large volumes of fluid tailings, including process water (tailings pond water, TPW, predominantly water associated with the caustic hot water extraction method used to separate the bitumen from the ore), soft fines that are a mixture of slowly densifying TPW and fines known as mature fine tailings (MFT, containing TPW, un-recovered bitumen, silts, and clays), and coarse tailings (predominantly sand saturated with TPW) (FTFC, 1995; Fedorak et al., 2003). The long-term approach for the reclamation of mined areas involves the construction of functional terrestrial and aquatic ecosystems using various reclamation strategies. One of these strategies, the wet landscape option, involved placing solid waste (predominantly MFT) into mined areas and capping them with water (TPW or natural surface water) to construct lakes and wetlands. Numerous experimental ponds and wetlands constructed over the period of 1975–1998 have been used to evaluate the development of viable aquatic ecosystems using different reclamation strategies. Field and microcosm studies demonstrated the effects of these differing aquatic reclamation options on phytoplankton (Leung et al., 2001; Hayes, 2005), invertebrates (Leonhardt, 2002; Ganshorn, 2002; Whelly, 1999; McCormick, 2000; Gould, 2000), fish (Lister et al., 2008; Nero et al., 2006; Murchie & Power, 2004; Siwik et al., 2000; van den Heuvel et al., 1999a, 1999b, 2000), amphibians (Pollet & Bendell-Young, 2000), and birds (Smits et al., 2000). The oil sands constituents of concern to reclamation success in these systems include salts (mainly Na^+, Cl^-, HCO_3^- and SO_4^{2-}, as well as NH_4^+), and

organic compounds such as naphthenic acids (NA) and poly-cyclic aromatic compounds (PAC).

One area that has received little attention to date is the cycling of carbon and nitrogen in reclaimed aquatic environments influenced by oil sands processed material (OSPM). The study presented here uses stable isotopes of carbon and nitrogen to assess the flow of these elements through some of the constructed systems already outlined. Stable isotope analyses have been used in ecotoxicological studies to determine carbon and/or nitrogen dynamics associated with exposure to municipal, agricultural, and/or industrial inputs (Wassenaar & Culp, 1996; Farwell, 2000; Jones et al., 2001; Wayland & Hobson, 2001; Anderson & Cabana, 2005; Galloway et al., 2003; Dube et al., 2005), as well as the dynamics of persistent organic pollutants (Broman et al., 1992; Kidd et al., 1995; Kiriluk et al., 1995; Schindler et al., 1995; Fisk et al., 2001; Stapleton et al., 2001), and oil sands constituents (Murchie & Power, 2004; Farwell et al., personal communication).

Constituents associated with OSPM, including organic carbon (NA and PAC) and nitrogen (mainly as NH_4^+ added with upgrading stripped sour water streams), may provide nutrient sources as aquatic reclamation sites develop into viable ecosystems. When OSPM is used to construct reclamation sites, NA concentrations can range from 10 to 100 mg/L in TPW, depending on age and source (MacKinnon, 1989; Holowenko et al., 2000; Scott et al., 2005), and PAC concentrations greater than 300 mg/kg can be found in whole MFT, while total PAC dissolved in the TPW will seldom exceed 2 μg/L (Madill et al., 2001; Ganshorn, 2002). There is biodegradation of NA in aquatic reclamation options (Headley & McMartin, 2004; Clemente & Fedorak, 2005; Scott et al., 2005), but it is unlikely to go to completion (Holowenko et al., 2001; Del Rio et al., 2006). Biodegradation and photooxidation of PAC proceed under natural conditions (Dutta & Harayama, 2000; Kropp & Fedorak, 1998). Ammonia (NH_3) is a by-product of the bitumen upgrading processes, where coking and hydrocracking transform the viscous raw bitumen product into a more commercial sweet synthetic crude (M. MacKinnon, personal communication). The organo-nitrogen components in the bitumen are degraded and transported in the reduced ammonia form to sour water streams. Most of this NH_3 is stripped and oxidized, while that portion not stripped ends up within the TPW in the settling basins (NH_4^+ in fresh TPW, 2–50 mg/L, M. MacKinnon, personal communication). Under anaerobic conditions, NH_3 is affected little, so even in settling basin seepage waters and in MFT pore waters concentrations remain elevated (FTFC, 1995; MacKinnon, 1989; Boerger et al., 1992). Carbon and nitrogen derived from oil sands processing may be consumed and assimilated directly or indirectly by bacterial and photosynthetic producers. In theory, increased levels of OSPM in reclaimed aquatic environments may result in changes in the $\delta^{13}C$ and $\delta^{15}N$ signatures of consumers depending on the degree of utilization of oil sands sources by producers and on the $\delta^{13}C$ and $\delta^{15}N$ signatures of the oil sands-derived material.

The objective of this study was to determine the utilization of carbon and nitrogen from OSPM in reclaimed aquatic environments using stable isotope analyses of benthic invertebrates and fish (where applicable). To accomplish this, a series of experimental reclamation ponds (referred to as the Test Ponds-1989 series) were used to examine changes in stable isotopes of aquatic organisms associated with differences in the quantity and quality of OSPM in these ponds. The $\delta^{13}C$ and $\delta^{15}N$ signatures of bitumen, as well as NA and PAC from a variety of oil sands sources, were also determined. Expanded studies examined benthic invertebrates and fish from other sites to determine the range of stable isotope values associated with different reclamation strategies. Stable isotope analysis may contribute to our understanding of carbon and nitrogen cycling in reclaimed environments and prove useful as a tool for tracing exposure to OSPM within reclamation areas and, in the future, at downstream sites when reclaimed watersheds are developed or an effluent is discharged.

