

Alberta oil sands development

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Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous class of hundreds of organic compounds composed of two or more aromatic rings that are released naturally and from human activities. Natural sources of PAHs include forest fires, oil seeps, and volcanic eruptions; anthropogenic sources include burning of fossil fuels and wood, production of coke and charcoal, petroleum refining, and petroleum spills (1). The US Agency for Toxic Substances and Disease Registry has ranked PAHs eighth on their list of hazardous substances (2).

In this issue of PNAS, Kelly et al. (3) demonstrate that the exploitation of the oil sands in Alberta, Canada, releases PAHs into terrestrial and aquatic environments. To estimate the potential of these PAHs to cause harm, this information can be incorporated into an exposure assessment and combined with dose–response information to form a risk assessment.

The International Energy Agency reports that global demand for oil will rise from 84.7 million barrels per day in 2008 to 105 million barrels per day in 2030 (4). The majority of this increase will take place in China and India, with China expected to overtake the United States as the world's largest importer of oil and gas by 2025. Currently, 85% of global energy demand is met by fossil fuels (4). However, reserves of conventional crude oil are declining, and the emphasis is shifting from conventional oil production to the development of nonconventional sources, including oil sands. Canada's proven petroleum hydrocarbon reserves include the oil sands in the Athabasca Basin of northeastern Alberta and Saskatchewan. These deposits, which are regarded as a safe and secure source of oil for North America, are the second largest in the world, containing an estimated 173.2 billion barrels of recoverable oil (5). In 2008, Alberta's oil sands industry produced 1,184,000 barrels per day (5).

Despite short-term economic benefits, the oil sands exploitation is controversial, especially relative to environmental ramifications. From 2000 to 2010, development and production activities are expected to lead to a total increase in gross domestic product of approximately \$885 billion (6). Currently, the majority of bitumen is recovered by surface-mining practices that require the clearing of large areas of land, resulting in loss of habitat, including migration corridors and breed-



Fig. 1. Aerial view of an oil sands extraction facility with adjacent OSPW holding ponds and the Athabasca River. Companies currently operate under a no-release strategy, so all OSPW must be stored in containment ponds to prevent release into the environment. The Athabasca River is the main source of fresh water used in the bitumen extraction process. (Copyright © The Pembina Institute, Calgary, Alberta, Canada. Photograph courtesy of Chris Evans, The Pembina Institute, www.OilSandsWatch.org.)

ing grounds for terrestrial and aquatic species. Methods for mitigating and remediating these effects are under development, but even when remediated the habitat will be considerably different from its previous state. These externalities are costs that should be considered when developing this resource.

Oil is extracted from surface-mined oil sands by use of the Clark hot (79–93 °C) water process that uses caustic soda to separate bitumen from other constituents such as clay, sand, dissolved metals, and organic compounds, including PAHs and naphthenic acids (NAs). The resultant oil sands process water (OSPW) is stored in on-site tailings ponds (7). Currently, two to four barrels of water are required to extract one barrel of oil, and 4 cubic meters of OSPW are produced for each cubic meter of oil sands processed (8). The Athabasca River is the source of fresh water (Fig. 1). Although recycling of OSPW reduces the demand for fresh water, the process has affected water quality by concentrating the organic and inorganic constituents within recycled OSPW; this process, in turn, has implications for water treatment and reclamation (9).

Oil sands companies are currently held to a zero-discharge policy by the Alberta Environmental Protection and Enhancement Act (1993). Thus, all OSPW produced must be held on site (4, 10). This requirement has resulted in over a billion cubic meters of tailings water held in containment systems (11). Ultimately, the companies are responsible for reclaiming

this water and finding a way to release it back into the local environment; this mandate presents a major challenge for the industrial and academic communities. The vast quantity of OSPW has led to public criticism and more recently to proposed targets for a reduction in the amount of liquid tailings by the Energy Resources Conservation Board of Alberta (12).

NAs are a group of naturally occurring acyclic, monocyclic, and polycyclic carboxylic acids that can account for up to 4% (by weight) of raw petroleum (13). These organic acids occur naturally in bitumen and become solubilized and concentrated in OSPW (14). NAs are a mixture of compounds, the relative proportion of which changes over time as the result of environmental weathering. The complex nature of the NA mixture presents challenges for their characterization both by analytical chemistry and toxicology. Ambient concentrations of NAs vary depending on the geological characteristics of the underlying area, but background concentrations for waterways in the Athabasca region typically have been less than 1 mg/L. In comparison, the NA concentrations in OSPW are as great as 110–120 mg/L (13). NAs in OSPW are

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both persistent and toxic to a range of aquatic organisms, including rainbow trout (*Oncorhynchus mykiss*) and *Daphnia magna* (15). NAs' mechanism of toxicity is not known, but they can act via narcosis (14) and other mechanisms (16). NAs are seen as the primary targets for treatment efforts and as the most important indicators of potential downstream effects after release.

Alkyl-substituted PAHs, including alkylated derivatives of phenanthrene/anthracene, fluoranthene/pyrene, and benz(a)anthracene/chrysene, are constituents of petroleum hydrocarbon products. These compounds are also the predominant PAHs in oil sands tailings ponds (17) and in sediments and surface water from tributaries of the Athabasca River (18, 19). These PAHs are derived from the erosion of naturally occurring bitumen along banks of the river and in the riverbed. Previous studies have shown that fishes inhabiting the Athabasca region are exposed to PAHs. Altered biochemical responses (ethoxyresorufin *O*-deethylase activities) have been demonstrated in several fish species native to the Athabasca River (19), including early life stages of some species (18).

Although PAHs exist as natural components of oil sands sediments, the results presented by Kelly et al. (3) suggest that fishes inhabiting the Athabasca River and its tributaries may be exposed to additional PAHs either liberated from oil sands sediments as a result of mining

practices or from emissions from upgrading facilities. Of particular concern is increased loading of PAHs into ecosystems, especially during the spring snowmelt, which occurs during fish spawning periods.

Exploitation of the oil sands in Alberta, Canada, releases PAHs into terrestrial and aquatic environments.

One aspect of PAHs that needs to be considered in assessing potential impacts of the concentrations of PAHs reported by Kelly et al. (3) is their photodynamic potential. Some of the three-, four- and five-ring PAHs exhibit photoenhanced toxicity to aquatic organisms (20). PAHs can become photoactivated by absorbing UV light that penetrates the atmosphere and aquatic systems (21). Photoactivated PAHs either in the water or in the tissues of organisms can transfer the energy through fluorescence or phosphorescence, or directly or indirectly, to biomolecules, thus resulting in damage to functional and structural proteins and lipids. In the presence of ambient solar light, some PAHs can be as much as 50,000-fold more toxic

than they are under laboratory conditions. Therefore, an assessment of the risk of even small concentrations of PAHs deposited into the environment must consider this aspect of chemical and physical interactions in the environment.

Global demand for oil and the resulting economic potential mean that development of oil sands will continue. This development has the potential to impact society and the environment significantly. It is essential that any detrimental effects be mitigated as much as possible and that development proceed in a manner that minimizes effects on the health and welfare of the environment, wildlife, and humans alike. Researchers at the Universities of Alberta and Saskatchewan are developing methods to treat OSPW and tailings, as well as analytical methods to better characterize the organic constituents and molecular markers of exposure to monitor for effects before population- or community-level effects are observed. These researchers also are investigating alternative methodologies to recover oil from bitumen that minimizes the use of water and energy and production of OSPW.

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