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Emissions databases for polycyclic aromatic compounds in the Canadian Athabasca oil sands region – development using current knowledge and evaluation with passive sampling and air dispersion modelling data

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S1 PAC emissions estimation and speciation methodology

S1.1 Tailings ponds

The PAH emission speciation profiles for oil sands tailings ponds is based on the paper by Galarneau et al. (2014). This study reported 1,069 kg/year emissions from tailings ponds for 13 PAH species during the JOSM field campaign (2011-2013). Based on the relative flux contributions among PAH species in Galarneau's paper, phenanthrene and pyrene dominated tailings pond PAH emissions. In our modelling practice, phenanthrene was given 50% mass fraction weight factor and pyrene was given 30% although they are not explicitly quantified in the paper. The remaining 20% weight factors are evenly distributed among the remaining 11 PAH species. As Galarneau et al. (2014) did not quantify naphthalene, acenaphthylene and acenaphthene, we do not include them in the tailings pond PAH emission. Although acenaphthylene and acenaphthene were excluded in tailings pond emissions, both of them are quantified in other PAH emission sources, such as mine fleet and point sources; therefore, they are included in total PAH emissions. However, in our study, we intentionally excluded naphthalene (NAPH) in our statistical analysis in the main paper due to its higher concentration and uncertainties compared with other PAHs species. This may lead to a bias in the modelling performance of total PAHs. Table S3 summarizes the PAH speciation profiles of tailings pond emissions. The profiles are presented as mass fractions of total PAHs.

In order to develop individual tailings pond PAH emissions for the JOSM-derived emissions database, we propagated the total annual PAH amount to each of the tailings ponds using the area size fraction of each pond and the PAH profiles in Table S3. Table S4 summarizes JOSM tailings pond total PAH emissions and the areas of each tailings pond.

The JOSM database tailings pond polygon areas in Table S4 were estimated from JOSM nonpoint emission source database shapefiles. Based on the coordinates of pond polygons, we calculated the areas of all tailings ponds. Environment and Climate Change Canada's JOSM emissions database files are available online (ECCC, 2016). The CEMA database tailings pond polygon areas in Table S5 were estimated from CEMA nonpoint emission source database files (Vijayaraghavan et al, 2010). We estimated CEMA tailings pond areas using the polygon coordinates supplied in the emissions files. Note that the pond numbers in Table S4 from JOSM are different from those in Table S5 from CEMA. Figure S1 shows the layouts of tailings ponds in the CEMA and JOSM emissions databases.

To maintain consistency in CEMA PAH emissions from tailings ponds, we estimated total tailings PAHs from CEMA by multiplying the JOSM tailings pond PAH total emissions with VOC emission ratios (of emission values from the two inventories), and then applied CEMA pond area size factors for individual ponds, as shown in Table S5.

S1.2 Mine face

There were no measurements of PAHs over oil sands mine face sources available at the time of this study. We made the assumption that PAH species emitted from mine faces should be similar to tailings ponds; thus the speciation profile of tailings pond PAH emissions in Table S3 was used for mine faces. However, PAH emissions intensity was assumed to be less than tailings ponds due to the fact that the total JOSM VOC emissions amount from mine face sources was only approximately 40% of that from tailings ponds (Table S1), although their areas were very close (tailings pond was 182.60 km^2 and mine face was 170.11 km^2). We also assumed that the PAH emission rates (unit: $g/s/m^2$) from mine faces were half of the rates from tailings ponds. In Tables S6 and S7, total PAH emissions from mine face sources were obtained by multiplying the PAH emission rate, the polygon area, and emissions duration (time) for CEMA and JOSM mines, respectively.

CEMA mine face polygon areas in Table S6 were estimated from CEMA nonpoint emissions database files (Vijayaraghavan et al, 2010). We estimated CEMA mine face areas with their polygon coordinates supplied in the emission files. Similarly, the JOSM mine face polygon areas in Table S7 were estimated from JOSM nonpoint emissions database shapefiles. We first estimated the coordinates of mine face polygons and then calculated their areas.

S1.3 Mine fleet

PAH emissions from mine fleet sources were speciated by mass fraction of total VOC emissions from mine fleet. The PAH speciation profiles were based on the CEMA study by Vijayaraghavan et al. (2010). If the total VOC emission rate is known, emissions of individual VOC and PAH compound groups can be calculated using the EPA SPECIATE database (USEPA, 2017). This EPA database provides the mass fraction of various hydrocarbon compounds. Note that the dominant species in mine fleet PAH emissions is naphthalene, which is not quantified in tailings pond emissions. Table S8 summarizes the PAH mass fractions of mine fleet VOCs. Tables S9 and S10 present PAH emissions for CEMA and JOSM mine fleet emissions, respectively. The CEMA mine fleet polygon areas in Table S9 were estimated from CEMA nonpoint emission source database files (Vijayaraghavan et al., 2010). The VOC emissions for mine fleet in the CEMA database were provided as both fleet area polygons and emissions for each of the 11 polygons. In the JOSM database, VOC emissions from mine fleet were provided as a facility total for each of the six facilities. Each facility was assigned one or more mine fleet polygon areas, and then the VOC emissions for each facility was distributed between the mine fleet polygon areas for a given facility. Note that the JOSM mine fleet polygon areas in Table S10 used the same polygon areas as mine face sources. This assumption is based on the fact that all the mine faces are covered by the operating mine fleet vehicles and infrastructure.

S1.4 Point sources, transportation, residential and area sources

In this study, CEMA PAH emissions (Vijayaraghavan et al., 2010) were used for oil sands modeling. Note that the majority of CEMA speciation profiles were based on a series of EIA studies in the oil sands area. Details can be found in the CEMA report (Vijayaraghavan et al.,

2010). For the sources that are not available in CEMA database, PAH species were estimated based on SPECIATE, the EPA's repository of organic and PM speciation profiles of air pollution sources (Simon et al., 2010). The profiles can be used to create speciated emissions inventories for ozone modelling (e.g. NO, NO2, and explicit VOC species) and to estimate hazardous and toxic air pollutant emissions from total PM and organic primary emissions. PAH species, such as acenaphthene, acenaphthylene, fluoranthene, etc., are available for the most common emission source types. Note that the SPECIATE database only contains profiles for typical sources operated in the U.S.; thus, speciation profiles may not be available for certain sources operated in northeastern Alberta, such as oil sands facilities. The current version of the SPECIATE database is 4.5.