METHODS

Site Descriptions

Test Ponds-1989 Series

The test ponds (TP1–7) are located on Syncrude's Mildred Lake Lease 17 within the Athabasca Oil Sands (AOS) deposit located about 40 km north of Fort McMurray in northeastern Alberta, Canada (57°05'102" N, 111°41'623" W) (Figure 1). They were excavated into clay overburden (Pleistocene and Cretaceous clays and tills) in an area that had not been previously mined and will be referred to as the Wet Landscape Field Research Facility. The ponds were constructed in 1989 and are similar in size (<0.1 ha), depth (7 m), and fluid containment volume (2000 m³). Each pond was filled with various fluid materials (water and MFT), with the in situ clay acting as an impervious liner, and after being filled there was no further water recharge or discharge occurring (Boerger et al., 1992). The method of construction allowed for a gradient to a maximum fluid depth of ~7 m, with littoral areas having clay substrates and only water contact. The banks of the ponds are steep and covered with sedge (*Carex* sp.) and grasses. Sedge and cattail (*Typha latifolia*) are found along the margins, and submerged macrophytes such as *Potamogeton* spp. are common. The submerged macroalga *Chara* sp. is abundant and often covers large areas in the test ponds. Fish were stocked in these ponds on occasion in previous years (Siwik, 1998); however, with oxygen depletion during winter ice cover periods, their survival was affected. At the time of this study, fish were found only in test ponds (TP) 1 and 3.

Four ponds (TP1, TP3, TP5, and TP7) were selected for the comparison of isotope values based on the types and quantities of OSPM used in construction. The construction material and water chemistry are summarized in Tables 1 and 2. These ponds have received no additional amendments since construction.
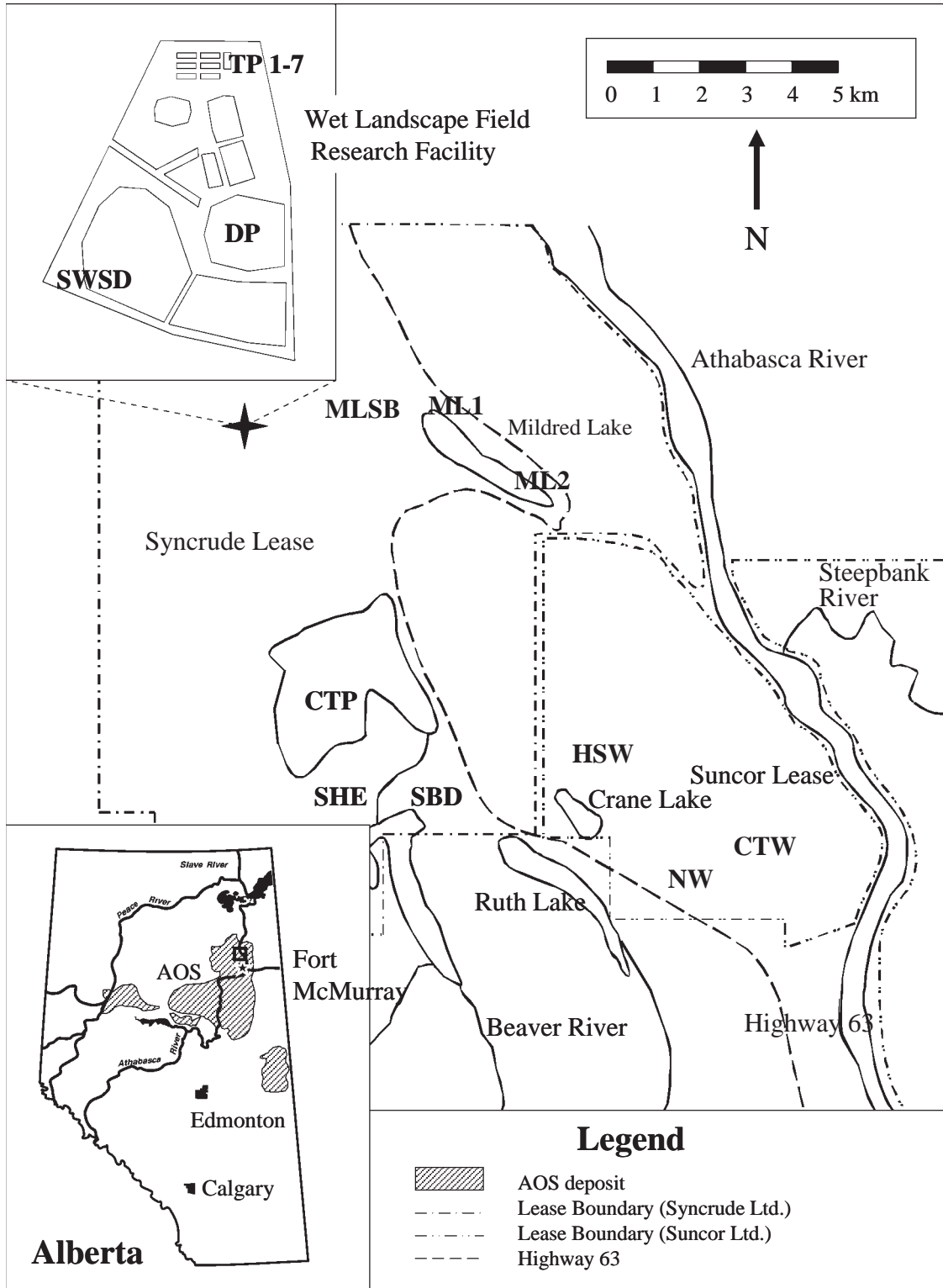
FIG. 1. Sampling sites located on the Athabasca oil sands (AOS) deposit north of Fort McMurray (Alberta, Canada). Sites include reclaimed systems containing mature fine tailings and/or tailings pond water (test pond 2, TP2; test pond 3, TP3; test pond 4, TP4; test pond 5, TP5; test pond 6, TP6; test pond 7, TP7; Demonstration Pond, DP) or consolidated tailings (Consolidated Tailing Wetland, CTW; Composite Tailings Pond, CTP; Natural Wetland, NW). Other natural or constructed sites located on reclaimed land or undisturbed oil sands (Mildred Lake, ML; Shallow Wetland South Ditch, SWSD; High Sulfate Wetland, HSW; Test pond 1, TP1; South Hydroline East, SHE; South Boundary Ditch, SBD). The location of Mildred Lake Settling Basin (MLSB) has also been included (map modified from Smits et al., 2000).

TABLE 1
Summary of the Materials Used for the Construction
of the Test Ponds (1989 Series)

Site	OSPM infill material	Water cap and source
TP1	None	2000 m^3 non-OSPM water from WID drainage[a]
TP3	1000 m^3 MFT	1000 m^3 non-OSPM muskeg runoff water from WID drainage[a]
TP5	1000 m^3 MFT	1000 m^3 TPW[a]
TP7	2000 m^3 MFT	Expressed (during consolidation of MFT) and precipitation water[b]

Note. OSPM-oil sands processed material; TP-test pond; WID-West Interceptor Ditch; MFT-mature fine tailings; TPW-tailings pond water.

