Evaluating officially reported polycyclic aromatic hydrocarbon emissions in the Athabasca oil sands region with a multimedia fate model

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Emissions of organic substances with potential toxicity to humans and the environment are a major concern surrounding the rapid industrial development in the Athabasca oil sands region (AOSR). Although concentrations of polycyclic aromatic hydrocarbons (PAHs) in some environmental samples have been reported, a comprehensive picture of organic contaminant sources, pathways, and sinks within the AOSR has yet to be elucidated. We sought to use a dynamic multimedia environmental fate model to reconcile the emissions and residue levels reported for three representative PAHs in the AOSR. Data describing emissions to air compiled from two official sources result in simulated concentrations in air, soil, water, and foliage that tend to fall close to or below the minimum measured concentrations of phenanthrene, pyrene, and benzo(a)pyrene in the environment. Accounting for evaporative emissions (e.g., from tailings pond disposal) provides a more realistic representation of PAH distribution in the AOSR. Such indirect emissions to air were found to be a greater contributor of PAHs to the AOSR atmosphere relative to reported direct emissions to air. The indirect pathway transporting uncontrolled releases of PAHs to aquatic systems via the atmosphere may be as significant a contributor of PAHs to aquatic systems as other supply pathways. Emission density estimates for the three PAHs that account for tailings pond disposal are much closer to estimated global averages than estimates based on the available emissions datasets, which fall close to the global minima. Our results highlight the need for improved accounting of PAH emissions from oil sands operations, especially in light of continued expansion of these operations.

The bitumen deposits underlying Alberta, Canada, represent the third largest proven reserve of crude oil in the world (1). It is predicted that investment in oil sands developments and its operations will contribute 2.28 trillion CAD to Canada's gross domestic product from 2010 to 2035 (2). Presently, most of the bitumen is extracted through surface-mining processes that necessitate clearing of overlying vegetation, resulting in loss of habitat, migration corridors, and breeding grounds (3). The surface mineable deposits cover 4,800 km^2 of the largest oil sands deposit, the Athabasca oil sands, and surround the region of Fort McMurray in northeastern Alberta.

During the surface mining process, bitumen is extracted from up to 100 m below the surface and is separated from other oil sands constituents using hot water (40–60 °C) and frothing processes. The residual fluids from the extraction process are transported to on-site settling basins, commonly known as "tailings ponds," and consist of a small percentage of residual bitumen in addition to sand, clay, dissolved metals, and organic compounds, including polycyclic aromatic hydrocarbons (PAHs), 16 of which are listed as priority pollutants by the US Environmental Protection Agency (EPA). Following extraction and separation of bitumen from the oil sands, the bitumen is subjected to upgrading, which often involves high temperatures (~460–500 °C). The left-over material from this process—known as petroleum "coke" and enriched in heavier compounds, such as heavier PAHs—may

be shipped abroad or left on-site (4) (e.g., as capping over tailings areas in a recently developed reclamation strategy), and is also subject to wind erosion and transport.

The Alberta government enforces a zero-discharge policy, which resulted in the on-site storage of ~720 million m^3 of oil sands process water in 2009 (5). Despite the presence of seepage-capture facilities and interceptor ditches to limit export of process waters from tailings ponds (6), it has been estimated that seepage from various tailings areas travels to the Athabasca River at a rate of 0.0864–5.6 million L/d (7). In addition, the quantities of PAHs reported by oil sands developers in the Athabasca Oil Sands region (AOSR) to the Canadian government's National Pollutant Release Inventory (NPRI) (8) as disposal to tailings ponds are up to five orders-of-magnitude larger than quantities reported as direct atmospheric emissions, highlighting the possibility of volatilization of PAHs from these ponds and their subsequent deposition to soils and waters. Other sources of PAHs resulting from oil sands operations include emissions from industry-associated vehicle traffic and stacks, in addition to wind erosion and transport of exposed bitumen from mine faces.