S1.5 Alkylated and DBT emissions

There is a lack of alkylated PAH and DBT speciation profiles from oil sands studies. U.S. EPA's SPECIATE program does not include oil sands related alkylated PAH species except mobile sources, such as mine fleet. In this study, we included mine fleet emissions profiles and estimated alkylated PAHs from mine fleet and transportation line sources. In addition, we roughly estimated alkylated PAHs and DBTs from tailings ponds indirectly based on the observed PAHs and alkylated PAHs, plus the observed tailings pond PAH emissions from Sect. S1. We made an assumption that the ratio (*R*) between total PAH emissions and total alkylated PAHs or DBTs emissions from tailings ponds is equivalent to the ratio of average PAHs concentration and average alkylated PAHs or DBTs concentration at all 17 passive monitoring sites (Fig. S1b; Schuster et al., 2015). In this sense, the total alkylated PAHs and DBTs emissions from tailings ponds can be calculated from the known PAH emissions from tailings ponds divided by the ratio, *R*. Regarding alkylated PAHs and DBTs emissions profiles (i.e., the percentage mass fraction for each of the species), it was assumed to be equivalent to the observed alkylated PAHs and DBTs speciation profiles of the 17 passive monitoring sites.

S2 CALPUFF model configuration

CALPUFF (Scire et al., 2000) is a multi-layer, multi-species, non-steady-state puff dispersion model that can simulate the effects of meteorological conditions, which vary with time and space, on pollutant transport, transformation, and deposition. CALPUFF can use the three-dimensional meteorological fields developed by the CALMET model, or simple, single-station winds in a format consistent with the meteorological files used to drive the ISCST3 steady-state Gaussian model. Details on CALPUFF and model guidance were obtained from AENV (2003), AESRD (2013), CEMA (2011), Lott (1984), Malm (2000), Scire et al. (2000), New Zealand Ministry of the Environment (2004), and USEPA (1995).

The major features and options of the CALPUFF model are summarized in Table S11. Some of the technical algorithms of relevance include:

- Wet and Dry Deposition: Not modelled in this study.

- Chemical Transformation: CALPUFF includes options to parameterize chemical transformation effects using the five-species scheme employed in the MESOPUFF II model, a modified six-species scheme adapted from the RIVAD/ARM3 method, or a set of user-specified, diurnally varying transformation rates.
- Building Downwash: The Huber-Snyder and Schulman-Scire downwash models are both incorporated into CALPUFF. An option is provided to use either model for all stacks, or make the choice on a stack-by-stack and wind-sector-by-wind-sector basis. Both algorithms have been implemented in such a way as to allow the use of wind-direction specific building dimensions. In addition, there is an option to use PRIME (Plume Rise Model Enhancements) as the method of calculating building downwash. PRIME includes two important features in downwash calculations: (1) enhanced plume dispersion coefficients due to turbulent wake effects, and (2) reduced plume rise due to descending streamlines and increased entrainment in the wake of the building.
- Dispersion Coefficients: Several options are provided in CALPUFF for the computation of dispersion coefficients: the use of turbulence measurements (σv and σw); the use of similarity theory to estimate σv and σw from modelled surface heat and momentum fluxes; the use of Pasquill-Gifford (PG) or McElroy-Pooler (MP) dispersion coefficients; or dispersion equations based on the Complex Terrain Dispersion Model (CDTM). Options are provided to apply an averaging-time correction or surface roughness length adjustments to the PG coefficients.

Model domain

The CALPUFF model requires the user to define locations where concentrations are to be calculated. The CALPUFF model domain (Table S12) was selected as 404 km by 580 km area at 4 km grid resolution in order to include a number of sources which might have the potential for impacting the selected Study Area (SA) of Alberta Oil Sands.

Meteorology

CALMET output was used to provide representative wind, temperature and turbulence fields. The three-dimensionally varying fields account for seasonal land-use differences.

Model options

The CALPUFF control file defines the 17 input groups as identified in Table S13. For many of the options, the default values were used in the absence of site/project specific data. Tables S14 to S28 identified the input parameters and the default options. Note that in the tables, values indicated by an asterisk (*) were allowed to vary spatially across the domain and were obtained from CALMET. A dash (-) indicates that the parameter was not applicable.

Table S1. Comparison of VOCs emissions (tonnes yr^{-1}) between CEMA and JOSM databases over the model domain. Data from ECCC (2016) and ECCC and AEP (2016).

Sources	CEMA 2010	JOSM 2013
Tailings pond	10,458	26,783
Mine face	3,655	10,053
Mine fleet	2,552	2,585
Residential and commercial	62	62
Non-industry (local traffic and airport)	26	26
Point sources[1]	5,092	5,092
Line sources	1,313	1,313

[1] Includes large upstream oil and gas (UOGs) but not small UOGs because most of them are outside the oil sands mining area and there are only a few of them

Table S2. Comparisons of model performance between JOSM-derived and CEMA-derived PAH emissions and over local and remote sites.

Local Sites			
PAHs	Monitored	Modeled-JOSM Emissions	Modeled-CEMA Emissions
Mean concentration (ng/m^3)	7.9	7.2	6.7
Percentage Error	-	17.1%	30.2%
RMSE (ng/m^3)	-	1.7	3.4
Remote Sites			
PAHs	Monitored	Modeled-JOSM Emissions	Modeled-CEMA Emissions
Mean concentration (ng/m^3)	4.8	2.5	1.7
Percentage Error	-	65.8%	67.1%
RMSE (ng/m^3)	-	3.6	3.5

RMSE: root mean square error

Table S3. Profile of PAH species in total tailings pond PAHs emissions

Species Name	Percentage of total PAH mass fraction (%)
Acenaphthene	0.0
Acenaphthylene	0.0
Anthracene	1.82
Benz[a]anthracene	1.82
Benzo[a]pyrene	1.82
Benzo[b]fluoranthene	1.82
Benzo[ghi]perylene	1.82
Benzo[k]fluoranthene	1.82
Chrysene	1.82
Dibenz[a,h]anthracene	1.82
Fluoranthene	1.82
Fluorene	1.82
Indeno[1,2,3-cd]pyrene	1.82
Naphthalene	0.0
Phenanthrene	50.0
Pyrene	30.0

Table S4. PAH emissions of tailings ponds from JOSM-derived emissions database

Polygon Name	Area(km^2)	PAH(kg/year)
Pond JOSM1	18.27	106.95
Pond JOSM2	1.48	8.65
Pond JOSM3	3.25	19.02
Pond JOSM4	1.71	9.99
Pond JOSM5	0.59	3.48
Pond JOSM6	1.46	8.57
Pond JOSM7	2.83	16.59
Pond JOSM8	6.86	40.16
Pond JOSM9	2.98	17.44
Pond JOSM10	7.76	45.45
Pond JOSM11	12.31	72.09
Pond JOSM12	0.43	2.50
Pond JOSM13	18.76	109.83
Pond JOSM14	28.42	166.40
Pond JOSM15	9.82	57.49
Pond JOSM16	4.83	28.26
Pond JOSM17	3.66	21.41
Pond JOSM18	13.22	77.97
Pond JOSM19	7.54	44.12
Pond JOSM20	1.80	10.54
Pond JOSM21	21.64	126.71

Pond JOSM22	8.31	48.63
Pond JOSM23	3.56	20.85
Pond JOSM24	1.01	5.88

Table S5. PAH emissions of tailings ponds from the CEMA-derived emissions database