[a]Nero et al. (2006).
[b]Siwik (1998).

The TPW and MFT used as fill material for the test ponds were drawn from Syncrude's Mildred Lake Settling Basin (MLSB), while non-OSPM waters were drawn from local muskeg runoff areas. Pond TP5 has maintained the highest NA concentration,

followed by TP7 (Table 2). Concentrations of total nitrogen (TN), total phosphorus (TP), and dissolved organic (DOC) and inorganic carbon (DIC) (CO_3^{2-} and HCO_3^{-}) tend to rise with increases in the volume of OSPM. The MFT used in pond construction had total extractable hydrocarbon (bitumen content) and PAC (parent and alkylated PAC) concentrations as high as 24,000 mg/kg and 374 mg/kg, respectively (Ganshorn, 2002). The non-OSPM clay substrates varied but in general were sodic clays representative of the area.

Expanded Study Sites

Additional aquatic environments were sampled to determine the degree of variability in the $\delta^{13}C$ and $\delta^{15}N$ values of invertebrates at sites on reclaimed materials or on undisturbed substrates (Figure 1; Tables 2 and 3). In addition, sites constructed using OSPM were included. Mildred Lake (ML) (~170 ha area, maximum depth of 8.2 m) is a lake located adjacent to Syncrude's MLSB, and acts as a clean (non-OSPM) water reservoir that is drawn from the Athabasca River. While it has not received OSPM materials directly, its location makes it susceptible to impacts associated with ongoing oil sands operations at Syncrude, such as sedimentation, seepage, and bank erosion due to the proximity of a constructed road at the contact berm with sand dykes of the MLSB (ML1). ML continuously

TABLE 2
Water Chemistry Parameters (Mean ± SE) for Study Sites

Site	pH	Cond. (μS/cm)	TN (mg/L)	NH$_4$ (mg/L)	NO$_2$+NO$_3$ (mg/L)	TP (mg/L)	o-PO$_4$ (mg/L)	CO$_3$ (mg/L)	HCO$_3$ (mg/L)	DOC (mgC/L)	NA (mg/L)
Test ponds (1989 series)											
TP1	8.4 ± 0.4	725 ± 92	0.68 ± 0.5	0.02 ± 0.01	0.006	0.01	<0.002	1.9	161 ± 43	24 ± 8	1.5 ± 0.7
TP3	8.9 ± 0.5	683 ± 102	1.05 ± 0.7	0.05 ± 0.05	0.021	0.02	<0.002	25.0	322 ± 48	28 ± 4	3.4 ± 0.9
TP5	9.0 ± 0.3	2540 ± 590	1.32 ± 1.7	0.09 ± 0.2	0.026	0.02	<0.002	63.5	553 ± 69	45 ± 6	24.8 ± 5
TP7	8.7 ± 0.4	1746 ± 398	1.76 ± 0.4	0.09 ± 0.2	0.017	0.05	<0.002	54	846 ± 157	50 ± 11	19.5 ± 4.4
Expanded C and N stable isotope study sites											
TP2	8.8 ± 0.3	661 ± 99	1.32 ± 0.7	0.04 ± 0.05	0.017	0.02	<0.002	17.5	368 ± 39	33 ± 5	3.7 ± 1.0
TP4	8.8 ± 0.7	611 ± 106	1.00 ± 0.7	0.04 ± 0.05	0.018	0.02	<0.002	21	283 ± 54	29 ± 6	3.4 ± 0.9
TP6	9.1 ± 0.7	1089 ± 220	1.76 ± 0.8	0.14 ± 0.2	0.015	0.05	<0.002	43.8	336 ± 57	37 ± 5	3.8 ± 1.2
DP	8.8 ± 0.4	1135 ± 196	1.79 ± 1.2	0.20 ± 0.2	0.109	0.04	<0.002	33.3	461 ± 81	31 ± 7	8.9 ± 2.7
SWSD	8.6 ± 0.7	622 ± 126	—	0.04 ± 0.05	<0.001	—	<0.002	6.8	262 ± 64	18 ± 2	1.4 ± 0.8
ML	7.9 ± 0.4	307 ± 37	0.75 ± 0.2	0.09 ± 0.05	0.030	0.03	<0.002	5.3	159 ± 19	13.5 ± 4	0.7 ± 0.3
SHE	8.1 ± 0.3	1855 ± 186	1.15 ± 0.3	0.16 ± 0.2	0.019	0.03	<0.002	0.4	238 ± 66	33 ± 5	6.9 ± 4.4
SBD	7.3 ± 0.2	317 ± 74	—	—	—	—	<0.002	0.0	184 ± 10	23 ± 10	1.8 ± 0.4
CTP	8.3 ± 0.9	5100 ± 850	1.87 ± 1.4	0.09 ± 0.3	0.04 ± 0.06	<0.1	<0.002	29	496 ± 125	56 ± 15	55 ± 11
CTW	8.5 ± 0.2	2350 ± 385	—	0.20 ± 0.1	—	—	—	25	775 ± 155	—	55 ± 12.9
NW	8.5 ± .6	1425 ± 420	3.1	0.6 ± 0.5	—	0.01	—	27	675 ± 200	57 ± 8	47 ± 13

Note. Values are mean for open water period, 1998–2004; TP-Test Pond; DP-Demonstration Pond; SWSD-Shallow Wetland South Ditch; ML-Mildred Lake; SHE-South Hydroline East; SBD-South Boundary Ditch; CTP-Composite Training Pond; CTW-Composite Tailing Wetland; NW-Natural Wetland; TN-total nitrogen; TP-total phosphorus; DOC-dissolved organic carbon; NA-naphthenic acids; —, not determined.