Past studies have found various aquatic species native to the AOSR suffer adverse health effects when exposed to oil sands process water and sediments produced in the region (e.g., refs. 9–12). The toxic nature of oil sands process waters discerned through controlled field and laboratory studies and the carcinogenic nature of some PAHs warrant concern when considered alongside the concentrated presence of PAHs in tailings ponds, and the pathways connecting these ponds to freshwater bodies in the AOSR. Recent findings by Kelly et al. (13) suggest that development in the AOSR during the 2 y preceding their study was related to increased concentrations of dissolved PAHs observed in the Athabasca River and its tributaries, and

Significance

Our study shows that emissions of polycyclic aromatic hydrocarbons estimated in environmental impact assessments conducted to approve developments in the Athabasca oil sands region are likely too low. This finding implies that environmental concentrations in exposure-relevant media, such as air, water, and food, estimated using those emissions may also be too low. The potential therefore exists that estimation of future risk to humans and wildlife because of surface mining activity in the Athabasca oil sands region has been underestimated.

that these concentrations fell within a range "likely toxic" to fish embryos.

The impact of oil sands development on PAH cycling through the AOSR remains unclear, in part because of monitoring programs that have been deemed inadequate by various review panels (e.g., refs. 14–16), and the difficulty in ascribing observed environmental residue levels to natural sources versus anthropogenic activity. However, a recent assessment of PAHs in lake-sediment cores provides compelling evidence that oil sands development has led to a significant increase in PAH levels in the AOSR environment (17). Although there have been studies providing insight into concentrations of PAHs in air (18), water (13), snow (13), sediments (10, 17, 19–21), tailings pond pore water (22), and tailings pond sediments (10, 21) in the AOSR, thorough characterization of PAH sources, pathways, and sinks within the AOSR is still lacking.

Given environmental monitoring data and emissions estimates, a multimedia environmental fate model can serve as a cost-effective method to describe PAH transport and fate in a particular region, not only helping to elucidate important sources, pathways, and sinks, but also highlighting those environmental parameters and processes that require better characterization through field studies (23–29). Environmental monitoring data relevant to the AOSR can be found in environmental impact assessment (EIA) reports compiled by consulting companies (30), in addition to studies reporting environmental residue levels, such as those mentioned above. Emissions estimates are available in EIA reports as well as in an online repository maintained by the NPRI. In light of the uncertainty surrounding water quality and contaminant cycling in the AOSR, the objectives of the present study are to: (i) assess whether reported emissions of PAHs in the AOSR can be reconciled with measured concentrations in air, water, soil, and foliage found in the AOSR and similar boreal environments; (ii) make an estimate of PAH emissions if reported emissions of PAHs are not found to be reasonable, in addition to first estimates of some alkylated PAHs and dibenzothiophene (DBT), considered oil sands marker compounds; and (iii) elucidate major transport pathways of PAHs in the AOSR, specifically with respect to supplying PAHs to aquatic systems.

Methods

The nonsteady-state multimedia fate model CoZMo-POP (Coastal Zone Model for Persistent Organic Pollutants) (31, 32) was used in all model simulations. First, the model was parameterized to better represent the AOSR environment and the contaminants being modeled: phenanthrene (PHE), pyrene (PYR), benzo(a)pyrene (BaP), DBT, C1-, C2-, and C3-naphthalenes (C1-NAP, C2-NAP, and C3-NAP), C1-fluorenes (C1-FLU), and C1-phenanthrenes/anthracenes (C1-P/A). Model simulations for PHE, PYR, and BaP were then run with two sets of officially reported emissions scenarios: one which included only emissions to air (AIR), and another which described emissions into a tailings pond compartment (TP). The emissions scenarios were first evaluated by comparing the model predicted concentrations with those measured in the environment. During a last set of model simulations for all contaminants, emissions scenarios were adjusted until simulated air concentrations matched those recently reported by Environment Canada (INV) (18). Finally, emissions densities (t/km²·y, where "t" is "ton") were calculated and compared for PHE, PYR, and BaP for all three emissions scenarios—AIR, TP, and INV—in addition to global per-country emission estimates compiled by Shen et al. (33).