Polygon Name	Area(km^2)	PAH(kg/year)
Pond CEMA1	7.5	35.68
Pond CEMA2	16.9	80.39
Pond CEMA3	3.04	14.46
Pond CEMA4	0.64	3.04
Pond CEMA5	1.6	7.61
Pond CEMA6	1.96	9.32
Pond CEMA7	3.24	15.41
Pond CEMA8	4.41	20.98
Pond CEMA9	1.44	6.85
Pond CEMA10	13.5	64.22
Pond CEMA11	11.5	54.70
Pond CEMA12	10.2	48.52
Pond CEMA13	6.25	29.73
Pond CEMA14	1.96	9.32
Pond CEMA15	3.61	17.17

Table S6. PAH emissions from each mine face of the CEMA-derived emissions database

Polygon Name	Area(km^2)	PAH(kg/year)
Mine Face CEMA1	1.21	1.66
Mine Face CEMA2	4.50	6.19
Mine Face CEMA3	11.52	15.9
Mine Face CEMA4	6.0	8.26
Mine Face CEMA5	8.14	11.2
Mine Face CEMA6	3.68	5.06

Table S7. PAH emissions from each mine face of the JOSM-derived emissions database

Polygon Name	Area(km^2)	PAH(kg/year)
Mine Face JOSM1	8.68	30.59
Mine Face JOSM2	3.53	12.44
Mine Face JOSM3	7.32	25.80
Mine Face JOSM4	3.24	11.42
Mine Face JOSM5	12.14	42.78
Mine Face JOSM6	4.97	17.52
Mine Face JOSM7	16.03	56.49
Mine Face JOSM8	4.31	15.19

Mine Face JOSM9	2.65	9.34
Mine Face JOSM10	8.59	30.27
Mine Face JOSM11	14.55	51.28
Mine Face JOSM12	17.46	61.53
Mine Face JOSM13	2.11	7.44
Mine Face JOSM14	25.90	91.28
Mine Face JOSM15	38.65	136.21

Table S8. Profile of PAH species as a mass fraction of total mine fleet VOCs

Species Name	Percentage of total VOC mass (%)
Acenaphthene	0.007360883
Acenaphthylene	0.026735644
Anthracene	0.0004767412
Benz[a]anthracene	0.0001136551
Benzo[a]pyrene	0.0
Benzo[b]fluoranthene	0.0
Benzo[ghi]perylene	0.002219707
Benzo[k]fluoranthene	0.0
Chrysene	0.001277666
Dibenz[a,h]anthracene	0.0
Fluoranthene	0.020213825
Fluorene	0.013196195
Indeno[1,2,3-cd]pyrene	0.0
Naphthalene	0.235319433
Phenanthrene	0.035507681
Pyrene	0.027422151

Table S9. PAH emissions of mine fleet from the CEMA-derived emissions database

Polygon Name	Area(km^2)	PAH(kg/year)
Mine Fleet CEMA1	4.5	2449.81
Mine Fleet CEMA2	0.06	68.47
Mine Fleet CEMA3	1.21	501.11
Mine Fleet CEMA4	0.06	2.84
Mine Fleet CEMA5	0.05	9.49
Mine Fleet CEMA6	0.02	27.92
Mine Fleet CEMA7	0.08	46.19
Mine Fleet CEMA8	11.52	4399.22
Mine Fleet CEMA9	6.00	822.32
Mine Fleet CEMA10	8.14	1115.34
Mine Fleet CEMA11	3.68	130.36

Table S10. PAH emissions of mine fleet from the JOSM-derived emissions database

Polygon Name	Area(km^2)	PAH(kg/year)
Mine Fleet JOSM1	8.68	501.45
Mine Fleet JOSM2	3.53	279.51
Mine Fleet JOSM3	7.32	302.78
Mine Fleet JOSM4	3.24	133.88
Mine Fleet JOSM5	12.14	501.84
Mine Fleet JOSM6	4.97	205.63
Mine Fleet JOSM7	16.03	662.78
Mine Fleet JOSM8	4.31	178.12
Mine Fleet JOSM9	2.65	109.39
Mine Fleet JOSM10	8.59	355.39
Mine Fleet JOSM11	14.55	882.11
Mine Fleet JOSM12	17.46	1058.21
Mine Fleet JOSM13	2.11	127.69
Mine Fleet JOSM14	25.90	1765.20
Mine Fleet JOSM15	38.65	2633.99

Table S11. Major features of the CALPUFF Model

Source Types	Point sources (constant or variable emissions) Line sources (constant or variable emissions) Volume sources (constant or variable emissions) Area sources (constant or variable emissions)
Non-steady-state emissions and meteorological conditions	Gridded 3-D fields of meteorological variables (winds, temperature) Spatially variable fields of mixing height, friction velocity scale, Monin-Obukhov length, precipitation rate Vertically and horizontally varying turbulence and dispersion rates Time-dependant source and emissions data
Efficient sampling functions	Integrated puff formulation Elongated puff (slug) formulation
Dispersion coefficient (σy,σz) options	Direct measurements of σv and σw Estimated values of σv and σw based on similarity theory Pasquill-Gifford (PG) dispersion coefficients (rural areas) McElroy-Pooler (MP) dispersion coefficients (rural areas) CTDM dispersion coefficients (neutral / stable) PDF formulation for the convective boundary layer
Vertical wind shear	Puff splitting Differential advection and dispersion
Plume rise	Partial penetration Buoyant and momentum rise Stack tip effects Vertical wind shear Building downwash effects
Building downwash	Huber-Snyder method Schulman-Scire method
Sub-grid Scale Complex Terrain	CTDM flow module Dividing streamline, Hd - Above Hd puff flows over the hill and experiences altered diffusion rates - Below Hd puff deflects around the hill, splits, and wraps around the hill

Interface to the Emissions Production Model (EPM)	Time-varying heat flux and emissions from controlled burns and wildfires
Dry Deposition	Not modelled in this study
Over Water and Coastal Interaction Effects	Over water boundary layer parameters Abrupt change in meteorological conditions, plume dispersion at coastal boundary Plume fumigation Option to introduce sub-grid scale Thermal Internal Boundary Layers (TIBL's) into coastal grid cells
Chemical Transformation Options	Pseudo-first-order chemical mechanism for SO2, NOX, HNO3, and NO3 (MESOPUFF II method) Pseudo-first-order chemical mechanism for SO2, SO4, NO, NO2, HNO3 and NO3 (RIVAD/ARM3 method) User-specified diurnal cycles of transformation rates No chemical conversion
Wet Removal	Not modelled in this study
Graphical User Interface	Point-and-click set-up and data input Enhanced error checking of model inputs On-line Help files

Table S12. CALPUFF Model Domain Coordinates (UTM Zone 12; NAD 83) (404 km x 580 km grid)

Domain Extent	Easting (km)	Northing (km)
Southwest	306.219	6054.418
Northwest	306.219	6634.418
Southeast	710.219	6054.418
Northeast	710.219	6634.418