TABLE 3
Description of the Oil Sands Sites from Which Samples Were Taken for the Expanded C and N Stable Isotope Study

Code	Site	Year of construction	Description
Sites without OSPM			
ML	Mildred Lake (SCL Lease 17)	N	Modified (1975) to act as a reservoir for plant makeup water [a]
SWSD	Shallow Wetland South Ditch (SCL Lease 17)	1993	Shallow wetland was used as a storage area for unprocessed WID water (muskeg drainage water)
HSW	High Sulfate Wetland (Suncor Lease 86)	1985	Lean oil sands mixed with overburden material (peat)[a]
SHE	South Hydroline East (SCL Lease 17)	—	High conductivity (saline) site constructed on waste materials (mining sands and/or consolidated tailings)[c]
SBD	South Boundary Ditch (SCL Lease 17)	1975	Constructed diversion, receives surface water[a]
Sites with OSPM			
TP2	Test pond 2 (SCL Lease 17)	1989	1000 m^3 MFT capped with non-OSPM muskeg surface runoff water, via WID[d]
TP4	Test pond 4 (SCL Lease 17)	1989	1000 m^3 MFT capped with non-OSPM muskeg surface runoff water, via WID; amended with biota inoculums from local wetlands[d]
TP6	Test pond 6 (SCL Lease 17)	1989	1,000 m^3 MFT capped with non-OSPM muskeg surface runoff water, via WID; nutrient amended with inorganic phosphorus and nitrogen[d]
DP	Demonstration Pond (SCL Lease 17)	1993	70,000 m^3 MFT capped with 70,000 m^3 non-OSPM muskeg surface runoff water, via WID[d]
CTP	Composite Tailings Pond (SCL Lease 17)	1997	CT (gypsum-treated tailings) release water from 1997/98 CT pilot test[a]
CTW	Consolidated Tailing Wetland (Suncor Lease 86)	1998	CT water from dyke seepage[a]
NW	Natural Wetland (Suncor Lease 86)	1986	surface water runoff and CT water[a,b]

Note. N refers to a natural site; —, indicates there is no information available; SCL-Syncrude Canada Ltd.; WID-West Interceptor Ditch; MFT-mature fine tailings; OSPM-oil sands processed material; CT-consolidated tailings.

[a]Ganshorn (2002).
[b]Smits et al. (2000).
[c]Leonhardt (2003).
[d]Golder Associates Ltd. (2002).

receives natural non-OSPM water from the Athabasca River at a rate of about 3–4 Mm^3/mo (ML2). The NA concentration (<0.7 mg/L) of ML is consistent with levels expected in other non-OSPM waters of the Athabasca River watershed (Headley & McMartin, 2004). Four of the sites are located either on oil sands land (South Hydroline East [SHE] and South Boundary Ditch [SBD]) or reclaimed land (Shallow Wetland South Ditch [SWSD] and High Sulfate Wetland [HSW]). Sites constructed with OSPM included test ponds (TP) 2, 4, and 6 at Syncrude's Wet Landscape Field Facility described earlier. Demonstration pond (DP) is a larger experimental pond, approximately 4 ha in area with a maximum depth of about 14 m (2.9 m of non-OSPM

water overlying about 10 m of MFT (van den Heuvel et al. 1999b), that was also sampled. Three of the reclaimed sites that were sampled, Natural Wetland (NW), Consolidated Tailing Wetland (CTW), and Composite Tailing Pond (CTP), contain consolidated tailings (CT) release water or CT substrate (gypsum [CaSO$_4$]-treated MFT augmented with tailings sand (FTFC, 1995). All three of these sites have elevated levels of NA (Table 2). Natural Wetland (NW) has been part of Suncor's surface water management system since the mid 1980s. It is located adjacent to one of the operating settling basins and continuously receives OSPM as dyke seepage CT water so it has elevated NA as well as elevated total petroleum hydrocarbon

(TPH) concentration (~8 mg/L in the water (Smits et al., 2000) and 130 mg PAC/kg organic carbon in the benthic zones (Ganshorn, 2002).

Sample Collection

Bitumen associated with sediments was collected from a variety of sources including an active settling basin (MLSB), a lake on the AOS deposit (ML), and a reclamation pond (DP). The samples were placed in cleaned glass 20-ml scintillation vials. TPW was collected in 20-L high-density polyethylene containers from MLSB (fresh) and TP5 (aged >11 yr). To separate the acid fraction containing NA, as well as some of the fulvic and humic acids, the water was extracted using the method described in Nero et al. (2006). In brief, the water was acidified to a pH of 2.5 to precipitate the acids; the precipitate was then extracted with dichloromethane, and dissolved in 0.1 N NaOH. The NaOH solution was filtered through a precombusted glass-fiber filter (GF-C). Both the filtrate, which may contain residual bitumen and PAC, and the soluble acid fraction were dried and analyzed for stable isotopes.

Biota and sediment samples were collected from the littoral zones from TP1, TP3, TP5, and TP7 in the fall of 2000 and 2001. For the expanded survey, benthic invertebrate collections were made in the fall of 2000 and 2001 and the summer of 2001. Small-bodied fish species were collected in beach seines and minnow traps and benthic invertebrates were collected using a D-frame aquatic net. Dorsal muscle samples of fish were collected, placed in cryovials, and immediately frozen (–20°C). Benthic invertebrates were picked live, cleaned of debris, held in filtered water for gut clearance (approximately 24 h), and stored in cryovials. All samples were immediately frozen and stored at –20°C prior to isotope analysis. Three groups of invertebrates were selected for isotope analyses based on their size and abundance within the collection samples.

Isotope Preparation and Analysis

Selected invertebrates and fish samples were freeze-dried, ground in a ball mill grinder, weighed, and analyzed for carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) isotope ratios along with reference standards (C standard, Pee Dee Belemnite; N standard, atmospheric nitrogen [N_2]) using a Micromass VG Isochrom continuous-flow isotope ratio mass spectrometer at the Environmental Isotope Laboratory, Department of Earth Sciences, University of Waterloo, Waterloo, ON. $\delta^{13}C$ and $\delta^{15}N$ values are derived from the difference between the isotope ratio ($R = {}^{13}C/^{12}C$ or $^{15}N/^{14}N$) of a sample and a reference standard such that δX ‰ = (R_{sample}) – ($R_{standard}$)/($R_{standard}$) × 10^3. The delta (δ) value is expressed as a parts per thousand, or per mil ‰. More negative $\delta^{13}C$ or $\delta^{15}N$ values represent a decrease in the quantity of the heavier isotopes ($^{13}C, ^{15}N$) relative to the lighter isotopes ($^{12}C, ^{14}N$) and are referred to as ^{13}C or ^{15}N depleted. In contrast, more positive $\delta^{13}C$ or $\delta^{15}N$ values represent an increase in the heavier isotopes ($^{13}C, ^{15}N$) and are referred to as ^{13}C or ^{15}N enriched.

