October 2013

SHELL CANADA ENERGY

Appendix 3.5: Aerial Deposition Assessment

Project Number: 13-1346-0001

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1.0   INTRODUCTION

This appendix provides technical information regarding the modelling assessment methods used to assess potential impacts of aerial deposition to snowmelt water and sediment concentrations. The modelling assessment methods described herein were applied to the Pierre River Mine (PRM) Local Study Area (LSA), and preliminary calibration was also carried out using Isadore's Lake. This lake was selected because it is in the vicinity of oil sands mines and upgraders, and a large baseline data set is available. Isadore's Lake serves as a representative test case for other lakes in the Regional Study Area. The assessment was done under existing conditions, 2013 Base Case, 2013 PRM Application Case and 2013 Planned Development Case (PDC) conditions.

Effects on water quality arising from deposition of airborne metals and Polycyclic Aromatic Hydrocarbons (PAHs) are of potential importance in cold climates because the metals and PAHs can be retained in the snow and released as a pulse during spring melt. Snow forms a porous medium that remains permeable to gases over depths of several metres (Albert et al. 2000) and therefore offers a large internal surface for interactions with atmospheric gases (Domine and Shepson 2002). Deposition of airborne constituents to snow may occur either by wet deposition or by dry deposition of aerosol particles (Simmleit et al. 1986). The snow cover, functioning as a temporary storage reservoir, may release constituents that have accumulated over the winter during a short melt period, resulting in temporarily elevated concentrations in air, water and soil (Daly and Wania 2004).

During snowpack aging and metamorphosis (changes to the snow crystal structure followed by increases in snow density and decreases in snow surface area), a constituent can be transported with the melt water to the terrestrial or aquatic environment underlying the snow pack, or it may volatilize back into the atmosphere. Thus, snowmelt controls the extent and timing of the delivery of constituents to surface waters (Meyer et al. 2005).

During snowmelt, the elution sequence of organic substances is strongly dependent on their partitioning properties and the physical properties of the snowpack (Meyer and Wania 2008). Water-soluble organic compounds can be discharged in elevated concentrations at an early stage of melting, while the bulk of the hydrophobic chemicals attached to particles are often released at the end of the melt period (Johannessen and Henriksen 1978; Meyer and Wania 2008; Schondorf and Herrmann 1987; Simmleit et al. 1986). Melting of a highly metamorphosed and deep snowpack can promote pulse load releases, whereas a shallow snow cover over a relatively warm ground experiencing irregular melting over the winter season is unlikely to generate notable peak releases of organic substances (Meyer and Wania 2008).

Recent studies in the Alberta Oil Sands Region have documented increases in snowpack and lake sediment concentrations. Kelly et al. (2009 and 2010) studied contributions of Polycyclic Aromatic Compounds (PAC) and metals from oil sands developments to the Athabasca River and its tributaries. They analyzed snowpack samples for PACs and metals. The results of their 2009 study indicated that PACs are deposited from the atmosphere in the vicinity of oil sands developments. In a subsequent study, Kelly et al. (2010) showed that metals were also being deposited on snow near oil sands developments. These metals were also measured in snowpacks and in regional watercourses (Kelly et al. 2010). The study described herein quantifies the effects of aerial deposition on snowpack and ultimately on receiving watercourses in the LSA.

In the Environmental Impact Assessment (EIA), the water quality assessment considered PAHs, whereas Kelly et al. (2009) examined PACs. These groups of compounds are similar, except that PACs also include

heteroatoms, as in the case of dibenzothiophene, which is not a PAH. The deposition modelling described below was applied to PAC, consistent with the substances examined in Kelly et al. (2009).

Kurek et al. (2013) studied five lakes near oil sands mining and upgrading operations and another lake 90 km to the northwest. They found elevated concentrations of PAHs in lake sediments relative to predevelopment conditions. Elevated concentrations may be an outcome of multiple factors including aerial deposition, because these lakes are located in the watersheds that are near oil sands developments. In 2011, PAH levels in these lake sediments ranged from 2.5 to 33 times higher than levels recorded before 1960. The PAH ratios measured in sediment over time indicated a shift from primarily wood combustion to petrogenic sources (i.e., those associated with oil sands).

This study was completed to evaluate the aerial deposition pathway as a potential source of metals and PAHs to the receiving environment. It examined potential effects from existing and approved projects, PRM, and other reasonably foreseeable projects. As discussed in Section 4.0, the study is considered a first step toward investigating this issue and as such it should be viewed as preliminary.

2.0 ASSESSMENT METHODS

This section summarizes the assessment methods used to quantify the fate and transport of aerially deposited PACs and metals to the snowpack. The substances considered in this assessment were:

- PACs: acenaphthene, anthracene, benzo(a)pyrene, biphenyl, dibenzothiophene, fluoranthene, fluorene, naphthalene, phenanthrene and pyrene.

- Metals: antimony, arsenic, cadmium, chromium, copper, lead, manganese, molybdenum, nickel, silver, vanadium and zinc.

These substances were selected if:

- oil sands development source emissions contain sufficient quantities of specific compounds to be included in air quality modelling (EIA, Volume 3, Section 3.1.3);

- they were measured in snowpack by Kelly et al. (2009); and

- they were identified as potentially relevant to the aquatic health (EIA, Volume 4A, Section 6.6) or human health risk assessments (EIA, Volume 3, Section 5.3).

To evaluate the contribution of snowmelt to surface water concentrations, a non-steady-state, mass-balance and multi-compartment fate model was used for PACs, and a conservative mass-balance assessment method was adapted for metals. More detailed information about these models is presented in the following sections.

2.1 Data Sources

Surface water and sediment quality predictions and assessments are based on the following data:

- deposition rates and ambient concentrations associated with the existing conditions and the assessment cases predicted using the CALPUFF model (Appendix 3.2);

- flow rates in watercourses during snowmelt derived from the Hydrological Simulation Program-Fortran (HSPF) model (EIA, Volume 4B, Appendix 4-2, Section 2.1.3);

■ chemical properties of PACs from a variety of literature sources; and

■ physical characteristics, surface hydrology, existing water and sediment quality, and meteorology for Isadore's Lake (Albian Sands 2005; RAMP 2011).

2.2 Polycyclic Aromatic Compounds

2.2.1 Models and Assumptions

Based on an extensive literature review of models available for simulating the interactions of airborne organic compounds and snow, the modified Coastal Zone Model for Persistent Organic Pollutants (CoZMo-POP) model (Daly and Wania 2004) was selected to evaluate the contribution of snowmelt to freshwater PAC levels. The CoZMo-POP model builds on the earlier studies simulating the fate of organic chemicals in an aging snowpack (Wania 1997; Wania et al. 1999, 2000). This model incorporates the results of research on quantifying the snow-specific surface area (Domine et al. 2002; Hoff et al. 1998; Legagneux et al. 2002) and chemical-specific interfacial partition coefficients (Goss and Schwarzenbach 1999; Roth et al. 2004). To build the modified CoZMo-POP model, snow was incorporated into the original CoZMo-POP model (Wania 1997; Wania et al. 1999, 2000), which is a dynamic, multimedia, organic chemical fate model. CoZMo-POP is a non-steady-state, mass-balance model for Persistent Organic Pollutants (POPs) based on the fugacity approach (Wania et al. 2000), which can be thought of as the escaping tendency of a substance from a heterogeneous system. Prior to the addition of snow, the model had compartments describing the atmosphere, forest canopy, forest soil, agricultural soil, fresh water, freshwater sediment, coastal water and coastal sediment. It allows for seasonally variable temperature, wind speed and hydroxyl radical concentrations.