Table S13. Input Groups in the CALPUFF Control File

Input Group	Description	Applicable to the Project
0	Input and output file names	Yes
1	General run control parameters	Yes
2	Technical options	Yes
3	Species list	Yes
4	Grid control parameters	Yes
5	Output options	Yes
6	Sub grid scale complex terrain inputs	No
7	Dry deposition parameters for gases	No
8	Dry deposition parameters for particles	No
9	Miscellaneous dry deposition for parameters	No
10	Wet deposition parameters	No
11	Chemistry parameters	Yes
12	Diffusion and computational parameters	Yes

13	Point source parameters	Yes
14	Area source parameters	Yes
15	Line source parameters	No
16	Volume source parameters	No
17	Discrete receptor information	Yes

Table S14. CALPUFF Model Options Group 1 (Input Group 1: General run control parameters)

Parameter	Default	Project	Comments
METRUN	0	0	All model periods in met file(s) will be run
IBYR	-	2010	Starting year
IBMO	-	10	Starting month
IBDY	-	1	Starting day
IBHR	-	1	Starting hour
IRLG	-	19752	Length of run (from Oct 2010 to the end of 2012)
XBTZ	-	7	Base time zone
NSPEC	5	16	Number of chemical species
NSE	3	16	Number of chemical species to be emitted
ITEST	2	2	Program is executed after SETUP phase
Input Group 1: General run control parameters (Continued)			
Parameter	**Default**	**Project**	**Comments**
MRESTART	0	0	Does not read or write a restart file
NRESPD	0	0	Restart file written every NRESPD period
METFM	1	1	CALMET binary file (CALMET.MET)
AVET	60	60	Averaging time in minutes
PGTIME	60	60	PG Averaging time in minutes

Table S15. CALPUFF Model Options Group 2 (Input Group 2: Technical Options)

Parameter	Default	Project	Comments
MGAUSS	1	1	Gaussian distribution used in near field
MCTADJ	3	3	Partial plume path terrain adjustment
MCTSG	0	0	Scale-scale complex terrain not modelled
MSLUG	0	0	Near-field puffs not modelled as elongated
MTRANS	1	1	Transitional plume rise modelled
MTIP	1	0	Stack tip downwash used

Parameter	Default	Project	Comments
MBDW	1	1	Building downwash simulated using PRIME method
MSHEAR	0	1	Vertical wind shear modelled
MSPLIT	0	0	Puffs are not split
MCHEM	0	0	Transformation rates computed internally using (RIVID/ARM3) scheme
MAQCHEM	0	0	Aqueous phase transformation not modelled
MWET	1	0	Wet removal not modelled
MDRY	1	0	Dry deposition not modelled
MDISP	3	2	PG dispersion coefficients from internally calculated sigma v, sigma w using micrometeorological variables (u*, v*, L, etc.)
MTURBVW	3	3	Use both σv and σw from PROFILE.DAT to compute σy and σz, (n/a)
MDISP2	3	3	PG dispersion coefficients from internally calculated sigma v, sigma w using micrometeorological variables (u*, v*, L, etc.)
MCTURB	1	1	Standard CALPUFF subroutines used to compute turbulence σv and σw
MROUGH	0	0	PG σy and σz adjusted for roughness
MPARTL	1	1	Partial plume penetration of elevated inversion
MTINV	0	0	Strength of temperature inversion computed from default gradients
MPDF	0	1	PDF used for dispersion under convective conditions
MSGTIBL	0	0	Sub-grid TIBL module not used for shoreline
MBCON	0	0	Boundary concentration conditions not modelled
MFOG	0	0	Do not configure for FOG model output
MREG	1	0	Do not test options specified to see if they conform to regulatory values

Table S16. CALPUFF Model Options Group 3 (Input Group 3: Species list-chemistry options)

CSPEC	Modelled (yes=1, no=0)	Emitted (yes=1, no=0)	Dry (0=none, 1=computed-gas, 2=computed particle, 3=user-specified)	Output group number
Naphthalene	1	1	1	0
Acenaphthylene	1	1	1	0
Acenaphthene	1	1	1	0
Fluorene	1	1	1	0
Phenanthrene	1	1	2	0
Anthracene	1	1	2	0
Fluoranthene	1	1	2	0
Pyrene	1	1	2	0
Benz(a)anthracene	1	1	2	0
Chrysene	1	1	2	0
Benzo(b)fluoranthene	1	1	2	0

Benzo(k)fluoranthene	1	1	2	0
Benzo(a)pyrene	1	1	2	0
Indeno(1,2,3-	1	1	2	0
Dibenz(a,h)anthracene	1	1	2	0
Benzo(g,h,i)perylene	1	1	2	0

Table S17. CALPUFF Model Options Group 4 (Input Group 4: Grid control parameter)

Parameter	Default	Project	Comments
NX	-	101	Number of X grid cells in meteorological grid
N		145	Number of Y grid cells in meteorological grid
NZ	-	10	Number of vertical layers in meteorological grid
DGRIDKM	-	4	Grid spacing (km)
ZFACE	-	0,20,40,80,160,300 600, 1000, 1500, 2200, 3000	Cell face heights in meteorological grid (m)
XORIGKM	-	306.219	Reference X coordinate for SW corner of grid cell (1,1) of meteorological grid (km)
YORIGKM	-	6054.418	Reference Y coordinate for SW corner of grid cell (1,1) of meteorological grid (km)
IUTMZN	-	12	UTM zone of coordinates
IBCOMP	-	1	X index of lower left corner of the computational grid
JBCOMP	-	1	Y index of lower left corner of the computational grids
IECOMP	-	101	X index of the upper right corner of the computational grid
JECOMP	-	145	Y index of the upper right corner of the computational grid
SAMP	T	F	Sampling grid is not used
IBSAMP	-	-	X index of lower left corner of the sampling grid
JBSAMP	-	-	Y index of lower left corner of the sampling grid
IESAMP	-	-	X index of upper right corner of the sampling grid
JESAMP	-	-	Y index of upper right corner of the sampling grid
MESHDN	1	1	Nesting factor of the sampling grid

Table S18. CALPUFF Model Options Group 5 (Input Group 5: Output Option)

Parameter	Default	Project	Comments
ICON	-	1	Output file CONC.DAT containing concentrations is created
IDRY	-	1	Output file DFLX.DAT containing dry fluxes is created
IWET	-	1	Output file WFLX.DAT containing wet fluxes is created
IVIS	-	0	Output file containing relative humidity data is not created
LCOMPRS	T	F	Perform data compression in output file

Parameter	Default	Project	Comments
IMFLX	0	0	Do not calculate mass fluxes across specific boundaries
IMBAL	0	0	Do not report mass balances
ICPRT	0	0	Do not print concentration fields to the output list file
IDPRT	0	0	Do not print dry flux fields to the output list file
IWPRT	0	0	Do not print wet flux fields to the output list file
ICFRQ	1	1	Concentration fields are printed to output list file every 1 hour
IDFRQ	1	1	Dry flux fields are printed to output list file every 1 hour
IWFRQ	1	1	Wet flux fields are printed to output list file every 1 hour
IPRTU	1	3	Units for line printer output are in $\mu g/m^3$ for concentration and $\mu g/m^2/s$ for deposition
IMESG	2	2	Messages tracking the progress of run are written on screen
LDEBUG	F	F	Logical value for debug output
IPFDEB	1	1	First puff to track
NPFDEB	1	1	Number of puffs to track
NN1	1	1	Meteorological period to start output
NN2	10	10	Meteorological period to end output