RESULTS

The $\delta^{13}C$ values of bitumen samples collected from the settling basin (MLSB, –30.4‰), the source of the TPW and MFT used in the construction of TP 2 through 7, as well as a lake on the oil sands deposit (ML, –30.3‰) and a reclamation pond (DP, –29.6‰), were similar. In contrast, the $\delta^{13}C$ values of the soluble acid fraction extracted from fresh TPW (MLSB, –25.8‰ to –23.8‰) were more ^{13}C enriched, as was the particulate carbon (filtrate) which may contain residual bitumen and PACs (–29.2‰ to –27.2‰).

Food Web Structure

The $\delta^{13}C$ and $\delta^{15}N$ signatures for selected invertebrate and fish components of the food web in DP, a site reclaimed using MFT, are given in Figure 2. In general, the $\delta^{15}N$ values for dragonflies and damselflies were similar to those for leeches and caddisflies and more ^{15}N enriched relative to other invertebrates, including chironomids. Fathead minnows from DP had the highest $\delta^{15}N$ values (12.6‰ ± 0.1, n = 10), consistent with their trophic position. The $\delta^{13}C$ values for dragonflies, damselflies and chironomids were generally similar to other invertebrate groups, as well as sediment detritus, periphyton and fine particulate organic matter. Other invertebrates including caddisflies, corixidae and notonectidae were quantitatively more ^{13}C depleted.

Test Ponds—1989 Series

Benthic invertebrates from the test ponds (TP) 1, 3, 5, and 7 showed ^{15}N enrichment and ^{13}C depletion (except chironomids) with increasing quantities of OSPM (Figure 3). All the invertebrates had incremental increases (≥1.0‰ per pond) in $\delta^{15}N$ values from the reference non-OSPM pond (TP 1) compared to ponds with higher quantities of OSPM (TP 3, 5, 7). Similar elevations in $\delta^{15}N$ values were evident for samples of surficial sediments (TP1, –0.6‰; TP3, below detection limit; TP5, 2.3‰; TP7, 4.3‰). The ^{15}N enrichment of the invertebrates relative to the sediments was somewhat variable, with chironomids showing values of 2 to 2.5‰, dragonflies values of 2.5 to 3.0‰ and damselflies values of 3 to 4‰. The $\delta^{13}C$ values (TP 1, 3, 5) for both sediments (TP1, –22.0‰; TP3, –21.2 ‰; TP5 –22.8‰) and chironomids (Figure 3) were similar among ponds. In comparison, dragonflies and damselflies from TP3 to TP7 become more ^{13}C depleted. Surficial sediments for TP7 were ^{15}N enriched (4.3‰) and ^{13}C depleted (–27.5‰), similar to the trends for dragonflies and damselflies.

Fish from TP1 and TP3 were ^{15}N enriched, indicative of their trophic position and showed species specific $\delta^{13}C$ trends. Fathead minnows from TP1 ($\delta^{13}C$, –28.8 ± 0.3‰, n = 10; $\delta^{15}N$, 6.2 ± 0.1‰, n = 10) were more ^{13}C and ^{15}N depleted compared

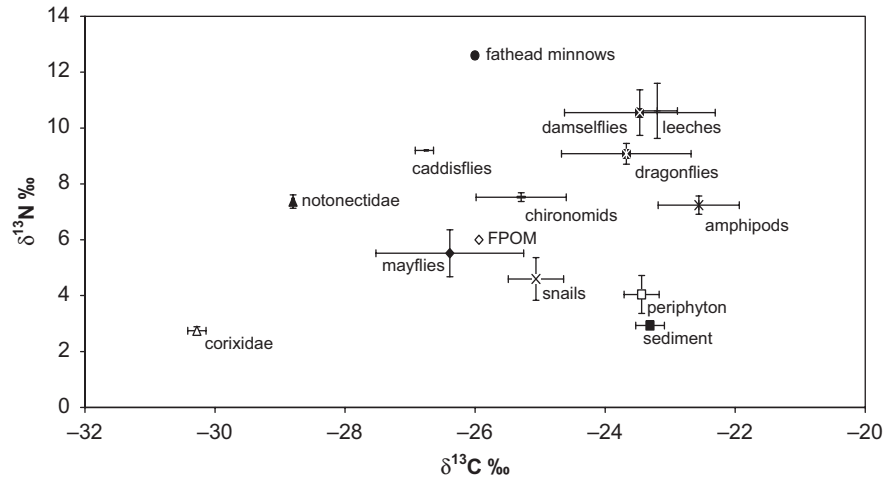**FIG. 2.** An example of the $\delta^{13}C$ and $\delta^{15}N$ values of components of a benthic food web at the oil sands reclamation site, Demonstration Pond.
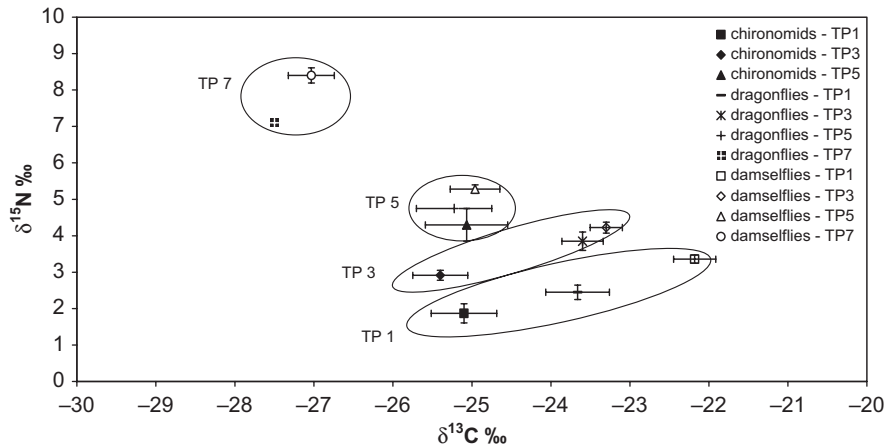

