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Polycyclic aromatic hydrocarbons in caribou, moose, and wolf scat samples from three areas of the Alberta oil sands

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ABSTRACT

Impacts of toxic substances from oil production in the Alberta oil sands (AOS), such as polycyclic aromatic hydrocarbons (PAHs), have been widely debated. Studies have been largely restricted to exposures from surface mining in aquatic species. We measured PAHs in Woodland caribou (*Rangifer tarandus caribou*), moose (*Alces americanus*), and Grey wolf (*Canis lupus*) across three areas that varied in magnitude of *in situ* oil production. Our results suggest a distinction of PAH level and source profile (petro/pyrogenic) between study areas and species. Caribou samples indicated pyrogenic sourced PAHs in the study area previously devastated by forest fire. Moose and wolf samples from the high oil production area demonstrated PAH ratios indicative of a petrogenic source and increased PAHs, respectively. These findings emphasize the importance of broadening monitoring and research programs in the AOS.

1. Introduction

The Alberta oil sands (AOS) is the third largest proven reserve of oil in the world underlying 142,200 square kilometres (km^2) of land (Alberta, 2013a). The bitumen (thick, heavy crude oil), which is refined for consumer and industrial use, is mixed with sand and water deep below the earth's surface. Extraction of these oil reserves has required *in situ* drilling technologies; steam assisted gravity drainage (SAG-D) is the predominant form of extraction in the AOS, particularly south of Fort McMurray. Steam mobilizes and separates the bitumen deep below the surface (e.g., 350 m), and only the bitumen is removed and transported. *In situ* technologies are advertised by the Canadian Association of Petroleum Producers to have lower environmental impact than surface mining as measured by greenhouse gas emissions, land use, water use, and tailings ponds (CAPP, 2014). Although this technology disturbs less land on the surface, it has been shown to have a spatial footprint equivalent to surface mining when considering increased landscape fragmentation due to seismic lines, access roads, pipelines, and well sites (Jordaan et al., 2009). The perceived environmental and public health impact of surface mining activity, north of Fort McMurray, has been the focus of controversy with demands to reduce or halt development in the AOS (Gibbins, 2010; Kelly et al., 2009; Timoney and Lee, 2009). However, few independent studies are available on the environmental and public health impacts of oil exploration and bitumen extraction using *in situ* methods south of Fort McMurray.

Attention surrounding the AOS stems from the perception that these reserves are integral to North American energy security coupled with local to international campaigns highlighting negative impacts on human, wildlife, and ecological health (Gibbins, 2010). Of particular concern are exposures to polycyclic aromatic hydrocarbons (PAHs), a diverse groups of compounds found in bitumen, among other sources such as forest fires and diesel exhaust, known to be carcinogens and mutagens, and rank in the top 10 hazardous substances by the United States Agency for Toxic Substances and Disease Registry (ATSDR, 2013; Baird et al., 2005; Culp et al., 1998; Xue and Warshawsky, 2005). PAHs can be resistant to degradation making it imperative for future planning initiatives to be grounded on an understanding of the impacts of PAH exposure on the maintenance of biodiversity and ecologic processes. The Woodland caribou of northern Alberta are listed as threatened (Alberta Woodland Caribou Recovery Team, 2005), yet the extent and routes of PAH exposure and potential long-term impacts on this population are poorly understood. A better understanding of PAH exposures in large terrestrial mammals is also imperative for the health of tribal and recreational hunters.

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Sustainable hunting communities in the AOS, particularly First Nations who have retained treaty rights to hunt and fish in their traditional homeland for subsistence (Alberta, 2013c), depend on the health of this ecosystem to ensure their game is pollutant free. Common big game in Alberta includes moose, caribou, and deer. Moose in particular are the most frequently consumed traditional food among First Nation groups (McLachlan, 2014).

Caribou feed largely on lichen, when available (Naughton, 2012; Wasser et al., 2011). Lichen can readily absorb airborne contaminants; including the lightweight and volatile 2–4 ring PAHs (Belis et al., 2011; Blasco et al., 2007, 2006; Kelly and Gobas, 2001), potentially exposing caribou to trace contaminants from long-range transport of the compounds. Kelly et al. (2009) calculated over 11,000 metric tons of airborne particles, consisting mostly of bitumen, as far as 50 km from upgrading facilities. PAHs can persist in environmental compartments, such as lichen, due to their slow growth and longevity (Blasco et al., 2006). As such, caribou may be exposed to PAHs from land disturbance or forest fire for a prolonged period after the event. Moose feed largely on riparian vegetation, particularly Red Oster Dogwood and various willow species that depend upon moist soils that may facilitate absorption of PAHs through ground water (Naughton, 2012). Although the uptake of PAH compounds varies by properties of the plant, the pollutants, and environmental conditions (Belis et al., 2011; Migaszewski et al., 2002), water and sediment is a well-established contamination source of PAHs in the AOS (Akre et al., 2004; Hall et al., 2012; Headley et al., 2001; Kurek et al., 2013; Wayland et al., 2008). PAH exposure may also occur through atmospheric transport and deposition on the woody vegetation. Exposure to PAHs in carnivores could occur through ingestion of PAH-laden prey. An evaluation of prey hair in wolf scat samples, analysed as part of this same ongoing work, demonstrated over 90% of the winter diet in wolves consisted of deer, moose, and caribou; 24% of wolf diet was comprised of moose, 11% of caribou, and 65% of deer after adjusting for biomass (Wasser et al., 2011). Similar findings have been reported from a separate study in Northeastern Alberta, including sites that overlap our study area (Latham et al., 2011).