Table S19. CALPUFF Model Options Group 6 (Input Group 6: Sub Grid Scale Complex Terrain Inputs)

Parameter	Default	Project	Comments
NHILL	0	0	Number of terrain features
NCTREC	0	0	Number of special complex terrain receptors
MHILL	-	2	Input terrain and receptor data for CTSG hills input in CTDM format
XHILL2M	1.0	1.0	Conversion factor for changing horizontal dimensions to metres
ZHILL2M	1.0	1.0	Conversion factor for changing vertical dimensions to metres
XCTDMKM	-	0	X origin of CTDM system relative to CALPUFF coordinate system (km)
YCTDMKM	-	0	Y origin of CTDM system relative to CALPUFF coordinate system (km)

Table S20. CALPUFF Model Option Group 9 (Input Group 9: Miscellaneous Dry Deposition Parameters)

PAC dry deposition was not modelled in this study. The modelled air concentrations do not account for dry deposition.

Table S21. CALPUFF Model Option Group 10 (Input Group 10: Wet Deposition Parameters, scavenging coefficients, units: s^{-1})

PAC wet deposition was not modelled in this study. The modelled air concentrations do not account for wet deposition.

Table S22. CALPUFF Model Option Group 11 (Input Group 11: Chemistry Parameters)

Parameters	Default	Project	Comments
MOZ	1	0	Use monthly ozone values
BCKO3	80-	40	Monthly background ozone concentration (ppb)
BCKNH3	10	10	Monthly background ammonia concentration (ppb)
RNITE1	0.2	0.2	Night time NO2 loss rate in percent/hour
RNITE2	2	2	Night time NO_X loss rate in percent/hour
RNITE3	2	2	Night time HNO3 loss rate in percent/hour
MH202	1	1	Background H2O2 concentrations (Aqueous phase transformations not modelled)
BCKH202	-	-1.00	Background monthly H2O2 concentrations (Aqueous phase transformations not modelled)

Table S23. CALPUFF Model Option Group 12 (Input Group 12: Dispersion/Computational Parameters)

Parameters	Default	Project	Comments
SYDEP	550	550	Horizontal size of a puff in metres beyond which the time dependant dispersion equation of Heffter (1965) is used
MHFTSZ	0	0	Do not use Heffter formulas for sigma z
JSUP	5	5	Stability class used to determine dispersion rates for puffs above boundary layer
CONK1	0.01	0.01	Vertical dispersion constant for stable conditions
CONK2	0.1	0.1	Vertical dispersion constant for neutral/stable conditions
TBD	0.5	0.5	Use ISC transition point for determining the transition point between the Schulman-Scire to Huber-Snyder Building Downwash scheme
IURB1	10	10	Lower range of land use categories for which urban dispersion is assumed
IURB2	19	19	Upper range of land use categories for which urban dispersion is assumed
ILANDUIN	20	20	Land use category for modelling domain
XLAIIN	3.0	3.0	Leaf area index for modelling domain
ZOIN	0.25	0.25	Roughness length in metres for modelling domain
ISIGMAV	1	1	Sigma-v is read for lateral turbulence data
IMIXCTDM	0	0	Predicted mixing heights are used
XMXLEN	1.0	1.0	Maximum length of emitted slug in meteorological grid units
XSAMLEN	1.0	10.0	Maximum travel distance of slug or puff in meteorological grid units during one sampling unit
MXNEW	99	60	Maximum number of puffs or slugs released from one source during one time step
MXSAM	99	60	Maximum number of sampling steps during one time step for a puff or slug
NCOUNT	2	2	Number of iterations used when computing the transport wind for a

Parameters	Default	Project	Comments
			sampling step that includes transitional plume rise
SYMIN	1.0	1.0	Minimum sigma y in metres for a new puff or slug
SZMIN	1	1	Minimum sigma z in metres for a new puff or slug

Stability Class	Parameter	
	SVMIN	SWMIN
	Minimum turbulence (σv) (m/s)	Minimum turbulence (σw) (m/s)
A	0.5	0.2
B	0.5	0.12
C	0.5	0.08
D	0.5	0.06
E	0.5	0.03
F	0.5	0.016

CDIV	0.0, 0.0	0.0, 0.0	Divergence criteria for dw/dz in met cells
WSCALM	0.5	0.5	Minimum wind speed allowed for non-calm conditions (m/s)
XMAXZI	3000	3000	Maximum mixing height in metres
XMINZI	50	50	Minimum mixing height in metres
WSCAT		1.54	wind speed category 1 [m/s]
		3.09	wind speed category 2 [m/s]
		5.14	wind speed category 3 [m/s]
		8.23	wind speed category 4 [m/s]
		10.8	wind speed category 5 [m/s]
SL2PF	10	10	Slug-to-puff transition criterion factor equal to sigma y/length of slug

Input Group 12: Dispersion/Computational Parameters (Continued)

Parameters	Default	Project	Comments
PTG0	0.02	0.02	potential temperature gradient for E stability [K/m]
	0.035	0.035	potential temperature gradient for F stability [K/m]
NSPLIT	3	3	Number of puffs that result every time a puff is split
IRESPLIT	0,0,0,0,00,0,0, 0,0,0,0,0,0,0,0,0, 0,1,0,0,0,0,0,0	0,0,0,0,00,0,0,0,0, 0,0,0,0,0,0,0,1,0,0 ,0,0,0,0	Time(s) of day when split puffs are eligible to be split once again

Stability Class	Parameter	
	PLX0	PPC
	Wind speed profile exponent	Plume path coefficient
A	0.07	0.8
B	0.07	0.7
C	0.1	0.6
D	0.15	0.5
E	0.35	0.4
F	0.55	0.35

ZISPLIT	100	100	Minimum allowable last hour's mixing height for puff splitting
ROLDMAX	0.25	0.25	Maximum allowable ratio of last hour's mixing height and maximum mixing height experienced by the puff for puff splitting
NSPLITH	5	5	Number of puffs that result every time a puff is horizontally split
SYSPLITH	1	1	Minimum sigma-y of puff before it may be horizontally split
SHSPLITH	2	2	Minimum puff elongation rate due to wind shear before it may be horizontally split

Parameters	Default	Project	Comments
CNSPLITH	1.00E-07	0	Minimum concentration of each species in puff before it may be horizontally split
EPSSLUG	1.00E-04	0	Fractional convergence criterion for numerical SLUG sampling iteration
EPSAREA	1.00E-06	0	Fractional convergence criterion for numerical AREA sampling iteration
DRISE	1	1	Trajectory step length for numerical rise

Table S24. CALPUFF Model Option Group 13 (Input Group 13: Point Source Parameters)