Model Parameterization. The present study used the version of the nonsteady-state model CoZMo-POP (32) that was modified in 2004 to include a seasonal snow compartment (31). Also included are compartments representing the atmosphere, forest canopy, forest soil, nonforested soil, freshwater, freshwater sediment, coastal water, and coastal sediment. To accommodate the TP scenario, the parameters related to the existing coastal water and coastal water sediment compartments in CoZMo-POP were altered such that they describe tailings areas and their underlying sediments (SI Appendix, Table S1). No direct exchange between the freshwater compartment and the compartments representing the tailings ponds occurs (refer to SI Appendix, Fig. S1 for schematic of model structure). The model is formulated in terms of fugacity using Z-values to express equilibrium partitioning and D-values to express transformation processes and transport

between compartments (34). A complete model description including the equations used to represent different transport and transformation processes can be found in Wania et al. (32).

The study area was delineated as a 22,500-km² (150 km × 150 km) region encompassing the center of oil sands surface-mining activity between the towns of Fort McMurray and Embarras in northeastern Alberta. Monthly average temperature, rainfall, and wind speed for the region were from Environment Canada's online repository of climate normals for Fort McMurray from 1971 to 2000 (35). Monthly OH radical concentrations were estimated based on Spivakovsky et al. (36). A complete list of the values used for environmental parameters and their respective sources, can be found in the SI Appendix, Table S1.

Three PAHs—PHE, PYR, and BaP—were used in all components of this study because of availability of emissions data and because they cover a broad range of physical-chemical properties. The remaining PAHs, in addition to DBT, were also used during one component of this study because of their status as oil sands marker compounds and the availability of relevant environmental monitoring data and key physical-chemical property data.

Equilibrium partition coefficients for PAHs were taken from Ma et al. (37), and those for alkylated PAHs and DBT from Mackay et al. (38) or the US EPA (39). Reaction rate constants with hydroxyl radicals in the gas phase were from Brubaker and Hites (40) or, if unavailable, estimated with EPISuite from the US EPA (39). Half-lives in the various environmental media for parent PAHs were taken from Daly et al. (41) and, in the case of the alkylated naphthalenes and DBT, taken from Mackay et al. (38) as per Daly et al. (41). Half lives for C1-FLU and C1-P/A were approximated using data for parent homologs as done for alkylated naphthalenes by Mackay et al. (38). Half-lives in forest canopy, snow, and tailings water and sediment were estimated using the same ratios between media found in Daly et al. (41). Soil half-lives for the alkylated PAHs and DBT were adjusted in the manner of Daly et al. (41) by increasing the default values by a factor of 22. A complete list of physical-chemical properties and their corresponding sources are listed in SI Appendix, Table S2.

Yearly emissions data were obtained from two sources: an EIA for a proposed oil sands development in the AOSR conducted for the year 2009 (42), and the NPRI (8). Both datasets were temporally and spatially limited. The NPRI dataset included direct emissions to air in addition to quantities described as "disposal" to tailings areas from only 4 of the approximately 10 existing in situ and surface-mining operations in the area. In contrast, the EIA estimates were defined for a 290-km × 700-km area, and included many possible sources of emissions—stacks, plant fugitives, mine vehicles, mine faces, and tailings areas—that accounted for all industries including oil sands development. Compound-specific emissions data for each emissions source were only provided for a "base case" accounting for operations that were currently operating, under construction, approved but not yet constructed, and soon likely to be approved, whereas only cumulative emissions for 14 PAHs were given for the "existing case." Thus, the ratios of the two cases for each emissions type were used to estimate compound-specific emissions for the existing case (SI Appendix, Table S3). Nonindustrial emissions, comprising 0–7% of total emissions for each compound, were excluded. Of note, naphthalene was the only PAH of the 14 assessed in the EIA with nonzero emissions from tailings areas, plant fugitives, and mine faces. Furthermore, the EIA did not include PAHs associated with fugitive dust.

The temporal range covered by the NPRI air emissions and tailings disposal data varied from 1 to 10 y, starting from any year between 2000 and 2009, whereas the EIA dataset was based on emissions-related information collected from 2006 to 2009. To generate complete emissions scenarios that ranged from 1967, the year the first oil sands development commenced operation, to 2009 it was assumed that emissions increased steadily from an initial value of approximately 2% of the most recent emissions. Thus, three model scenarios were compiled for each chemical: two describing direct emissions to air and one describing emissions to tailings ponds. Given that the two emissions datasets from the NPRI and EIA describing emissions to air were extremely similar, the three emissions scenarios were reduced to two emissions scenarios for use in model simulations: "AIR" describing emissions to air and taken from the NPRI, and "TP" describing emissions to tailings ponds, also taken from the NPRI (SI Appendix, Table S4). Direct emissions to air were excluded from the TP scenarios as they made up less than 1% of total emissions.