FIG. 3. $\delta^{13}C$ and $\delta^{15}N$ values for chironomids, dragonflies, and damselflies collected from the 1989 series of test ponds. Site abbreviations are as noted in Figure 1.

to the five-spined sticklebacks ($\delta^{13}C$, -23.7 ± 0.4‰, $n = 8$; $\delta^{15}N$, 7.1 ± 0.2‰, $n = 8$). The isotope values of the five-spined sticklebacks for TP3 ($\delta^{13}C$, -23.6 ± 0.1‰, $n = 10$; $\delta^{15}N$, 7.3 ± 0.1‰, $n = 10$) were similar to TP1. In TP1 fathead minnows were 2.8–4.3‰ more ^{15}N enriched compared to invertebrates. The five-spined sticklebacks had ^{15}N enrichment in the range of 3.7–5.2‰ and 3.1–4.4‰ compared to invertebrates from TP1 and TP3, respectively.

Expanded Study Sites

Among the 16 sites surveyed in this study, $\delta^{13}C$ and $\delta^{15}N$ values of the selected invertebrates varied by ~15‰ (Figure 4). Invertebrates from sites with CT (NW, CTP, CTW) consistently had the highest $\delta^{15}N$ values relative to all other sites. Reclaimed sites with elevated levels of MFT (TP7 and DP) had the second highest $\delta^{15}N$ values for dragonflies and damselflies.

In comparison, chironomids from ML and SHE had high $\delta^{15}N$ values, similar to those seen at sites with elevated levels of MFT (TP7 and DP) (Figure 4a). Invertebrates with high $\delta^{15}N$ values also had decreased $\delta^{13}C$ values at CT sites, consistent with the trend observed in the 1989 series of test ponds with elevated levels of MFT (TP7). There was a wide range of decreased $\delta^{13}C$ values (-38 to -28‰) for chironomids from sites containing no direct inputs of OSPM. There were also decreased $\delta^{13}C$ values for chironomids collected from ML1 (mean -35.3‰) compared to ML2 (mean -29.4‰) indicating spatial variability within ML.

DISCUSSION

Based on data for the 1989 series of test ponds, the higher $\delta^{15}N$ values for invertebrates in this study are unique to sites with OSPM and the degree of elevation is a function of the
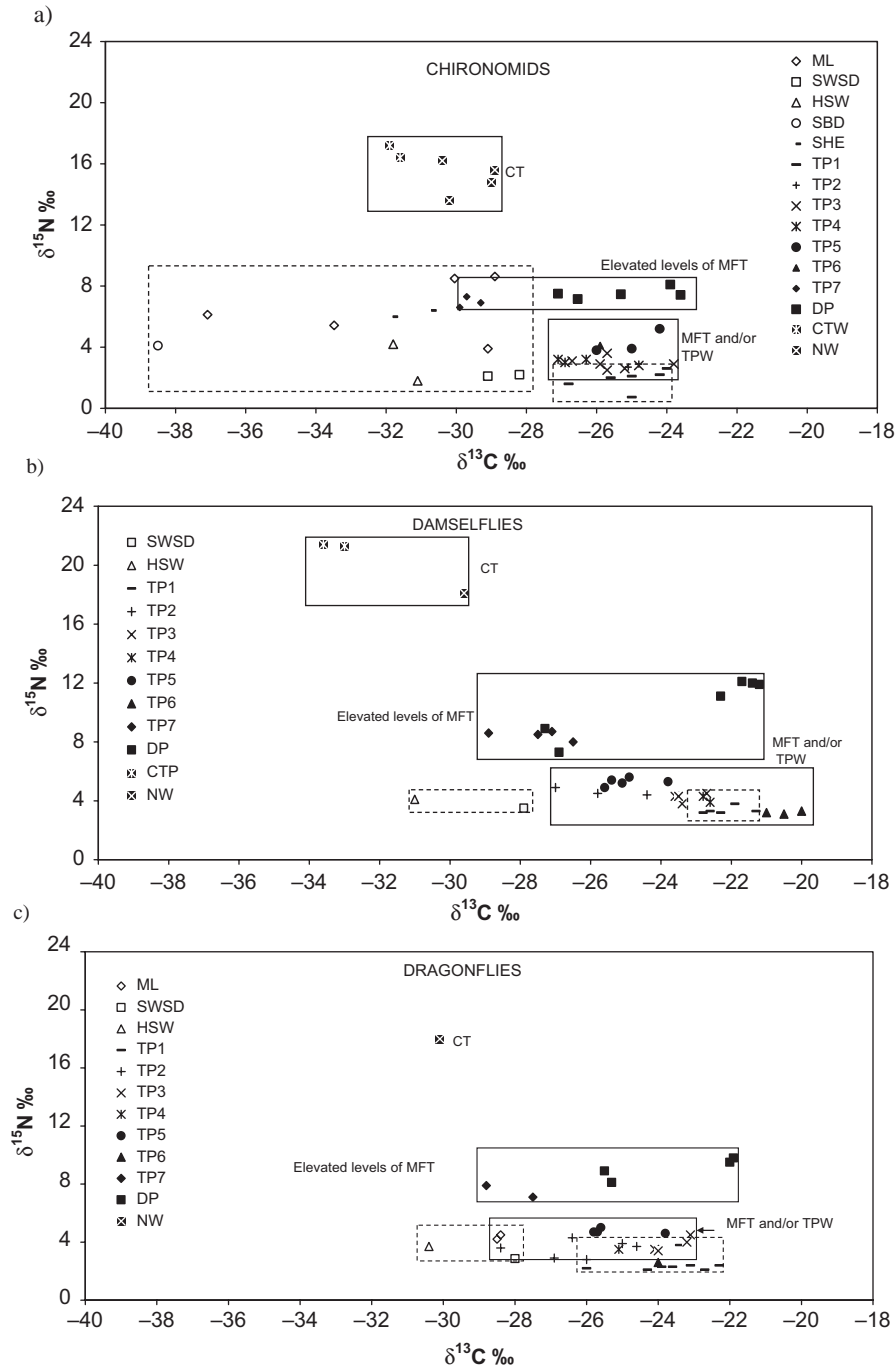
FIG. 4. The $\delta^{13}C$ and $\delta^{15}N$ values of (a) chironomids, (b) damselflies, and (c) dragonflies collected from a variety of sites containing various quantities and qualities of natural or processed oil sands material. Solid boxes were sites constructed with oil sands processed material (OSPM) (i.e., CT; elevated levels of MFT; MFT and/or TPW). Dashed boxes were either natural or constructed sites that contained no direct inputs of OSPM. Site abbreviations are as noted in Figure 1.

quantity of that material used to construct the reclaimed aquatic habitat. Based on the expanded survey, waste management strategies involving the addition of gypsum to tailings had the strongest impact on the $\delta^{15}N$ values for invertebrates.