Parameters	Default	Project	Comments
NPT1	-	689	Number of point sources with constant stack parameters or variable emission rate scale factors
IPTU	1	1	Units for point source emission rates are g/s
NSPT1	0	0	Number of source-species combinations with variable emissions scaling factors
NPT2	-	0	Number of point sources with variable emission parameters provided in external file

Table S25. CALPUFF Model Option Group 14 (Input Group 14: Area Source Parameters)

Parameters	Default	Project	Comments
NAR1	-	87	Number of polygon area sources
IARU	1	1	Units for point source emission rates are g/ m^2/s
NSAR1	0	880	Number of source-species combinations with variable emissions scaling factors
NAR2	-	0	Number of buoyant polygon area sources with variable location and emission parameters

Table S26. CALPUFF Model Option Group 15 (Input Group 15: Line Source Parameters)

Parameters	Default	Project	Comments
NLN2	-	-	Number of buoyant line sources with variable location and emission parameters
NLINES	-	29	Number of buoyant line sources
ILNU	1	1	Units for line source emission rates is g/s
NSLN1	0	0	Number of source-species combinations with variable emissions scaling factors.
MXNSEG	7	7	Maximum number of segments used to model each line
NLRISE	6	6	Number of distance at which transitional rise is computed
XL	-	22.81	Average line source length (m)
HBL	-	2.0	Average height of line source height (m)
WBL	-	10.0	Average building width (m)
WML	-	0.5	Average line source width (m)

DXL	-	2.0	Average separation between buildings (m)
FPRIMEL	-	50.0	Average buoyancy parameter (m4/s3)

Table S27. CALPUFF Model Option Group 16 (Input Group 16: Volume Source Parameters)

Parameters	Default	Project	Comments
NVL1	-	0	Number of volume sources
IVLU	1	1	Units for volume source emission rates is grams per second
NSVL1	0	0	Number of source-species combinations with variable emissions scaling factors
IGRDVL	-	-	Gridded volume source data is not used
VEFFHT	-	-	Effective height of emissions (m)
VSIGYI	-	-	Initial sigma y value (m)
VSIGZI	-	-	Initial sigma z value (m)

Table S28. CALPUFF Model Option Group 17 (Input Group 17: Discrete Receptor Information)

Parameters	Default	Project	Comments
NREC	-	9300	Number of non-gridded receptors

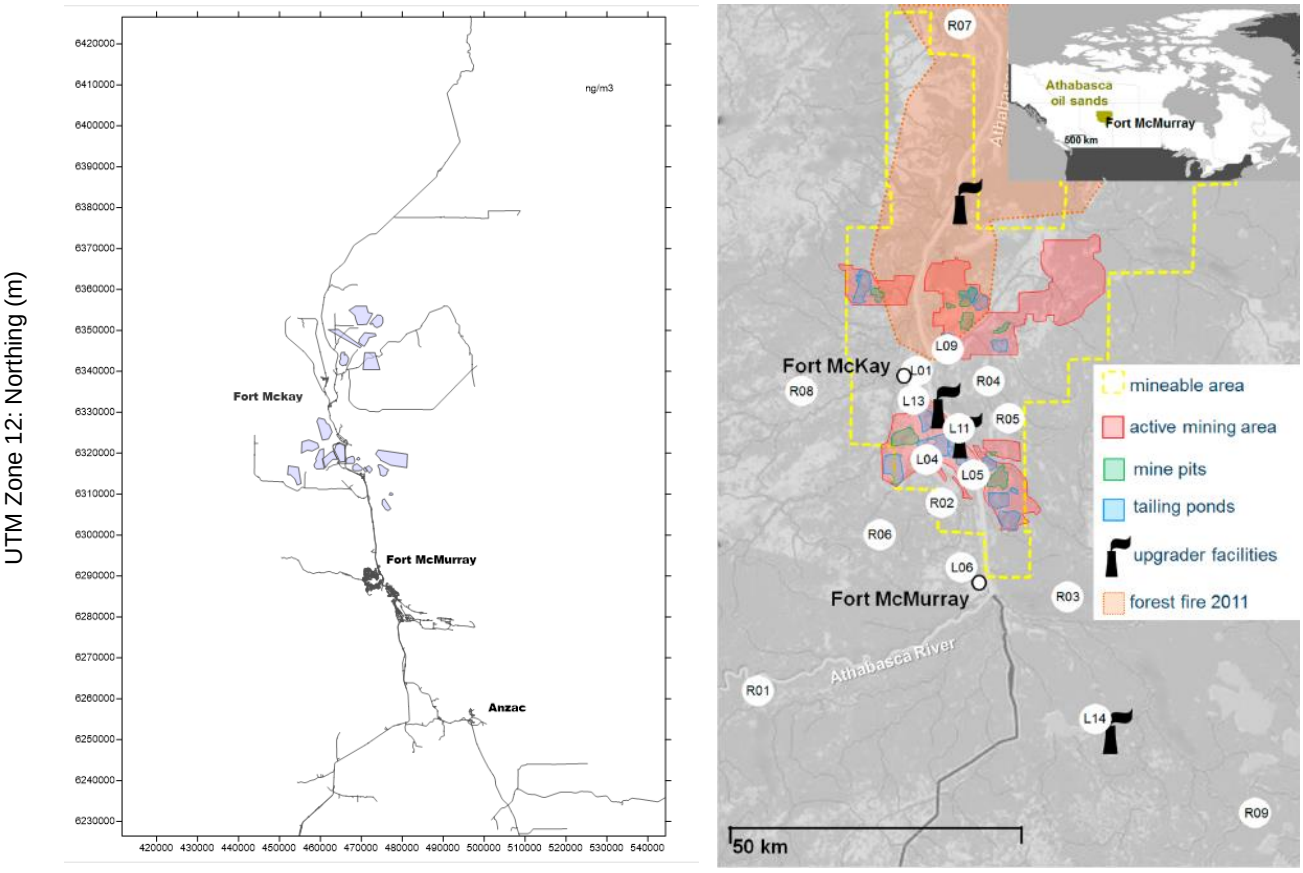

Figure S1. Map of tailings pond locations (shown in blue) in the CEMA emissions database (a) and PAC passive air monitoring locations from JOSM activities and oil sands operations obtained from Schuster et al. (2015) (b).