Our study measured polycyclic aromatic hydrocarbons in scat (fecal) samples collected over a 2500 km^2 area with varying degrees of *in situ* oil production activity, providing an unprecedented opportunity to non-invasively monitor levels of PAHs in three terrestrial species with markedly different resource utilizations. We evaluated three wide-ranging terrestrial mammals that inhabit the AOS, Woodland caribou (*Rangifer tarandus caribou*), moose (*Alces americanus*), and Grey wolf (*Canis lupus*). This allowed us to compare levels across species that have markedly distinct dietary differences, life histories, and associated routes of exposure for a comprehensive look at potential contamination of different environmental resources.

2. Material and methods

2.1. Study area

Scat samples from caribou, moose and wolf were collected over a 2500 km^2 area south of Fort McMurray, spanning three caribou ranges within the East Side of the Athabasca River caribou herd that differed in oil production activity and fire histories (Fig. 1). The extent of oil development and exploration was evaluated using the Alberta Energy Regulation's List of Wells in Alberta, Statistical Report 37 (AER, 2014), including all reported wells starting in 1957 up through and including 2009 in locations defined using the Alberta Township System (ATS) (ATS, 2014). The Egg Pony (EP) range, located in meridian 4 including ranges 7–13 and townships 77–83, was the site of the greatest amount of oil development and exploration activity during our winter 2009 study period. The EP area had 4 active wells and 34 wells drilled and cased. The Wiau range, to the immediate south of the EP, located in meridian 4 including ranges 9–12 and townships 76–77, included oil exploration and extraction activity at a lower intensity than the EP, with no active wells and 7 wells drilled and cased. In addition, an extensive fire in 2002 (the House River fire) burned over 238,000 ha of the range (Alberta, 2013b) including the entire Wiau sampling area. No other fires on record in the three study areas since 1996 were larger than 20,000 ha. The Algar range, approximately 160 km to the north of the EP and 70 km west-southwest of Fort McMurray, along the Athabasca River, located in meridian 4 including ranges 13–17 and townships 84–87, had no active or capped wells on record although historical exploration may have occurred, as evidenced by survey lines visible on Google Earth (Google Inc; Mountain View, CA). These 3 major geographic areas sampled allowed for a spectrum of oil development and exploration activity to be represented and evaluated, even in the absence of a true reference site.

2.2. Sample collection

Scat samples were located by trained detection dogs between mid-December of 2008 and mid-March of 2009, as part of the ongoing work on the impacts of AOS development on caribou, moose, and wolf (Wasser et al., 2011). The survey included 36 cells in the EP, four cells in the Wiau, and eight cells in the Algar. DNA was extracted from all scat samples and used to confirm the species, sex, and individual identities (Wasser et al., 2011). Available funding restricted the number of samples that could be analysed in each species. We aimed to randomly select one fecal sample from 15 genetically unique individuals of each sex per species and area. However, the number of samples analysed from each sex and species varied across study areas based on sample detections in the field. For example, only one wolf sample was collected in the Algar (not analysed) and no male caribou or female wolf samples were collected in the Wiau.

2.3. Laboratory and analytical methods

PAH extraction, purification, and quantification methods were developed and performed at the University of Washington, Seattle using modified procedures from other studies (Cochran et al., 2012; Forsberg et al., 2011; Mazéas and Budzinski, 2005; United States Environmental Protection Agency, 1996). All samples were spiked with a surrogate standard (Acenapthylene-d10) (Accustandard; New Haven, CT USA) prior to extraction to monitor extraction recovery and for internal standard quantification using isotope dilution methods. All samples were previously lyophilized (Wasser et al., 2011). For caribou and moose samples, 1.0 g of dry fecal material was saponified (alkaline decomposition of lipids) using 9.0 mL of 1 M potassium hydroxide:ethanol (80% ethanol:20% Millipore water) then extracted with 10.0 mL of hexane. Due to matrix interference and poor recovery of internal standards in the wolf sample, 0.35 g of dry fecal material was first extracted in 10.0 mL of hexane, then saponified as described above. This modification served to saponify only the extract, not other components of the fecal bulk (e.g., prey hair). The final extract solution for all species received 20.0 mL of magnesium sulfate and sodium chloride (4:1). The resulting hexane extract was evaporated to approximately 1.0 mL, and loaded onto a 500 mg Discovery-aminopropyl Solid Phase Extraction cartridge (Supelco; Bellefonte, PA USA). The target compounds were eluted using 12.0 mL hexane. The final extract was evaporated to 0.5 mL and stored in the