Key assumptions applicable to all model simulations included: (i) air entering the region from outside of the system was less contaminated than air within the system; specifically contaminant fugacities in incoming air could be estimated using the average of concentrations measured by Harner et al. (18) by passive sampling at two stations designated "remote" just adjacent to the study region from early November 2010 to early February 2011; and (ii) soil in the region contained background contaminant levels comparable

to those measured in the remote Rocky Mountains in Canada ($n = 10$) by Choi et al. in 2003 and 2004 (43). Both the incoming air fugacity and background soil contamination were assumed constant.

Model Simulations I: AIR and TP Emissions Scenarios. Simulations using the AIR and TP scenarios were run for each of PHE, PYR, and BaP, and model output subsequently compared with reported environmental residue levels. Simulations could not be run for alkylated PAHs or DBT because of lack of reported emissions. Model output was compared with concentrations measured in the AOSR in air by Harner et al. (18) and freshwater by Kelly et al. (PYR; dissolved) (13; see also ref. 44). Air concentrations were measured with passive samplers at eight "near-source" sites within 50 km of Fort McMurray (18). Dissolved water concentrations for individual compounds were not specified in Kelly et al. (13), and thus were estimated from bar graphs of the total PAH concentrations and compound-specific relative concentrations. Water samples were taken at 17 sites along the Athabasca River and 10–20 tributaries within 100 km of Fort McMurray, with most within 150 km (13, 45). As an extra evaluative measure, model concentrations in the forest canopy and soils were compared with concentrations measured in these media in the climatologically similar boreal forests of Sweden and Norway respectively. Foliage concentrations were compared with those measured in spruce needles in southwestern Sweden ($n = 4$) by Brorström-Lundén and Löfgren (46) and model soil concentrations were compared with those measured in central Norway ($n = 9$) by Aamot et al. (47). Simulated foliage concentrations (PHE) and soil concentrations were further compared with those measured by Korosi et al. (48) in the Cold Lake region of northern Alberta ($n = 11$ and 18, respectively), where several in situ oil sands operations are located. The concentrations from the latter work were estimated from bar graphs in the supporting information of ref. 48. Modeled sediment concentrations were not compared with measured data because of limited sample sizes or the influence of natural sources of bitumen. Additionally, the resulting modeled cumulative fluxes and masses were used to ascertain the preferred transport pathways to freshwater and fates of each chemical.

Model Simulations II: Estimating Emissions Using Inverse Modeling. Inverse modeling was used to estimate the emissions to air that would be required to explain concentrations of PHE, PYR, and BaP measured in air in the AOSR from early November 2010 to early February 2011 by Harner et al. (18). Similar to the previous emission scenarios, emissions were assumed to increase linearly from 1967 onwards, at which time they were approximately 2% of 2009 values. The emissions scenarios (INV) were adjusted until modeled air concentrations between November to December 2009 and January 2009 fell within the ranges of concentrations measured at various sites in the study region designated "local" from early November 2010 to early February 2011. This procedure was also used to provide first emissions estimates for DBT, in addition to those groups of alkylated PAHs also measured during the sampling campaigns by Harner et al. (18) for which key physical-chemical property data (e.g., equilibrium partition coefficients) could be found. Similar to the previous simulations, contaminant levels in air entering the AOSR from outside of the region were set equal to levels found by Harner et al. (18) during late 2010 to early 2011, although no preexisting soil contamination was specified for the alkylated PAHs and DBT.

Evaluating Emissions Scenarios Using Emission Densities. The three emissions scenarios, AIR, TP, and INV, in addition to the air emissions presented in ref. 42 for the year 2004 (EIA), were compared with a global per-country PAH emissions inventory compiled by Shen et al. (33) using their corresponding emissions densities to air (t/km^2·y) [i.e., the emissions of each of PHE, PYR, and BaP to air in tons (t), normalized to land area (km^2) and a time period of 1 y (y)]. The emissions to air in 2009 were used to calculate emissions densities for the AIR, INV, and EIA scenarios, and the net fluxes from the tailings pond to the atmosphere in 2009 were used to calculate the emissions densities for each of the TP scenarios. An area of 22,500 km^2 was used for the AIR, TP, and INV scenarios, and an area of 203,000 km^2 used for the EIA scenario.