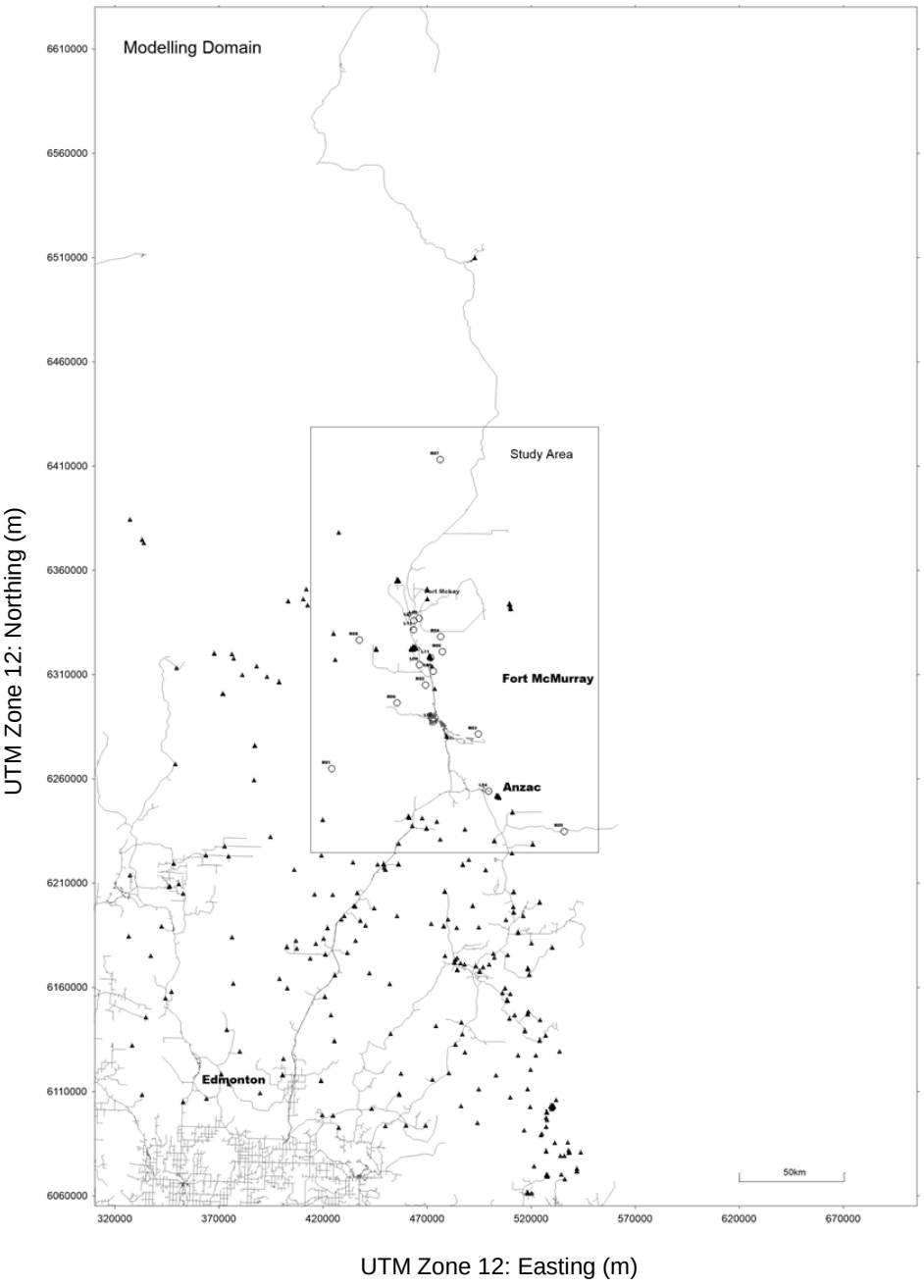

Figure S2. Map showing the point sources accounted for in the model domain and the study area where modelled concentrations are compared with measured air concentrations (Fig. S1). Black triangles indicate VOC point source locations are from the CEMA emissions database (Vijayarahavan et al., 2010) and the Capital Region Particulate Matter Air Modelling Assessment (Nopmongcol et al., 2014), which are converted to PAH emissions.

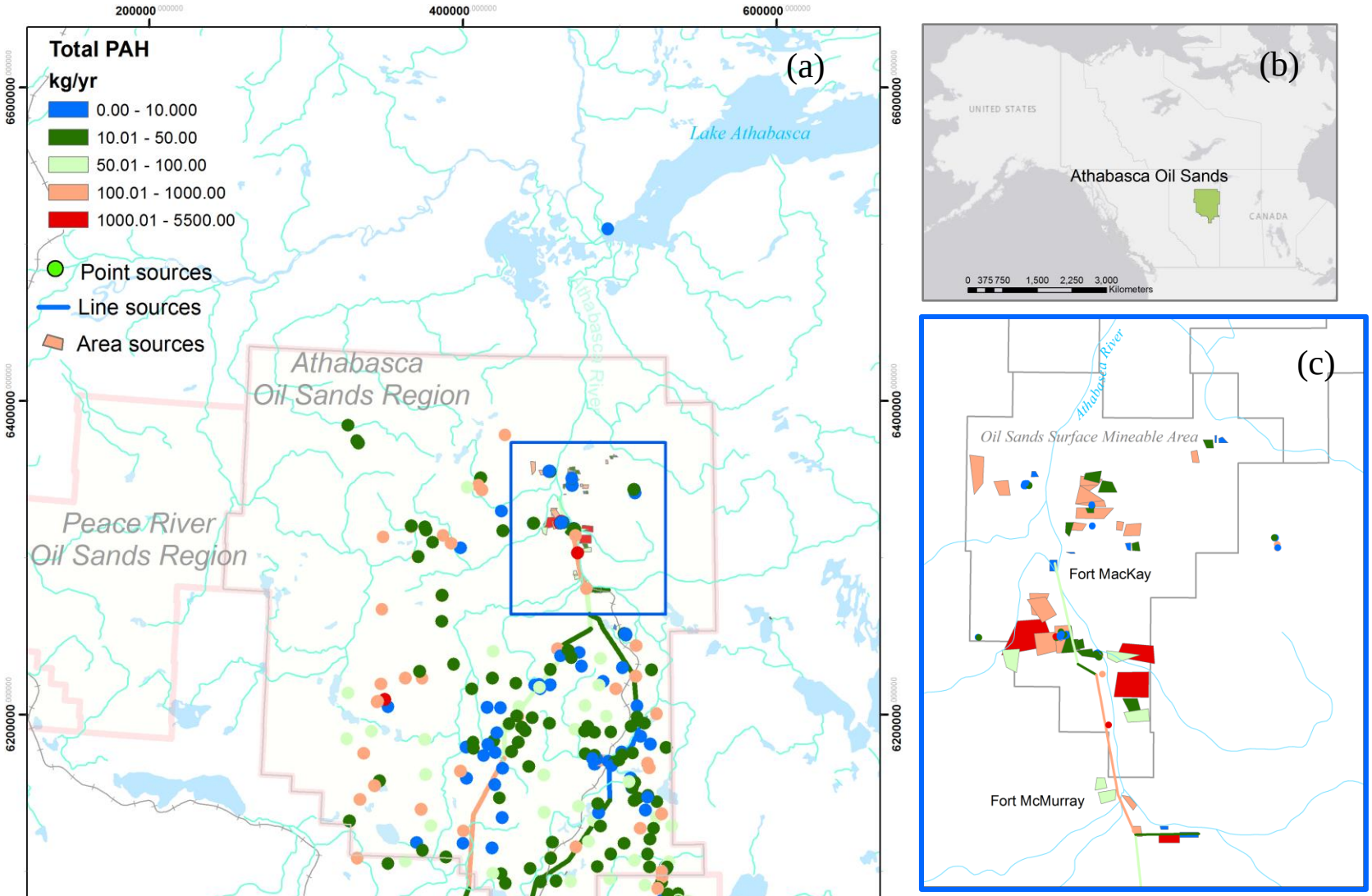

Figure S3. (a) Map of unsubstituted PAH emissions in the AOSR derived from the JOSM emissions database. (b) Inset map of western Canada showing the AOSR. (c) Zoomed-in map of emissions over the surface mineable area. Line sources include transportation emissions. Area sources include tailings pond, mine face, mine fleet, community heating, and airport and traffic emissions. Note: oil sands region boundaries are based on 2009 data.