Using surficial sediments to establish a baseline for nitrogen isotopes in the 1989 series of test ponds, each invertebrate group was feeding at a similar trophic position independent of the quantity of OSPM in the system. Chironomids were generally feeding at a lower trophic level ($\leq 2.5‰$ ^{15}N enrichment) compared to the predatory invertebrates ($\geq 2.5‰$ ^{15}N enrichment). Ganshorn (2002) also found that the trophic positions of predatory and benthic chironomids, adjusted using detrital material, were

similar in wetlands in the presence and absence of OSPM. This is consistent with studies that showed that $\delta^{15}N$ values of consumers become increasingly more ^{15}N enriched (~3–5 ‰ per trophic level) at higher trophic levels due to the preferential excretion of ^{14}N during metabolism (DeNiro & Epstein, 1981; Minigawa & Wada, 1984).

As was the case with the 1989 series of ponds, sites from the expanded survey with high levels of MFT (i.e., TP 7 and DP with ~2000 and 70,000 m³ MFT, respectively), also had invertebrates with higher $\delta^{15}N$ values. The $\delta^{15}N$ values of invertebrates were even higher when tailings amended with gypsum (i.e., CT) were used in the construction of aquatic systems. Since invertebrate trophic levels were likely unaffected by the presence of oil sands material, the increases in $\delta^{15}N$ values exhibited by benthic invertebrates are probably a function of elevated levels of nitrogen, principally ammonia, released from oil sands during processing (M. MacKinnon, personal communication) and used in primary and microbial production. The levels of NH_4^+ seen in the water zones of all these sites were low compared to the concentrations measured in MFT porewaters that might be released into the capping water (M. MacKinnon, personal communication). Since the MFT is anaerobic, no post-deposition oxidation would be expected and this is what is seen. However, the capping waters at or above the sediment interface are aerobic and with the low flux of MFT porewater release, oxidation processes (nitrification) convert ammonia to nitrite and nitrate in the surface waters (M. MacKinnon, personal communication). Other potential sources of ammonia include the mineralization of organic nitrogen sources, occurring naturally in oil sands but at elevated levels in OSPM, and raw sewage inputs into the settling basin prior to reclamation. The high $\delta^{15}N$ values at some of the sites with no apparent direct inputs of OSPM suggest that there may be oil sands-derived nitrogen sources present. The higher $\delta^{15}N$ values of chironomids at ML may be due to natural exposure to oil sands or increased exposure resulting from sedimentation and bank erosion due to the proximity of a constructed road or inputs from the Athasbasca River. Similarly, the higher $\delta^{15}N$ values of chironomids at SHE may be influenced by surface runoff from constructed/reclaimed areas.

Although water chemistry data on nitrogen species and/or TN is limited for a few of the sites studied, general trends have been reported. Boreal forest lakes in the area of oil sands deposits, but free of the influence of oil sands extraction activity, had the highest TN concentrations (3.3–3.7 mg/L) followed by MFT reclaimed sites (DP, 2.48 mg/L), wetlands or ponds on reclaimed pasture (Deep Wetland, 1.26 mg/L; South Bison Pond, 0.91 mg/L), and ML (0.8 mg/L); the NH_4^+ concentrations were low for all of these sites (≤0.11 mg/L) (van den Heuvel et al., 1999b). In the 1989 series of test ponds, TN increased with the amount of OSPM present (TP3, 1.05 mg/L; TP5, 1.32 mg/L; TP7, 1.76 mg/L) compared to the pond with no OSPM (TP1, 0.68 mg/L) (this study). Concentrations of NH_4^+ (TP3, 0.05 mg/L; TP5 and TP7, 0.09 mg/L) rose quantitatively with an increase in OSPM, whereas nitrite + nitrate

($NO_2 + NO_3$) concentrations remained similar (TP3, 0.02 mg/L; TP5, 0.03 mg/L; TP7, 0.02 mg/L) (this study). In the larger reclaimed test pond (DP), the water cap zone had 0.2 mg/L NH_4^+ and 0.1 mg/L $NO_2 + NO_3$ (Table 2), while the pore waters of the underlying MFT zone had elevated concentrations of NH_4^+ (4.5 mg/L) but similar $NO_2 + NO_3$ (0.07 mg/L) (Siwik, 1998). As the MFT densifies over time, this water would be released to the cap layer and provide a continuous source of ammonia used as a nutrient. With release from the anaerobic MFT zone to the aerobic water cap, nitrification also provides nitrite and nitrate used as nutrients in the water cap. A constant recharge of CT water, with elevated ammonia content, is also occurring in the Natural Wetland (NW), which receives dyke seepage CT water (TPW contained in the sand dyke system of one of Suncor's settling basins). The recharge of this dyke seepage CT water resulted in the maintenance of high NH_4^+ concentrations (Table 2). With this continuous loading of ammonia from the OSPM water, elevated levels of NH_4^+ are maintained at levels greater than the other test sites (Table 2).