The contaminant transport processes that make up the CoZMo-POP model are described in detail in Wania et al. (2000). The model treats water content in soils, snowpack and fresh water as functions of time, dynamically determined by the balance of water flowing in and out of these compartments (Table 2.2-1). The fluxes are calculated based on user-defined rate constants (k) in units of reciprocal time and a term for the size of the water reservoirs in each compartment (e.g., soil moisture, freshwater depth). Snowmelt is an exception; it is assumed that snow melts at a constant rate, independent of the size of the snow compartment. The k values describing runoff from soils are functions of soil moisture, while evaporation k values increase with temperature.

Three seasons are defined in the model based on temperature:

■ a snow accumulating season starts when temperature drops below 0°C; no melting occurs in this period, and snow coverage is always complete (i.e., no partial snow cover);

■ a snow melting season starts when temperature rises above 0°C, and the user defines a fixed length; and

■ a summer season starts when the snow has completely melted.

Table 2.2-1   Equations Used to Describe the Water Content in the Model Compartments and the Water Fluxes Between Them

Water Balance Equations

Snowpack $dh_{sp}/dt = (wG_{a\text{-}sp} - wG_{sp\text{-}a} - wG_{sp\text{-}w} - wG_{sp\text{-}e})/(A_{sp} \cdot vf_{swe\text{-}sp})$

Soil $dvf_{we}/dt = (wG_{ae} + wG_{sp\text{-}e}) / V_e - (k_{evap\text{-}e} + k_{runoff\text{-}e}) \cdot vf_{we}$

Fresh water $dV_w/dt = wG_{aw} + wG_{sp\text{-}w} + wG_{ew} - (k_{evap\text{-}w} + k_{runoff\text{-}w}) \cdot V_w$

Parameter	Equation	Description
wG		*Water fluxes in m³/h*
$wG_{a\text{-}w}$	$U_3 \cdot A_w$	air-fresh water (*w*)
$wG_{a\text{-}e}$	$U_3 \cdot A_e$	air-soil (*e*)
$wG_{a\text{-}sp}$	$U_3 \cdot A_{sp}$	air-snow (*sp*)
$wG_{w\text{-}a}$	$V_w \cdot k_{evap\text{-}w}$	water-air
$wG_{e\text{-}a}$	$vf_{we} \cdot V_e \cdot k_{evap\text{-}e}$	soil-air
$wG_{sp\text{-}a}$	$vf_{swe\text{-}sp} \cdot h_{sp} \cdot A_{sp} \cdot k_{sub}$	snow-air
$wG_{sp\text{-}w}$	$vf_{swe\text{-}sp} \cdot h_{sp\text{-}max} \cdot A_w \cdot k_{melt}$	snow-fresh water
$wG_{sp\text{-}e}$	$vf_{swe\text{-}sp} \cdot h_{sp\text{-}max} \cdot A_e \cdot k_{melt}$	snow-soil
$wG_{e\text{-}w}$	$vf_{we} \cdot V_e \cdot k_{runoff\text{-}e}$	soil-fresh water
$wG_{w\text{-}c}$	$V_w \cdot k_{runoff\text{-}w}$	fresh water-coastal (*c*)
U_3		precipitation rate in m/h
A_x		surface area of compartment x in m²
V_x		volume of compartment x in m³
vf_{we}		volume fraction of water in soil
$vf_{swe\text{-}sp}$		volume fraction of snow water equivalent in snowpack
h_{sp}		height of snowpack in m
$h_{sp\text{-}max}$		maximum height of snowpack in m
k_{evap}		evaporation rate in hr⁻¹
k_{sub}		sublimation rate in hr⁻¹
k_{melt}		melting rate in hr⁻¹
$k_{runoff\text{-}e}$		soil runoff rate in hr⁻¹
$k_{runoff\text{-}w}$		fresh water outflow rate in hr⁻¹

Source: Daly and Wania 2004.

It is assumed that the snowpack is homogeneous with respect to temperature, physical properties and chemical concentrations. Physical snow characteristics, such as snow surface area and porosity, are time-variant, user-defined functions. The snowpack's particle content is determined from the rates of particle scavenging with falling precipitation and dry particle deposition.

The processes involved in the delivery and loss of organic contaminants in a seasonal snow cover in the modified CoZMo-POP model is shown in Figure 2.2-1. During the snow accumulation season, there is no air-surface exchange except with the snowpack. The contaminant exchange between the snowpack and the surface compartments is also zero. There is no runoff from soil to fresh water when temperatures drop below 0°C.

During the snowmelt period, air-surface exchange resumes with the forest canopy, and substances can be transferred from snow to surface media with meltwater and particles.

Figure 2.2-1   *Processes Involved in the Delivery and Loss of Organic Contaminants in a Seasonal Snow Cover in the Modified CoZMo-POP Model*
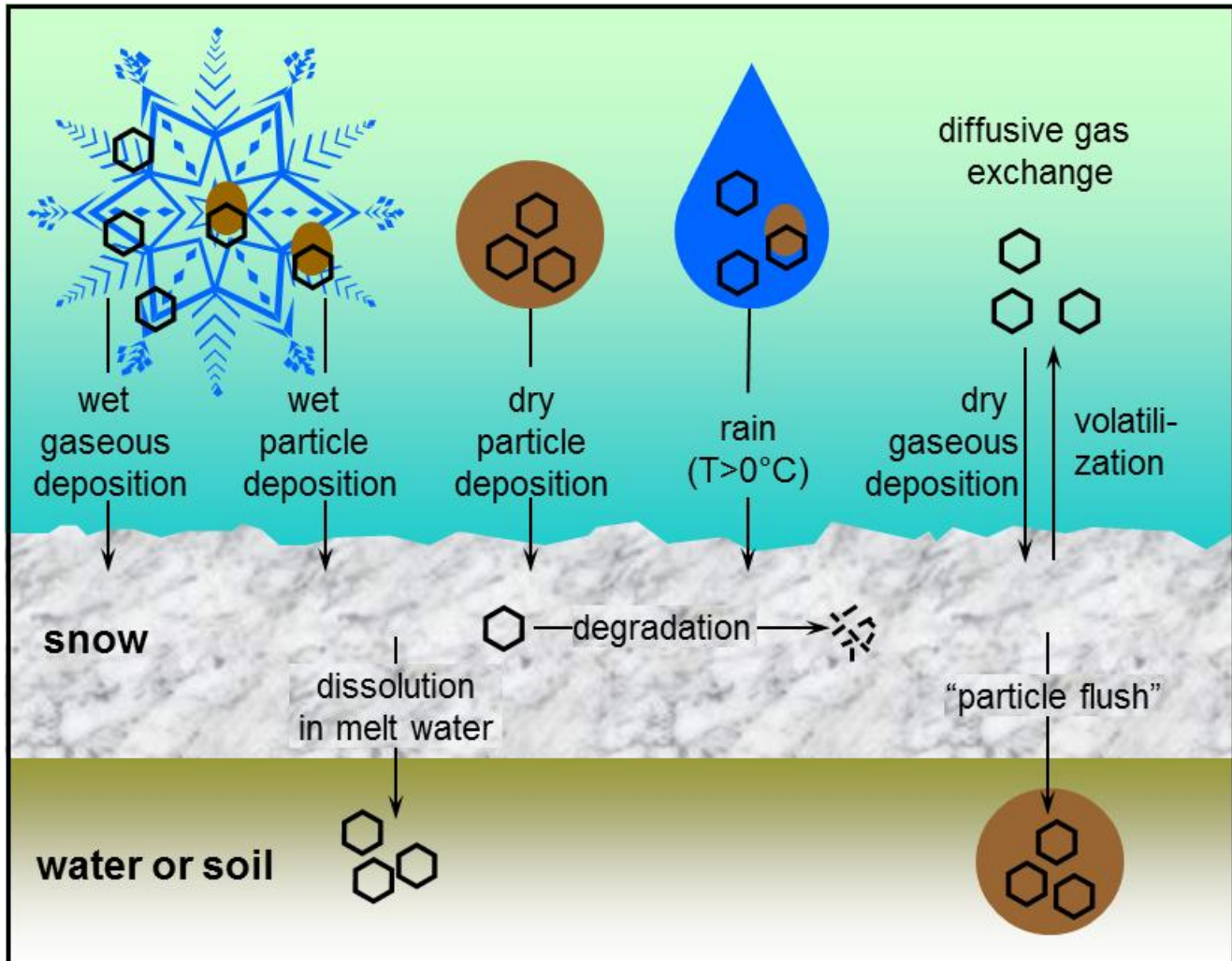
Note: T = temperature.
Source: Daly and Wania 2004.