Results and Discussion

Simulating Contaminant Fate: The Importance of Tailings Ponds. Model simulations using only direct emissions to air (AIR scenario) resulted in air, water, soil, and foliage concentrations of PHE, PYR, and BaP that tended to fall toward or below the minimum measured in the AOSR and other boreal environments (Fig. 1). Modeled concentrations of all chemicals in AOSR air were close to or below the minima measured; below the minima measured in boreal Norwegian and Cold Lake soils but within the range measured in

the remote Rockies (except BaP, which was still too low); below the minima measured in boreal Swedish spruce needles (except PHE, which fell within the range); and toward the minima measured in AOSR freshwater (except PHE, which fell higher within the range). The superior match between modeled and measured freshwater data may be because of the limited spatial extent of EIA data, taken from within a 30-km × 50-km area ~100 km north of Fort McMurray. In addition, only dissolved concentrations were measured in Kelly et al. (13), whereas only concentrations of pyrene could be reliably estimated from the bar graphs provided.

The inconsistencies between modeled and measured data suggest that emissions estimates considering only direct emissions of PAHs to air in the AOSR are underestimates. In the case of the NPRI data, this may have been because of the limited number of facilities reporting emissions information. However, this possibility is unlikely because the emissions quantities were approximately equal to those taken from the EIA, which was considered spatially too extensive as it estimated emissions from
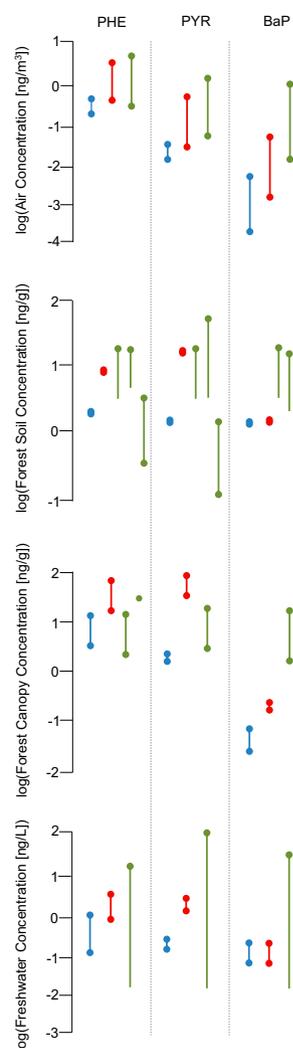
Fig. 1. Comparison of concentrations of PHE, PYR, and BaP measured in the environment (green) and modeled using only direct emissions to air (scenario AIR, blue) and emissions to tailings ponds (scenario TP, red). Closed ends represent minima and maxima; open-ended lines indicate minimum measurement below quantifiable levels, or, for the second measured range in soil (48), the average of data at 16 sites. The third measured range for forest soil represents Rocky Mountain data collected by Choi et al. (43). The second data point for PHE in foliage is the average of 11 sites from Korosi et al. (48). See text for remaining references and sampling details.

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various industrial sources in a 290-km × 700-km area extending beyond the AOSR. Despite taking into account PAH emissions from stacks, mine vehicles, mine faces, plant fugitives, and tailings areas, the estimated EIA emissions were insufficient to explain contaminant levels measured in the environment. This insufficiency may be because the EIA estimates zero emissions of all PAHs except naphthalene from tailings areas, plant fugitives, and mine faces, an unrealistic estimation considering the oil sands extraction and upgrading processes. The extraction and upgrading processes, which involve mixing with water at high temperatures in addition to aeration and thermal cracking, should facilitate the transfer of even higher molecular weight PAHs to the gas phase. These inconsistencies suggest major alteration is required in the methodology used to estimate PAH emissions from different sources in environmental impact assessments, such as that described in ref 42.