Nitrate and ammonia from different sources may influence the $\delta^{15}N$ values of primary and secondary consumers (Wayland & Hobson, 2001). Major sources of nitrate generally have $\delta^{15}N$ values in the range of –5 to 10‰ for atmospheric nitrate, –10 to 5‰ for soil nitrate, and 7 to 30‰ for human and animal waste (Kendall, 1998). Ammonia from sewage is usually ^{15}N enriched (Wayland & Hobson, 2001; Jordan et al., 1997) due to isotope fractionation associated with the volatilization of NH_3 (Heaton, 1986; Macko & Ostrom, 1994). Volatilization of NH_3 depends on high pH and most of the test systems with OSPM had pH values greater than 8.5. Oxidation processes may also convert the NH_4^+ species into the oxygenated nitrogen nutrient forms. The availability of OSPM associated ammonia could explain the high $\delta^{15}N$ values of invertebrates associated with elevated levels of MFT and CT that were found (Figure 4). Along the Athabasca River, there were no changes in the $\delta^{15}N$ values of fish species associated with natural exposure to oil sands; quantitative increases in the $\delta^{15}N$ values of longnose sucker may be attributed to sewage treatment discharge (Farwell et al., personal communication). Natural exposure to oil sands in natural habitats does not influence the nitrogen isotope signatures of aquatic organisms, but there are high $\delta^{15}N$ values associated with biota exposed to MFT or CT that contain TPW and may be influenced by the upgrading by-products entering the tailings water systems in the settling basins. As a result, a high $\delta^{15}N$ signature might be a valuable tool for defining exposure to TPW in OSPM. Defining exposure to OSPM known to be elevated in PAC and NA using stable isotopes of C and N may allow eventually for actual quantification of biota exposure to OSPM constituents and their potential metabolites. The alternative, to characterize these complex mixtures in water and sediment habitats and follow their uptake and pathway to exposed organisms, is a challenge.

In general, there are trends of decreased $\delta^{13}C$ values associated with increased $\delta^{15}N$ values, evident in the 1989 series of tests

ponds and at reclamation sites with CT. Among the sites, there is a wide range of δ^{13}C values for chironomids (–39‰ to –24‰), which tend to be more ^{13}C depleted relative to damselflies (–33‰ to –20‰) and dragonflies (–30‰ to –22‰). This may indicate that there are many sources of carbon both autochthonous and allochthonous fueling the aquatic food web. The 1989 series of ponds are situated in close proximity to each other in an area that includes a reclaimed pasture area constructed on tailings sand deposit, as well as areas that had yet to be disturbed by Syncrude's mining operations, where forest and muskeg habitat dominated. This may limit the importance of allochthonous material in these systems. In these ponds (TP 1, 3, and 5), the δ^{13}C values for chironomids were similar, suggesting the utilization of similar carbon sources. Since all chironomids were collected from the shallow-water habitats, it is probable that the detrital base of decomposing aquatic plants and charophytes overlying the construction material is a significant carbon source as indicated by the similar δ^{13}C values of the surficial sediments. In comparison, dragonflies and damselflies showed trends of decreased δ^{13}C values in TP5 and TP7, which may reflect differences in feeding habits and thus differences in benthic exposure to OSPM (bitumen, TPW release). In addition, TP7 is different from the other ponds in that it is highly turbid, an important factor in limiting primary production and affecting the detrital base developing in this constructed system. As a result, the ^{13}C depleted surficial sediments and invertebrates from TP7 may indicate the utilization and assimilation of carbon from ^{13}C-depleted oil sands constituents.

Understanding carbon cycling in these systems is particularly challenging since bitumen and PAC tend to partition to the sediments, while NA are generally water-soluble. Unfortunately, at MFT and CT sites where the ^{13}C depletion of invertebrates may be attributed to oil sands constitutents, there are generally elevated levels of bitumen, PAC, and NA. To complicate things further, the contribution of NA to DOC varies between sites, and at sites with similar DOC concentrations, there may be differences in DIC concentrations (TP5 vs. TP7, Table 2). Residual NA (δ^{13}C value, –13.9‰ after 10+ yr of aging (TP5) was more ^{13}C enriched than fresh NA (MLSB) (δ^{13}C, –24.0‰ from a similar source. The presence of labile and refractory fractions of the NA may result in ^{13}C enrichment over time, which reflects the more recalcitrant components of the NA envelope of compounds (Clemente & Fedorak, 2005). The stable isotope data may be interpreted to suggest that microbial degradation preferentially utilizes ^{12}C from the NA source, resulting in a shift to ^{13}C enrichment of the residual NA mixture. Microbes utilizing more ^{12}C could result in ^{13}C-depleted production and/or respiration. At CT sites where NA and total petroleum hydrocarbon concentrations were highest (Smits et al., 2000), invertebrates were ^{13}C depleted, suggesting the utilization of oil sands constituents as energy.

Clearly, for stable carbon isotopes to be useful as a tracer or for understanding the contribution of oil sands constituents to the carbon budget, there is a need for more focused study on production, beyond the scope of this study. Current studies are in progress to estimate microbial production from CO_2 production in situ, and to establish seasonal and spatial trends in primary and microbial production, as well as DOC and DIC concentrations and δ^{13}C values. This requires a coordination of field studies and controlled biodegradation studies of NA under laboratory conditions using stable isotopes.

CONCLUSIONS

Based on this study, stable isotopes of carbon and nitrogen, as well as their relative changes, may be useful in tracing the levels and pathways of exposure of biota to OSPM. Aquatic reclamation options currently under investigation incorporate OSPM into the water, substrate, and watershed components of these systems, and their acceptance and role as viable reclamation landscapes require that impacts on and pathways of delivery to the colonizing aquatic biota or regional wildlife need to be understood. Stable isotopes may provide a valuable tool in showing the effects of exposure on food chain and community development. Invertebrates with high δ^{15}N values and low δ^{13}C values were associated with elevated quantities of MFT or CT, which will be used as reclamation materials. Elevated levels of NH_4^+ at sites with MFT or CT may explain the high δ^{15}N values of invertebrates. In this case, the use of stable nitrogen isotopes may be a useful tool in tracing exposure to OSPM. This is equally applicable for detecting OSPM waters at discharge sites where biota may be exposed under seepage or groundwater transport mechanisms. As such, the stable isotope fingerprints may become a valuable tracer for water transport and exposure to a receiving environment. Another possible application uses the high δ^{15}N values of benthic invertebrates to trace exposures to MFT or CT in wildlife that will be directly using the reclaimed OSPM areas or food originating in them. This may be used to assess impacts and responses of waterfowl (nesting, rearing), other birds (insectivores where they consume emerging insects), or mammals (water, food) exposed to reclamation sites with elevated levels of TPW/MFT or CT.

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