The model is formulated in terms of fugacity using Z values to describe equilibrium partitioning, and D values to describe transport and transformation processes (Mackay 2001). The mass balance equation for the snow compartment and the expressions used to calculate the snow-related Z and D values are given in Table 2.2-2. An interfacial partition coefficient (KSA, in metres) defines the capacity of the snow surface for organic chemicals. Partitioning properties of the organic matter in snow and organic matter in atmospheric particles are assumed to be the same (Wania and Daly 2002).

Gaseous air-snow exchange of chemicals occurs by sequential molecular diffusion through the snowpack's air-filled pore space and the boundary layer above it. A wind-pumping factor describes the snow ventilation, which may increase substance movement within the snowpack beyond the rate of molecular diffusion.

Table 2.2-2   Model Equations Related to Contaminant in the Snowpack

Mass Balance Equation for the Contaminant in the Snowpack

$$dM_{sp}/dt = D_{a\text{-}sp} \cdot f_A - (D_{sp\text{-}a} + D_{sp\text{-}e/w} + D_{pf\text{-}e/w} + D_R) \cdot f_{sp}$$

M_{sp} amount of contaminant in the snowpack in mol
t time in hours
f_A, f_{sp} fugacity in air and snow pack in Pa

Parameter	Equation	Description
D-values in mol/Pa·h		
D_R	$k_{sp} \cdot V_{sp} \cdot Z_{sp}$	reaction in snow pack
$D_{sp\text{-}e}$	$wG_{sp\text{-}e} \cdot Z_w$	melt water runoff to soil
$D_{sp\text{-}w}$	$wG_{sp\text{-}w} \cdot Z_w$	melt water runoff to fresh water
$D_{pf\text{-}e}$	$G_{pf} \cdot Z_w + A_e/A_{sp} \cdot M_{o\text{-}max} \cdot Z_o / \rho_o$	particle flush to soil
$D_{pf\text{-}w}$	$G_{pf} \cdot Z_w + A_w/A_{sp} \cdot M_{o\text{-}max} \cdot Z_o / \rho_o$	particle flush to fresh water
$D_{sp\text{-}a}$	$A_{sp} / (1/U_{S/A\text{-}bl} \cdot Z_A) + 1/(wpf \cdot U_{S/A\text{-}ps} \cdot Z_A))$	snow to air transfer
$D_{a\text{-}sp}$	$D_{sp\text{-}a} + A_{sp} \cdot DDV_{sp} \cdot vf_A \cdot Z_Q + wG_{a\text{-}sp} \cdot BZ_x$	air to snow transfer ($BZ_x = BZ_{rain}$ at T > 0°C, $BZ_x = BZ_{snow}$ at T > 0°C
Z-values in mol/m³·Pa		
Z_a	$1 / (R \cdot T)$	air
Z_w	$K_{WA} \cdot Z_a$	water
Z_I	$K_{IA} \cdot Z_a$	interface
Z_o	$K_{OA} \cdot (\rho_{part}/\rho_{oct}) \cdot Z_a$	organic matter
Z_{sp}	$Z_a \cdot v_a + Z_w \cdot v_w + Z_i \cdot A_{snow} \cdot \rho_{mw} + Z_o \cdot v_o$	snow pack
BZ_{rain}	$Z_w + W_{p1} \cdot vf_A \cdot Z_o \cdot f_{oa}$	rain
BZ_{snow}	$Z_i \cdot A_{snow} \cdot \rho_{mw} + W_{p2} \cdot vf_A \cdot Z_o \cdot f_{oa}$	falling snow
k_{sp}		reaction rate of contaminant in snow pack in hours^{-1}
V_{sp}		volume of snow pack in m³
wpf		wind pumping factor
$M_{o\text{-}max}$		maximum mass of organic carbon in the snowpack in g
ρ_o		density of organic matter in g/m³
$U_{S/A\text{-}ps}$	$B_a \cdot (vf_{sa}^{10/3} / (vf_{sa} + vf_{sl})^2 / (\ln(2) \cdot h_{sp})$	mass transfer coefficient for air-filled pore space in m/h
$U_{S/A\text{-}bl}$		mass transfer coefficient for the air boundary layer above snow in m/h
B_a		molecular diffusivity in air in m²/h
vf_{sl}		volume fraction of liquid water in the snow pack in m³/m³
vf_{sa}		volume fraction of air in the snow pack in m³/m³
vf_A		volume fraction of aerosols in air in m³ solid/m³ bulk phase
DDV_{sp}		dry particle deposition velocity to snow in m/h
K_{WA}		dimensionless partition coefficient between water and air
K_{OA}		dimensionless partition coefficient between octanol and air
K_{IA}		partition coefficient between water/ice surface and air in m
R		gas constant in J/(mol·K)
T		absolute temperature in K
ρ_{part}, ρ_{oct}, ρ_{mw}		density of atmospheric particles, octanol and snow melt water in g/m³
v_a, v_w, v_o		volume fraction of air, liquid water and organic matter in snow pack
A_{snow}		snow surface area in m²/g
W_p		particle scavenging ratio for rain (1) and snow (2)
f_{oa}		mass fraction of organic matter in atmospheric particles

Source: Daly and Wania 2004.

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The surface area accessible to gases for a given mass of snow (specific snow surface area, A_{snow} in m^2/g) is a key parameter determining the capacity of the snow phase for organic substances. A_{snow} of falling snow controls the extent of vapour scavenging, and A_{snow} in the snowpack has a strong influence on diffusive snow-atmosphere exchange, in particular the potential for evaporation from the aging snowpack. For the simulations, a seasonally dependent A_{snow} was defined for the snow accumulation period (0.1 m^2/g) and for the snowmelt period (a linear decrease from 0.1 to 0.01 m^2/g).

The liquid water content in the snowpack was also defined based on season. During the snow accumulation season, the amount of liquid water contained in the snowpack is determined using the specific surface area assuming an average thickness of the quasi-liquid layer of 10 nm (Fletcher 1973). During the snowmelt period, the volume fraction of liquid water in the snowpack increases rapidly which was described using a power function increasing from the initial value to a maximum of 0.40 at the end of snowmelt. A constant snow density of 0.433 g/cm^3 was assumed throughout winter (Wania et al. 1999).