Model simulations using the TP scenario for all three PAHs result in concentrations in most media that are within the range of measured concentrations (Fig. 1). The concentrations of the three chemicals are within the range of measured concentrations in air, soil, water, and foliage, with the exception of BaP, for which the addition of tailings pond emissions is still insufficient to increase BaP levels in soil and foliage to match measured quantities. Furthermore, there is no substantial increase in air concentrations of BaP; resulting air concentrations are instead at the minimum measured by Harner et al. (18). The results of the TP simulations reaffirm that emissions estimates for the AOSR that take into account only direct emissions to air do not appear to be adequate representations of actual emissions in the region. Furthermore, indirect emissions of PAHs from secondary sources, such as tailings ponds to the atmosphere, may be a more significant contributor of oil sands PAHs to the AOSR atmosphere relative to direct emissions to air. The results also suggest that these alternative emissions sources (e.g., blowing dust from mine faces or waste coke disposal) require better quantification for low K_{AW} PAHs in particular. The relatively low modeled concentrations of BaP in air, foliage, soil and, to a lesser degree, freshwater may also be indicative of longer half-lives in these media than those that were used in this study. In the case of the soil, the estimated initial contamination may also have been too low.

The mass balances for PHE, PYR, and BaP reveal varied fates that correspond closely to contaminant physical-chemical properties; in particular, their respective partition coefficients (*SI Appendix*, Fig. S2). As such, the model predicts that approximately two-thirds of the PHE emitted to the tailings pond compartment volatilizes to the atmosphere, because of its relatively high air–water equilibrium partition coefficient. Of the remaining PHE, most (∼80%) is degraded in the tailings pond, whereas the remainder is transported to the sediments underlying the tailings pond where it is subsequently buried or degraded. Of the quantity transported to the atmosphere, most (∼80%) is degraded and the remainder is advected out of the region. In contrast, approximately half of the initially emitted BaP has been degraded in the tailings pond or tailings pond sediments by the end of the simulation period. About 25% persists in the tailings pond sediments and the rest is buried deeper in the sediments. Very little (<1%) of the initially emitted BaP volatilizes from the tailings pond. With intermediate partitioning properties, PYR is not as strongly subject as PHE or BaP to a particular environmental fate; instead, it is subject to a broader range of fates involving different environmental media. The model predicts that about half of the total emitted PYR volatilizes from the tailings ponds, which is mostly degraded in the atmosphere or advected out of the region in equal proportions. Elimination of PYR in the atmosphere and in the tailings pond and its underlying sediments each account for ∼30% of total PYR emissions, and about 10% persists in the tailings pond sediments.

The mass balances further show that the indirect pathway from the tailings pond via the atmosphere may be a significant supplier of oil sands PAHs to aquatic systems (*SI Appendix*, Fig. S3). Model simulations suggest that direct atmospheric deposition of tailings pond-derived PHE to freshwater contributes a larger quantity of PHE than PHE that is first deposited to snowpack and soils before it reaches the aquatic environment via snowmelt and runoff, respectively. Although the EIA (42) assumes naphthalene is the only priority pollutant PAH that volatilizes from tailings areas, the mass balances indicate that substantial proportions of low-volatility chemicals, such as PYR, also exhibit volatilization. These results further emphasize the need to evaluate currently used methods to estimate PAH emissions, such as that used in ref. 42, and indicate that the air-water partition coefficient (i.e., the ratio of solubility in air and water) should be considered as an indicator of emission potential rather than vapor pressure alone. The relatively low proportion of tailings pond BaP that volatilizes from the tailings areas does not render BaP emissions to tailings ponds insignificant, as the mass balance suggests that most of the remaining BaP in the region is in the tailings pond sediment, which may have serious implications for ongoing efforts to reclaim tailings areas.

Examination of the simulated seasonal concentration variability also gives some insight into transport pathways and drivers of contaminant transport (*SI Appendix*, Figs. S4–S6). In the case of PHE, the state of the tailings pond, particularly the presence of ice cover, is the main determinant of concentrations in the remaining environmental media. Ice cover prevents diffusive gas exchange with the atmosphere during the winter months, effectively eliminating the supply of PHE to the rest of the environment during the period with complete ice cover. The close linkage between the state of the tailings pond and concentrations in the remaining environmental media is less pronounced with PYR and BaP because of their relative inability to revolatilize and stronger preference to remain in a sorbed state, also resulting in less seasonally variable simulated concentrations in these media. More detailed description of seasonal concentration patterns can be found in *SI Appendix, Seasonal Patterns*.