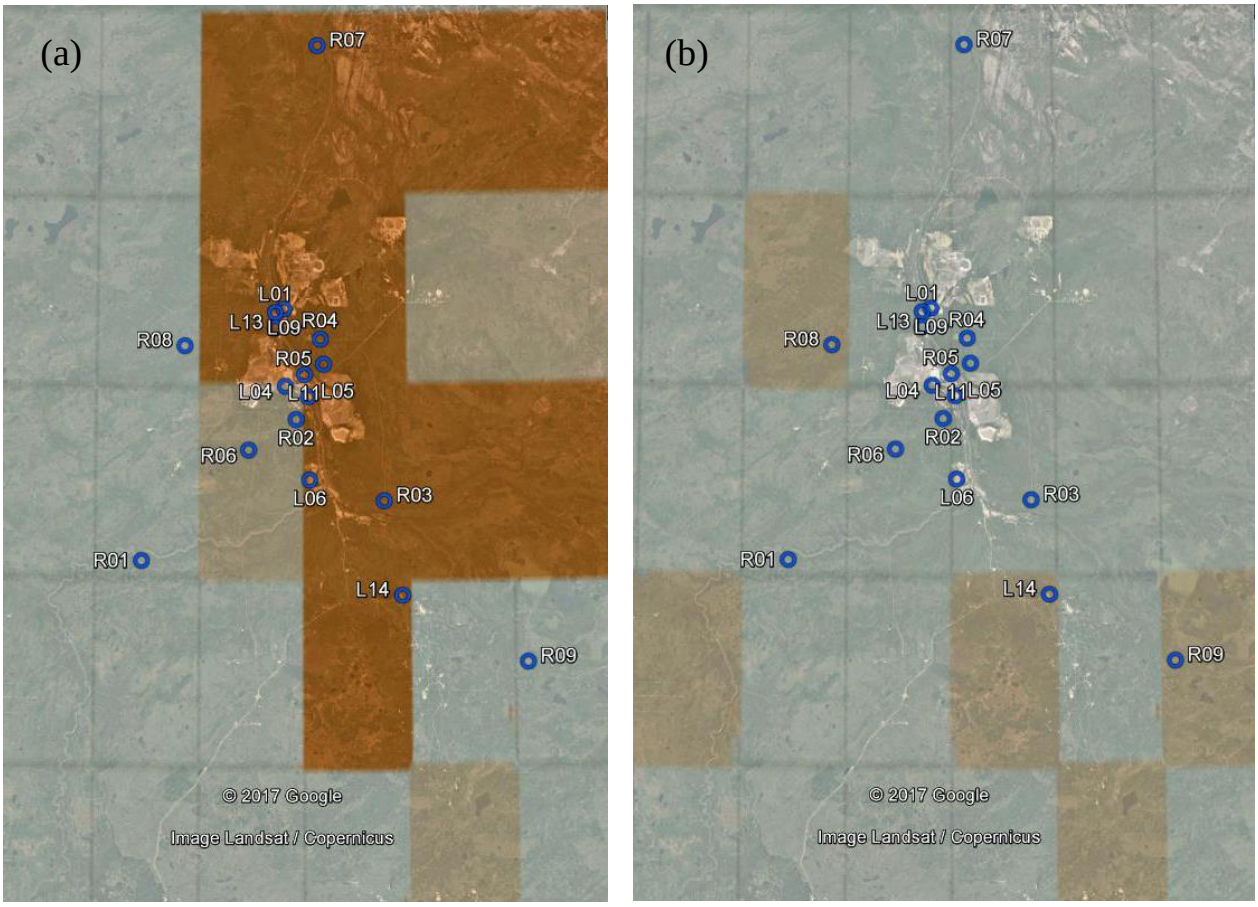

Figure S4. Mean fire radiative power (FRP in megawatts) during the active forest fire period from April 2011 to July 2011 (a) and excluding the April 2011 to July 2011 period in 2011 and 2012 (b). FRP is a measure of the intensity of biomass burning emissions; the data were obtained from MODIS (NASA, 2017). Dark orange: high intensity (80-220 MW); light orange: low intensity (10-39 MW); gray: zero intensity; blue circles: passive air monitoring sites.

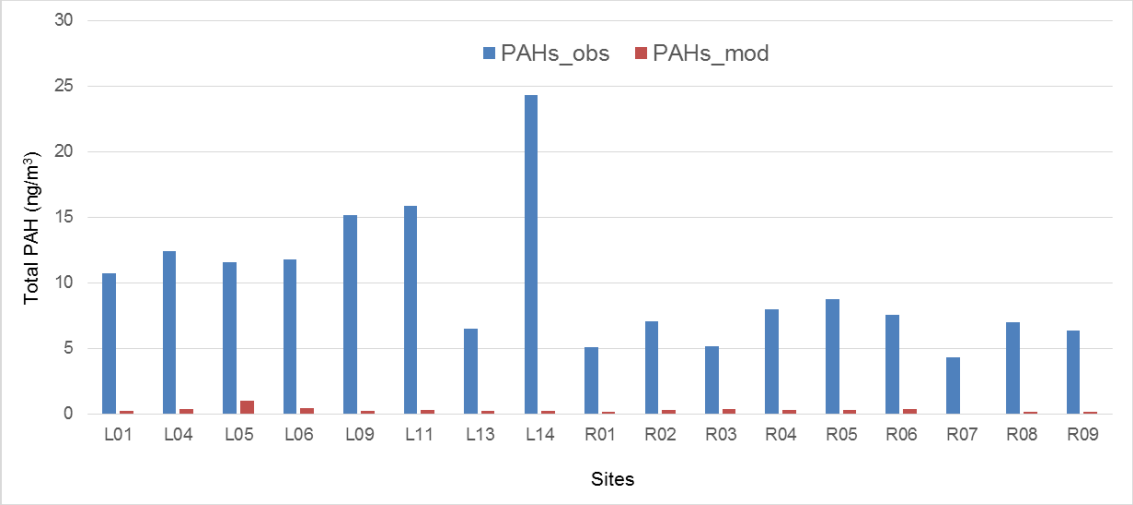

Figure S5. Model sensitivity analysis on the impact of point and line (transportation) source emissions (PAHs_mod) on total PAH concentrations at 17 passive sampling sites (PAHs_obs). PAHs_mod refers to the simulation where only the point and line sources were included in the model.

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