The snow-air exchange process for a chemical vapour has two steps: first, the chemical diffuses through the air-filled pore space to the top of the snowpack and then through a boundary layer to the bulk atmosphere. The latter is parameterized with a snow-air boundary layer mass transfer coefficient ($U_{S/A-bl}$, m/h), whereas, the mass transfer coefficient for molecular diffusion through the air-filled pore space ($U_{S/A-ps}$, m/h) is a function of the molecular diffusivity in air, the volume fraction of air in the snowpack, and the mean diffusion path length, which is related to snow depth (Wania 1997). Gas exchange would always take place, even when the snowpack gets deeper and the diffusion path longer, and thus the calculated resistance to molecular diffusive transport within the snowpack becomes large. This exchange occurs for two reasons: a chemical in the surface layer of the snowpack only has to diffuse a small distance to the top of the snowpack, and wind-driven advective motion through the snowpack may greatly accelerate vapour transport in the snow pores. As mentioned, a wind pumping factor is used in the model to account for this increase in mass transfer.

Water-sediment processes were also modelled mechanistically in CoZMo-POP. The CoZMo-POP model is designed for persistent organic pollutants (e.g., PACs), which preferentially attach to organic material, within both terrestrial and aquatic environments. Advective fluxes of contaminants between all compartments (e.g., soil, air, water, forest) comprise advection with organic matter, as attachment to mineral surfaces can be considered negligible. In CoZMo-POP, advective fluxes of Particulate Organic Carbon (POC) between model compartments are derived to calculate advective transport of contaminants with POC. Therefore, POC fluxes are a key component in deriving contaminant fluxes.

Two advective processes and four diffusive processes contribute to the exchange of contaminants across the water-sediment interface. The advective processes are physical sedimentation and re-suspension of contaminants sorbed to POC. For diffusion, on the water side there is a resistance to transfer through the stagnant benthic boundary layer above the sediment surface, quantified using a benthic boundary layer mass transfer coefficient. There are three parallel diffusive processes on the sediment side of the water-sediment interface. The first is molecular diffusion through the water-filled pore spaces in the sediment, quantified by the diffusivity in water, corrected for the sediment porosity. Bioturbation of sediment solids and sediment pore water is treated as two pseudo-diffusive processes invoking two equivalent "bioturbation diffusivities". In all three cases, the diffusion path length is calculated as the log mean depth of the sediment compartment.

2.2.2   Model Application

For this assessment, the modified CoZMo-POP (hereafter referred to as "CoZMo-POP") simulations were conducted for PACs to estimate the contribution of snowmelt to concentrations in surface waters, as well as the impact of long-term contaminant transfer to sediments. The model predicted incremental concentrations of substances in snowmelt water, averaged over the snowmelt period. The final sediment concentration following a 20-year period of emissions was also modelled.
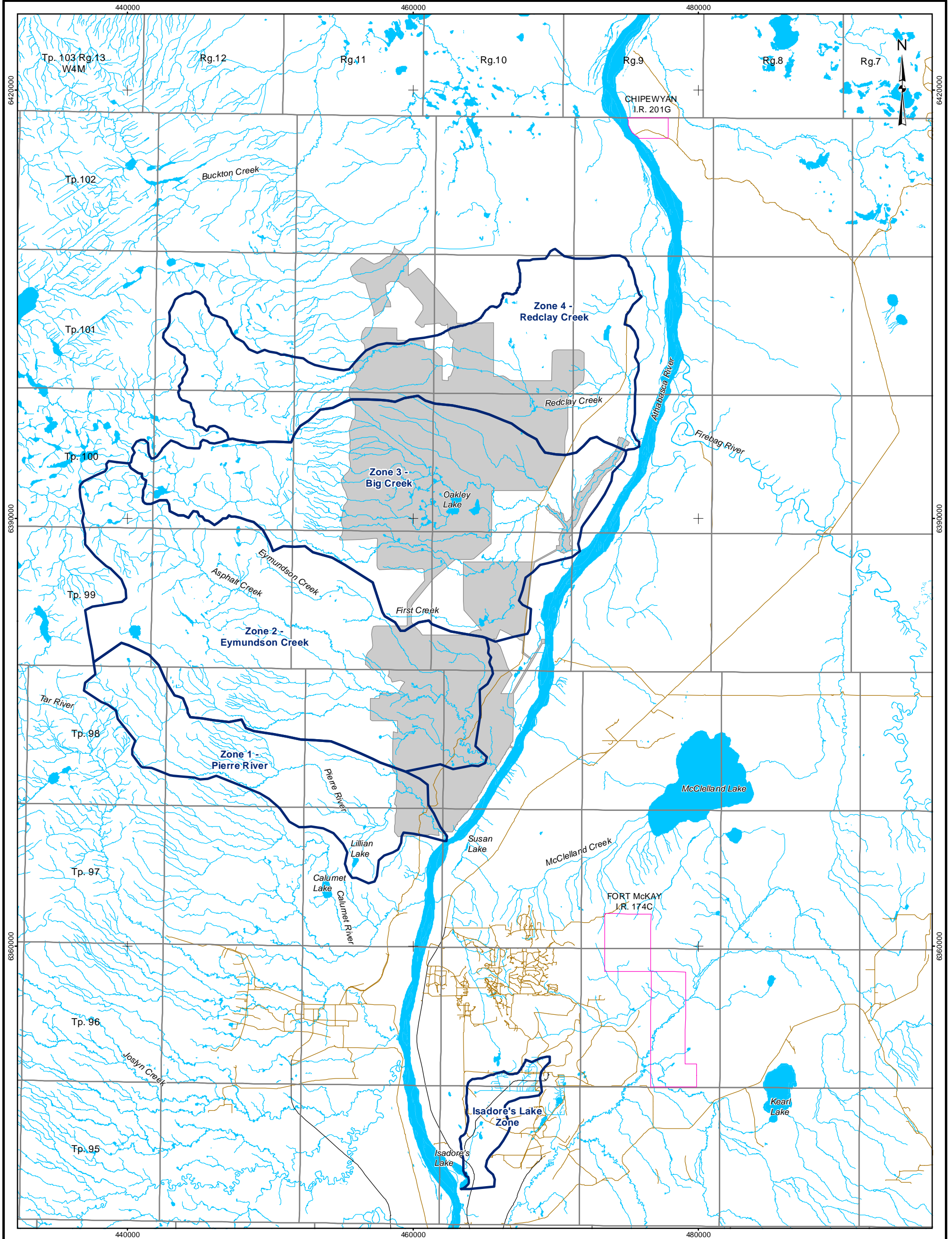
The model was applied to the Aquatics LSA, because that is where the 'worst-case' effects from PRM were expected to be observed. The LSA falls entirely within the oil sands development airshed, whereas, by comparison, a relatively small portion of the Athabasca River watershed would be potentially affected by aerial deposition. Additionally, PAC concentrations in water and sediment were predicted for Isadore's Lake. Observed sediment concentrations in Isadore's Lake were used for preliminary calibration of the PAC model. This lake was selected because it is in the vicinity of oil sands mines and upgraders, and a large baseline data set is available for this lake from the Regional Aquatics Monitoring Program (RAMP) and from the Muskeg River Mine Expansion Baseline Report (Albian Sands 2005). Isadore's Lake serves as a representative test case for other lakes in the Regional Study Area.

To apply the model to the small streams in the LSA, four zones were defined as discrete model segments: Pierre River – Zone 1, Eymunsdon Creek – Zone 2, Big Creek – Zone 3, and Redclay Creek – Zone 4 (Figure 2.2-2). Within each zone, site-specific land types were characterized and represented in the model. Land type characterization was consistent with the HSPF model setup (EIA, Volume 4B, Appendix 4-2, Section 2.1.3).

Separate simulations were completed with CoZMo-POP for each zone under the following scenarios: existing conditions, 2013 Base Case, 2013 PRM Application Case and 2013 PDC. The existing condition was added to the assessment cases for this study so that model predictions could be validated by contemporary snowpack monitoring data, once available. The existing condition represents development conditions as of the period from 2006 to 2012, which is the period of record for the various inputs to the model. It differs from the 2013 Base Case in that air modelling for the existing condition incorporates emissions from this period, whereas the 2013 Base Case assumes that all existing and approved facilities are operating at full capacity.