The sensitivity and uncertainty analyses conducted because of the uncertainty surrounding parameterization of the tailings pond compartment indicate that although modeled air and water concentrations are sensitive to tailings water temperatures, the parameters related to the tailings pond contribute little to the uncertainty in these exposure relevant output parameters (*SI Appendix*, Fig. S7, and Tables S5 and S6). Detailed discussion related to the sensitivity and uncertainty analyses can be found in *SI Appendix, Sensitivity and Uncertainty*. However, we note that the sensitivity and uncertainty analyses are only valid for the parameter ranges considered. In addition, there may also be characteristics of tailings areas affecting PAH fate and transport that presently remain unaccounted for in the model structure, and thus also in the sensitivity and uncertainty analyses. For example, oil films forming at the surface of tailings areas may slow down evaporative release of PAHs.

To date, evaporation of contaminants from tailings ponds and end-pit lakes and the possibility of indirect contaminant transfer to freshwater bodies from these ponds and lakes have received little attention in the ongoing debate over environmental impacts of oil sands development. The NPRI (49) states that emissions reported as "disposal" are reported as such because "…they are contained within managed disposal sites and are not being released directly into the environment." Our results suggest that this description of disposal to tailings areas is inadequate as it ignores the potential for volatilization from (open) water bodies, thereby also underscoring the need for better characterization of the various possible contaminant transfer pathways between environmental media in the AOSR. This situation requires better accounting of all of the possible sources of PAHs, which will be of varying importance depending on the PAH under consideration. For example, perhaps the tailings areas are a significant source of chemicals with K_{AW} similar to that of PHE or PYR,

whereas other sources, such as blowing dust from mine faces, are larger suppliers of relatively low K_{AW} chemicals, such as BaP.

Emissions Estimates and Comparison of Emissions Scenarios. Inverse modeling (INV scenario) suggests that the emissions to air required to explain measured concentrations of PHE, PYR, and BaP in the atmosphere of the AOSR are two to three orders-of-magnitude larger than those reported as direct emissions to air by the NPRI and as total emissions to air by the EIA report. Although the emissions densities resulting from the EIA and NPRI's AIR scenarios both fall close to the global minima of national emission densities for PHE, PYR, and BaP as found in Greenland, the emissions densities corresponding to the INV scenarios are much closer to the reported global average calculated based on Shen et al. (33) (Fig. 2). The low emissions densities corresponding to the EIA and AIR scenarios are inconsistent with the types and intensities of key industrial sectors in the AOSR relative to Greenland, in addition to the low population density (<1 in Greenland vs. 2.7 people per square kilometer in the study region) and lack of natural sources of PAHs (e.g., forest fires) in Greenland. Whereas the AOSR is characterized by oil extraction, Greenland's economy depends heavily on the export of fish and shellfish (50).
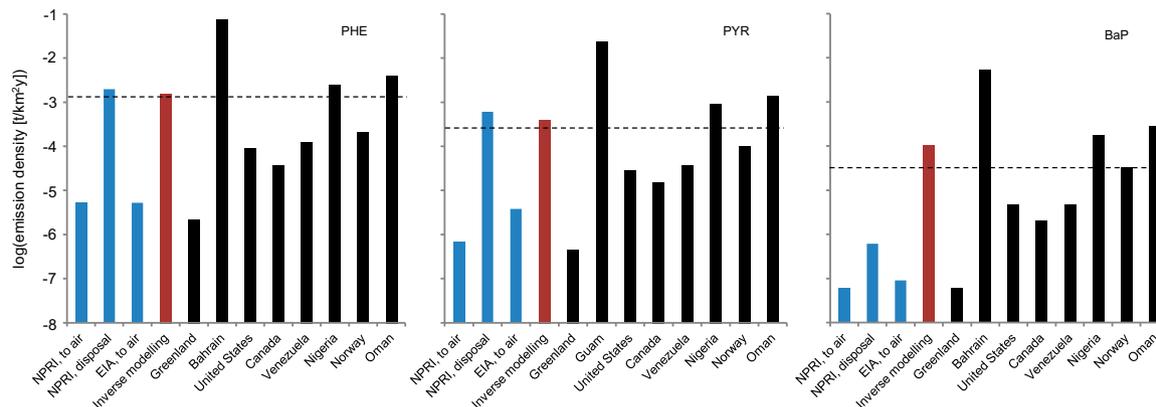
The emissions densities for the new emissions estimates are close to those for Oman, which has a relatively low population density (nine people per square kilometer) and whose economy relies in major part on petroleum resources (51). The estimates are also well within the range of those for major oil-producing nations, including the United States, Norway, and Nigeria, that also span a broad range of population densities and likely exhibit varying PAH emissions source profiles. The large discrepancies between the currently reported emissions to air for the AOSR and the emissions reported by Shen et al. (33) imply that currently available officially reported oil sands emissions data are underestimates of actual oil sands emissions in the AOSR. It appears that this may be due in large part to underestimation of indirect sources of emissions to air.