For each assessment case, the model used ambient air concentrations predicted by the air quality model, CALPUFF. The air quality model considered cumulative air quality effects from emission sources included in each assessment case, assuming full operation within the region, as well as estimated emissions from transportation and residential activities (EIA, Volume 3, Section 3 and Appendix 1, Section 2.2).

Closed-circuited areas, which were also set to represent each assessment case, were excluded from the areas contributing to surface water concentrations. The 2013 Base Case, 2013 PRM Application Case and 2013 PDC closed-circuited areas were based on a development snapshot circa 2029, representing the mid-life of operations and the highest mine fleet emissions. This snapshot does not correspond with the maximum closed-circuited area, which is anticipated to occur in 2042. The combination of maximum aerial emissions with mid-life closed-circuited areas is conservative, because maximum emissions were consequently applied over a larger land surface, which ultimately released larger quantities of affected snowmelt to surface waters.

N

Tp. 103 Rg.13 W4M   Rg.12   Rg.11   Rg.10   Rg.9   Rg.8   Rg.7

Tp.102

Buckton Creek

CHIPEWYAN I.R. 201G

Tp.101

Zone 4 - Redclay Creek

Tp. 100

Redclay Creek

Zone 3 - Big Creek

Athabasca River

Firebag River

Oakley Lake

Eymundson Creek

Asphalt Creek

Tp. 99

First Creek

Zone 2 - Eymundson Creek

Tar River

Tp. 98

Zone 1 - Pierre River

Pierre River

McClelland Lake

Lillian Lake

Susan Lake

McClelland Creek

Tp. 97

Calumet Lake

Calumet River

FORT McKAY I.R. 174C

Tp. 96

Joslyn Creek

Kearl Lake

Isadore's Lake Zone

Tp. 95

Isadore's Lake

LEGEND

— PAVED ROAD
— UNPAVED ROAD
— WATERCOURSE
☐ INDIAN RESERVE
☐ ZONE BOUNDARY
☐ CLOSED CIRCUITED AREA
☐ OPEN WATER

10   0   10

SCALE 1:250,000   KILOMETRES

PROJECT

PIERRE RIVER MINE PROJECT

TITLE

LAYOUT OF THE DEFINED ZONES AND CLOSED-CIRCUITED AREAS IN THE PIERRE RIVER WATERSHED IN THE 2013 PLANNED DEVELOPMENT CASE (2029)

REFERENCE
ALBERTA DIGITAL BASE DATA OBTAINED FROM ALTALIS LTD. © GOVERNMENT OF ALBERTA 2013.
DATUM: NAD83 PROJECTION: UTM ZONE 12N

Shell Canada Limited

	PROJECT	13-1346-0001	FILE No.		
DESIGN	SD	10 Jun 2013	SCALE AS SHOWN	REV.	0
GIS	SB	24 Jun 2013			
CHECK	CW	05 Jul 2013			
REVIEW	WES	05 Jul 2013	**FIGURE: 2.2-2**		

2.2.3   Model Inputs

The model relied on emission data from oil sands facilities and regional meteorological data. Ambient air concentrations associated with existing conditions and the assessment cases were predicted using the CALPUFF model (EIA, Volume 3, Appendix 3-8) and entered into CoZMo-POP as inputs.

2.2.3.1   *Isadore's Lake Environmental Inputs*

Site-specific air temperatures and wind speed were consistent with those used in the CALPUFF model. Site-specific water temperatures and precipitation rates were derived from existing studies on Isadore's Lake (Albian Sands 2005 and RAMP 2011). Isadore's Lake was modelled for a 20-year period to provide an estimate of long-term surface water and sediment concentrations. The value of $k_{runoff-w}$, which controls the water outflow from the fresh waterbodies within the zone to the lake was set at 0.0042 hr^{-1}, as this generates an inflow rate of 0.1 m^3/s, which is an upper estimate of the total surface and groundwater inflow to Isadore's Lake (Albian Sands 2005).

Site-specific environmental input parameters were compiled for Isadore's Lake and the surrounding watershed; where these input parameters were not available, the generic parameters reported by Daly and Wania (2004) and Wania et al. (2000) were used. For the sediment modelling, some of the generic parameters provided in Wania et al. (2000) were adjusted to increase the contaminant flux to sediment, as part of the calibration process. The input value for primary productivity was increased from the generic value from Wania et al. (2000), consistent with observations by Kurek et al. (2013) that indicate an increase in primary productivity over time for waterbodies in the Oil Sands Region. Site-specific environmental input parameters for Isadore's Lake are presented in Table 2.2-3.

Table 2.2-3   Site-Specific Environmental Input Parameters for Isadore's Lake

Parameter	Value	Reference
Fraction of drainage basin covered by forest	0.20	GIS land-use maps
Fraction of forest area covered by coniferous trees	0.08	GIS land-use maps
Deciduous canopy development		
Start of growth [day of year]	133	
End of growth [day of year]	144	Downing and Pettapiece (2006)
Start of leaf falling [day of year]	261	
End of leaf falling [day of year]	283	
Hydrology		
Drainage basin surface area [m^2]	25,500,000	GIS maps
Fraction of drainage basin covered by lakes and rivers	0.31	GIS land-use maps
Lake surface area [m^2]	3,500	Albian Sands (2005)
Average lake depth [m]	0.45	Albian Sands (2005)
Water parameters		
Particulate organic carbon (POC) concentration [mg/L]	1	Albian Sands (2005) and RAMP (2011)
Primary productivity [g C/m^2/yr]	250	Kurek et al. (2013)
POC mineralization in water column [fraction of input]	0.50	
Sediment depth [m]	0.03	
Mass fraction organic carbon in sediment solids	0.06	Based on Wania et al. (2000) and adjusted as part of model calibration
Volume fraction of solids in sediment	0.15	
Bioturbation diffusivity [m^2/h]	10^{-9}	

2.2.3.2   *Local Study Area Environmental Inputs*

Site-specific meteorological data, including air temperature, wind speed and precipitation, were used as model inputs and were consistent with those in the CALPUFF model. The meteorological data for all years modelled was based on 2002, consistent with historical CALPUFF modelling.   For the purposes of identifying the maximum surface water concentration that may result from snowmelt, the model was run for six months, including the snow accumulation and snow melt periods.   While a snapshot in time is appropriate for surface water, which instantaneously mixes and dilutes contaminant input, sediments accumulate contaminants over time and a longer modelling time frame is needed.   For all assessment cases, sediment concentrations were modelled considering accumulation over a 20-year time frame. Considering that the cases represent maximum emission estimates, assuming accumulation over 20 years is generally equivalent to assuming 40 years of input at a linearly increasing rate.   A 40-year time span is appropriate for the existing conditions because this is approximately the duration that the Alberta oil sands have been in operation.   A 20-year time span was considered appropriate for the future assessment cases because it is close to the expected PRM lifetime. While these timelines are approximate, they reflect the preliminary nature of this assessment.

The initial height of the freshwater compartment is set at a negligible value, because the goal of the modelling was to determine the flux of PACs and water to the freshwater bodies from snowmelt. The water outflow rate from the freshwater compartment was also set to a negligible level so substances delivered to the freshwater compartment from the snowpack largely remain in the system.   Water was allowed to accumulate in the waterbody for the duration of the snowmelt period, thus giving an average concentration for constituents over one snowmelt event.

The site-specific environmental input parameters were collected for each zone; where these input parameters were not available, the generic parameters reported by Daly and Wania (2004) and Wania et al. (2000) were used.   Site-specific environmental input parameters for one zone (Zone 1, 2013 PRM Application Case) are presented in Table 2.2-4.

Table 2.2-4   Site-Specific Environmental Input Parameters for Zone 1 – 2013 PRM Application Case

Parameter	Value	Reference
Fraction of drainage basin covered by forest	0.70	GIS land-use maps
Fraction of forest area covered by coniferous trees	0.16	GIS land-use maps
Deciduous canopy development		
Start of growth [day of year]	133	Downing and Pettapiece (2006)
End of growth [day of year]	144	
Start of leaf falling [day of year]	261	
End of leaf falling [day of year]	283	
Hydrology		
Drainage basin surface area [m^2]	128,000,000	GIS maps
Fraction of drainage basin covered by lakes and rivers	0.098	GIS land-use maps
Adjusted water parameters		
Primary productivity [g C/m^2/yr]	250	Kurek et al. (2013)
Particulate organic carbon (POC) concentration [mg/L]	2.5	Based on Wania et al. (2000) and adjusted as part of model calibration
POC mineralization in water column [fraction of input]	0.50	
Sediment depth [m]	0.03	
Mass fraction organic carbon in sediment solids	0.06	
Volume fraction of solids in sediment	0.15	
Bioturbation diffusivity [m^2/h]	10^{-9}	

2.2.4   Aerial Emission Data

The CALPUFF model generated spatially variable ambient air concentrations across the LSA. These concentrations were input to the CoZMo-POP model as follows:

- average annual air concentration for each PAC for each zone was modelled in CALPUFF;

- the fugacity that corresponds to this air concentration was calculated using the average annual air temperature and applied as the fugacity in incoming air in CoZMo-POP, for each PAC and each zone;

- air concentrations were written to a file and average air concentrations were calculated;

- the ratio between the modelled air concentration and the target average air concentration was calculated, and this ratio was used to adjust the incoming fugacity; and

- the adjusted incoming fugacity was used to run CoZMo-POP, generate the air concentrations, and confirm that the calculated average air concentration matched the target value.

The height of the atmospheric compartment in CoZMo-POP was set equal to that in the CALPUFF model (812 m) (EIA Volume 3, Appendix 3-8, Section 2.2). The atmospheric residence time in CoZMo-POP was set to 7.5 hours; a short residence time increases the advection rate and reduces the ratio between the modelled air concentration and the target average air concentration.

2.2.5   CoZMo-POP Physical-Chemical Property Data

The physical-chemical property data selected for the chemicals of interest are shown in Tables 2.2-5 and 2.2-6. For the partitioning and enthalpy values, if one value is missing (e.g., K_{oa} missing, octanol-water partition coefficient [K_{ow}] and air-water partition coefficient [K_{aw}] available, heat of enthalpy of octanol-water partitioning [ΔH_{ow}] missing, heat of enthalpy of air-water partitioning [ΔH_{aw}] and heat of enthalpy of octanol-air partitioning [ΔH_{oa}] available) the CoZMo-POP model will calculate the missing value to conform to thermodynamic relationships. Therefore, only two of the three partitioning/enthalpy values are needed. Where data for parameters could not be located, a surrogate approach was used, adopting the value for a chemical with similar structure.

The degradation half-lives for soil were also used for the forest canopy. Reaction half-lives in water were adopted from Daly and Wania (2004) for the snowpack. This approach provides a reasonable estimate of the persistence of chemicals in snow, but results in a fairly wide range of uncertainty, given the limited studies of contaminant reactivity in snow under field conditions. To minimize the potential for underestimating the contribution of snowmelt, the half-lives in snow for all chemicals were set at 99,999 hours, resulting in essentially no degradation over the course of one winter.

Table 2.2-5   Selected Physical-Chemical Property Data – Partitioning and Enthalpy

Parameter	Log K_{ow}	Log K_{aw}	Log K_{oa}	Reference	ΔH_{ow} [kJ/mol]	Reference	ΔH_{aw} [kJ/mol]	Reference	ΔH_{oa} [kJ/mol]	Reference
Acenaphthene	3.95	-2.24	6.44	Ma et al. (2010)	-	-	51.9	Bamford et al. (1999)	49.7	Odabasi et al. (2006)
Anthracene	4.57	-2.69	7.7	Ma et al. (2010)	19.7	Lei et al. (2000)	-	-	63.5	Odabasi et al. (2006)
Benzo(a)pyrene	6.05	-4.51	11.48	Ma et al. (2010)	25.4	Lei et al. (2000)	-	-	103.1	Odabasi et al. (2006)
Biphenyl	4.0	-1.9	-	Mackay et al. (2006)	-	-	24	Mackay et al. (2006)	67.4	Mackay et al. (2006)
Dibenzothiophene	4.38	-1.75	-	Mackay et al. (2006)	-	-	31.8	Mackay et al. (2006)	34.8	Mackay et al. (2006)
Fluoranthene	4.97	-3.27	8.81	Ma et al. (2010)	20.8	Lei et al. (2000)	-	-	74.8	Odabasi et al. (2006)
Fluorene	4.11	-2.44	6.85	Ma et al. (2010)	19	Lei et al. (2000)	-	-	54.2	Odabasi et al. (2006)
Naphthalene	3.4	-1.73	5.19	Ma et al. (2010)	15.7	Lei et al. (2000)	44.65	Mackay et al. (2006)	-	-
Phenanthrene	4.47	-2.76	7.64	Ma et al. (2010)	19	Lei et al. (2000)	-	-	63	Odabasi et al. (2006)
Pyrene	5.01	-3.27	8.86	Ma et al. (2010)	19.2	Lei et al. (2000)	-	-	76.3	Harner et al. (1998)

Notes: ΔH_{aw} and ΔH_{oa} values were unavailable for dibenzothiophene; thiophene was used as a surrogate. ΔH_v for thiophene was used as an approximation of ΔH_{oa}.

ΔH_{oa} values unavailable for biphenyl; 4-chlorobiphenyl was used as a surrogate.

Table 2.2-6   Selected Physical-Chemical Property Data – Solute Descriptors, Half-Lives and Reaction Rates

Parameter	α	β	L16	Reference	Soil $t_{1/2}$ [hours][a]	Water $t_{1/2}$ [hours]	Sediment $t_{1/2}$ [hours]	Reference	k_{OH} [cm^3/molec/s]	Reference
Acenaphthene	0	0.21	6.68	Lei and Wania (2004)	121,000	550	17,000	Mackay (2001)	6.69E-11	U.S. EPA (2011)
Anthracene	0	0.26	7.73	Lei and Wania (2004)	121,000	550	17,000	Mackay (2001)	4E-11	U.S. EPA (2011)
Phenanthrene	0	0.26	7.73	Lei and Wania (2004)	121,000	550	17,000	Mackay (2001)	1.3E-11	U.S. EPA (2011)
Fluorene	0	0.21	7.0	Lei and Wania (2004)	121,000	550	17,000	Mackay (2001)	8.85E-12	U.S. EPA (2011)
Fluoranthene	0	0.29	8.70	Shunthirasingham et al. (2007)	374,000	1,700	55,000	Mackay (2001)	2.92E-11	U.S. EPA (2011)
Naphthalene	0	0.19	3.35	Lei and Wania (2004)	37,400	170	5,500	Mackay (2001)	2.16E-11	U.S. EPA (2011)
Pyrene	0	0.33	9.42	Lei and Wania (2004)	374,000	1,700	55,000	Mackay (2001)	5E-11	U.S. EPA (2011)
Benzo(a)pyrene	0	0.39	11.8	Lei and Wania (2004)	374,000	1,700	55,000	Mackay (2001)	5E-11	U.S. EPA (2011)
Dibenzothiophene	0	0.26	7.73	ACD Labs (2013)	37,400	550	5,500	Mackay (2001)	8.1E-12	U.S. EPA (2011)
Biphenyl	0	0.13	8.5	Lei and Wania (2004)	12,100	170	1,700	Mackay (2001)	2.14E-11	U.S. EPA (2011)

[a] Soil half-lives from Mackay (2001) were increased by a factor of 22 for a better fit with measured soil concentrations, as described in Daly et al. (2007).