The emissions densities resulting from the PHE and PYR INV emissions scenarios are also much closer to those obtained from the TP emissions scenario, indicating that the current methodology used to estimate emissions for oil sands operations is lacking in its accounting of different emissions types. Only BaP had an emissions density resulting from the TP scenario that was closer to the global minimum. Considered together with the relatively low modeled concentrations, particularly in soil, it appears that BaP emissions are underestimated, even when accounting for disposal to tailings areas. In the case of the EIA,

discounting fugitive emissions from blowing dust could be a major reason for this discrepancy. First estimates of DBT, C1-C3-NAP, C1-FLU, and C1-P/A emissions are also provided in *SI Appendix*, Table S7. Emissions of these chemicals range from ~5–110 tons emitted in 2009. With the exception of C1-FLU, the estimated emissions of the alkylated PAHs, of great concern from a toxicological perspective (13), are all greater than those of the unsubstituted PAHs, which range from 0.25 (BaP) to 25 (PHE) tons. Uncertainty remains in the division of the estimated emissions between various sources, such as tailings ponds and mine-associated vehicles and smokestacks.

A thorough understanding of contaminant cycling in the AOSR is currently absent from the tapestry of environmental studies that include several investigations into land reclamation and process water toxicity and treatment. Improving upon the use of a multimedia environmental fate model, such as CoZMo-POP, to simulate the transport and fate of polycyclic aromatic compounds and other contaminants in the AOSR is worthwhile to pursue as chemical fluxes in the region, particularly in and out of the tailings ponds, remain poorly characterized. Lack of reliable environmental monitoring data and emissions information has made this characterization difficult, and prevents optimal use of transport and fate models, including those estimating risk to humans and other biota. Although we were able to identify an important source of relatively high K_{AW} chemicals to aquatic systems in the AOSR (i.e., the tailings ponds), it is also clear that our understanding of key sources of relatively low K_{AW} chemicals, such as BaP in the AOSR, is deficient.

A recent long-term monitoring plan outlined by the Alberta and Canada governments attempts to address this lack of understanding with a more holistic monitoring scheme that aims to characterize chemical presence and cycling across various environmental media (52). Early stages of the monitoring plan include development of emissions inventories, which will hopefully be more exhaustive in their accounting of various emissions sources. Flux measurements near tailings ponds will also be carried out to better describe tailings pond emissions and perhaps clarify the effects of oil films, ice cover, and other tailings pond characteristics on chemical transport. Using the data obtained from this revamped environmental monitoring campaign, contaminant cycling and the relative importance of various sources of contaminant release in the AOSR can be more accurately described, thereby better informing management strategies for the region.

Fig. 2. Comparison of log PHE, PYR, and BaP emission densities in t/km²·y based on: per country emissions estimates from Shen et al. (33) (black), AOSR data from the NPRI and an EIA (blue), and estimated emissions from inverse modeling for the AOSR (red). Average emissions densities from Shen et al. (33) are represented by the dashed black line. Note: Although Monserrat had a lower BaP emissions density (5.60×10^{-9}) than Greenland, it was excluded from the dataset because of the presence of an active volcano that was unaccounted for in the study by Shen et al. (33).

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