Notes: α, β and L16 values were unavailable for some chemicals and surrogates were used; dibenzo(a,h)anthracene – surrogate: chrysene, indeno(1,2,3-cd)pyrene – surrogate: benzo(a)pyrene.

Degradation half-lives were unavailable for some chemicals and surrogates were used; acenaphthene – surrogate: phenanthrene, fluorene – surrogate: phenanthrene, fluoranthene – surrogate: pyrene, dibenzothiophene – surrogate: benzothiophene.

2.2.6   Model Simulations

2.2.6.1   Isadore's Lake

The purpose of the Isadore's Lake modelling was to compare predictions for the existing conditions to measured concentrations and calibrate the model, and to predict long-term surface water and sediment concentrations for each assessment case. The comparison will aid in understanding the accuracy, uncertainty and limitations of the CoZMo-POP modelling. Simulations were run with a time step of one hour, and results were stored at a time step of 8,760. The cumulative fluxes (i.e., total flux over the 20-year period for interphase transfer and degradation) along with the final modelled lake volume and lake sediment mass were used to calculate surface water and sediment concentrations.

2.2.6.2   Snowmelt Within the Local Study Area

The objective of the model simulations was to determine the substance flux to freshwater from snowmelt. Based on observed meteorological data, temperatures generally drop below 0°C in November and rise above 0°C in April. The model simulation period was therefore set to run over the six-month period corresponding to the snow accumulation and melting period.   This period captured chemicals that are scavenged by snow and are subsequently transferred to fresh water. The model simulation stopped after the snow was completely melted so that concentrations would not be diluted with rain water.

Simulations were run with a time step of one hour; results were stored at a time step of 24 hours. After the model simulation was completed for each zone, each chemical and each assessment case, the fluxes, cumulative fluxes and concentrations were exported. The net flux to fresh water was calculated by adding the cumulative input fluxes (air to fresh water, non-forested soil to fresh water, forested soil to fresh water, snow-fresh water) and subtracting the cumulative loss fluxes (water to sediment, water to air, degradation in water, water outflow). This net flux was divided by the final fresh water volume to yield an average concentration over the melt period. This concentration was close to the maximum fresh water concentration that is calculated directly in CoZMo-POP.

To apply the model to the small streams in the LSA, the site-specific land types were characterized within each zone (Figure 2.3-1). Separate simulations with modified CoZMo-POP were completed for each zone existing conditions and each assessment case (2013 Base Case, 2013 PRM Application Case and 2013 PDC).

### 2.2.6.3   *Sediment Within the Local Study Area*

The objective of these model simulations was to determine the sediment concentration that would result following 20 years of continuous atmospheric emissions and contaminant transport within the model. Simulations were run for 20 years with an hourly time step, and results were stored at a time step of 8,760 hours. The final sediment concentrations (i.e., the sediment concentration at the end of the model simulation) were reported. The environmental parameters and assessment cases applied were consistent with the surface water modelling.

2.3   Metals

The contribution of snowmelt to freshwater metal concentrations was evaluated using a conservative mass-balance approach. Similar to the approach used for PACs, CALPUFF results were applied to the four zones. However, for metals, the deposition rates, as opposed to the ambient concentrations, were applied. For each zone, the deposition of metals on snowpack was calculated over a six-month period. Separate calculations were completed for each zone's existing conditions and each assessment case (2013 Base Case, 2013 PRM Application Case and 2013 PDC). Based on a hydrograph separation, volumes of surface runoff, interflow and active groundwater were estimated at the mouth of the four zones at the end of the snowmelt period (Figure 2.2-3). The calculations were completed for one spring melt event, corresponding to the meteorological data for the year 2002. Data from 2002 was used for the air quality modelling completed for PRM. It was assumed that the metals associated with surface runoff and interflow, which comprise the majority of snowmelt, were transported directly into surface waters, whereas aerially deposited metals that entered the active groundwater flow would be retained within the soil matrix. The resulting mass of transported metals were then used to calculate an incremental concentration of metals in receiving surface waters for each zone.

Figure 2.2-3   Meteorological and Flow Conditions Used to Estimate Snowmelt Period
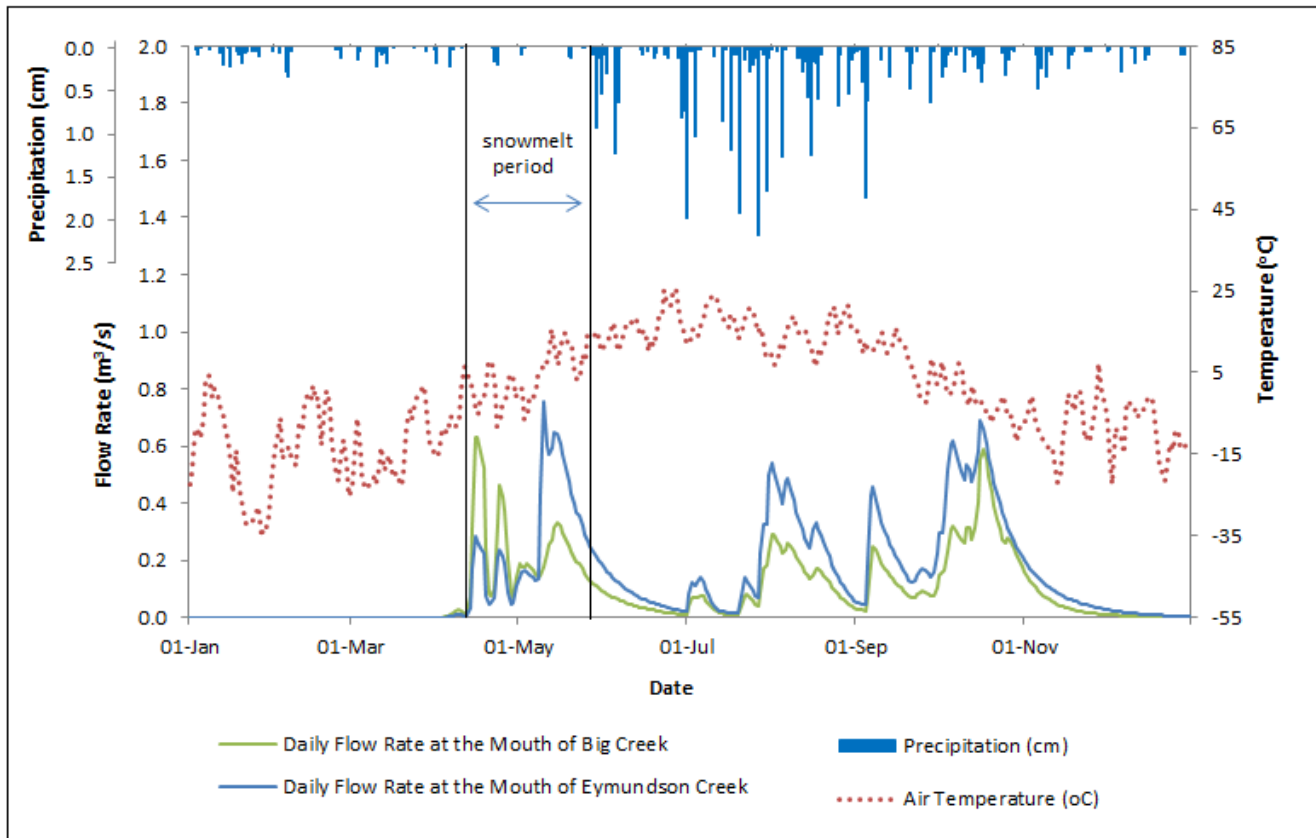
3.0   RESULTS

3.1   Isadore's Lake

Surface water and sediment concentrations were measured in Isadore's Lake and reported by Albian Sands (2005). The ranges of measured concentrations are compared to the predicted 2013 Base Case concentrations for Isadore's Lake in Table 3.1-1. Predicted concentrations of both water and sediment for acenaphthene, anthracene, fluorene, naphthalene and phenanthrene were within an order of magnitude of measured values. Given the amount of data available at this stage of modelling and the number of processes in the model, the agreement between measured and modelled values was considered acceptable for the preliminary calibration of these compounds. Concentrations of biphenyl and dibenzothiophene were under-predicted by the model, whereas benzo(a)pyrene, fluoranthene and pyrene were over-predicted for both water and sediment concentrations. The reasons for the under and over-predictions are not presently known; the most likely causes would be either under- or over-predicted air emissions for these compounds, or incorrect rates and coefficients within the CoZMo-POP model. Future model refinement will require additional snowpack data.

Table 3.1-1   Predicted Concentrations of Polycyclic Aromatic Compounds in 2013 Base Case vs. Measured Concentrations

Parameter	Surface Water Measured [µg/L] n=1	Surface Water 2013 Base Case [µg/L]	Sediment Measured [µg/g] n = 8	Sediment 2013 Base Case [µg/g]
Polycyclic Aromatic Compounds				
Acenaphthene	0.00075	0.00073	0.00087 to 0.0038	0.0008
Anthracene	0.00011	0.0009	0.00031 to 0.0015	0.0083
Benzo(a)pyrene	0.000072	0.002	0.0051 to 0.011	0.53
Biphenyl	0.0025	0.000004	0.0025 to 0.0057	0.000013
Dibenzothiophene	0.00032	0.0000032	0.0014 to 0.0048	0.000011
Fluoranthene	0.00025	0.033	0.0025 to 0.0083	0.90
Fluorene	0.00024	0.0022	0.0019 to 0.0046	0.0076
Naphthalene	0.0071	0.012	0.006 to 0.012	0.0052
Phenanthrene	0.0013	0.0078	0.0093 to 0.019	0.059
Pyrene	0.00022	0.072	0.0055 to 0.014	2.06

3.2   Snowmelt Within the Local Study Area

Under existing conditions, the incremental surface water concentrations of all modelled PACs and metals following aerial deposition and snowmelt are predicted to be below guidelines (Table 3.1-2). In the 2013 Base Case, chromium, cadmium and silver concentrations are predicted to exceed guidelines during the snowmelt period. Concentrations of PACs and metals increased from existing conditions to the 2013 Base Case, due to emissions from the approved projects. No other compounds are predicted to exceed guidelines under the 2013 PRM Application Case or the 2013 PDC.

The results presented in Table 3.1-2, for the snowmelt period, indicate that the concentrations of metals are predicted to increase in the 2013 PRM Application Case compared to the 2013 Base Case. Under the 2013 PRM Application Case, concentration of metals are predicted to increase in Zone 2 - Eymundson Creek (36% to 54%), more than Zones 3 and 4 (<20%). Metal concentrations are predicted to be lower than the 2013 Base Case in Zone 1 due to close circuiting of drainage areas. Under the 2013 PRM Application Case, concentrations of all metals are predicted to remain below guidelines, except for chromium, cadmium and silver, which were predicted to exceed guidelines under the 2013 Base Case.

Metals concentrations were generally predicted to increase in the 2013 PDC compared to the 2013 PRM Application Case except for antimony, cadmium, manganese and silver. Concentrations of PACs were predicted to increase under the 2013 PRM Application Case but remain low overall for all cases (i.e., less than 3 ng/L). The PAC concentrations were generally predicted to decrease in the 2013 PDC compared to the 2013 PRM Application Case except for biphenyl and naphthalene.

Increases in concentrations were due to addition of planned projects under each assessment case. Decreases in concentrations were due to the combined effects of changes in the different projects' emissions (Appendix 3.2), an increase in closed-circuited areas under each assessment case, and a decrease in the proportion of lakes and rivers (which receive aerial emissions directly) in the 2013 PDC zones. The 2013 PRM Application Case has close-circuited areas in the LSA while the 2013 Base Case does not, resulting in a smaller depositional area and thus a decreased pathway to receiving waters. Closed-circuited areas will not contribute

runoff to the receiving environment during operations, so they were excluded from the areas contributing to surface water concentrations in the assessment. Additionally, the local study area is located beyond the primary depositional area for oil sands mining and upgrading facilities, which are mainly centred further south.

Table 3.1-2   Predicted Concentrations of Metals and Polycyclic Aromatic Compounds in Snowmelt in the Local Study Area

Parameter	Units	Aquatic Life Guidelines [a][b]		Existing Conditions	2013 Base Case	2013 PRM Application Case	2013 PDC
		Acute	Chronic				
Metals							
Antimony	µg/L	-	-	0.003 to 0.0048	0.0052 to 0.0068	0.0044 to 0.0096	0.0039 to 0.0089
Arsenic	µg/L	340	5	0.011 to 0.017	0.051 to 0.065	0.046 to 0.098	0.071 to 0.15
Cadmium	µg/L	3.7	0.4	0.13 to 0.21	**1.3** to **1.7**	**1.3** to **2.6**	**1.5** to **2.7**
Chromium	µg/L	16	1	0.32 to 0.51	0.92 to **1.2**	0.89 to **1.8**	0.99 to **2**
Copper	µg/L	23	3	0.065 to 0.1	0.4 to 0.52	0.41 to 0.78	0.49 to 0.96
Lead	µg/L	163	6.3	0.062 to 0.099	0.34 to 0.44	0.34 to 0.66	0.39 to 0.76
Manganese	µg/L	-	-	0.12 to 0.2	0.42 to 0.55	0.42 to 0.82	0.44 to 0.87
Molybdenum	µg/L	-	73	0.08 to 0.13	0.32 to 0.41	0.29 to 0.61	0.42 to 0.87
Nickel	µg/L	742	83	0.49 to 0.79	1.2 to 1.5	1 to 2.2	1.3 to 2.6
Silver	µg/L	10.3	0.1	0.022 to 0.035	**0.19** to **0.24**	**0.19** to **0.37**	**0.19** to **0.35**
Vanadium	µg/L	-	-	0.25 to 0.41	0.81 to 1.1	0.72 to 1.5	1 to 2.1
Zinc	µg/L	190	30	2.3 to 3.7	9.5 to 12	9.1 to 18	12 to 25
Polycyclic Aromatic Compounds							
Acenaphthene	ng/L	-	5,800	0.0003 to 0.0006	0.0049 to 0.0098	0.0052 to 0.017	0.0096 to 0.016
Anthracene	ng/L	-	12	0.0005 to 0.0011	0.0084 to 0.017	0.0092 to 0.055	0.016 to 0.020
Benzo(a)pyrene	ng/L	-	15	0.025 to 0.056	0.36 to 0.75	0.33 to 0.74	0.50 to 0.55
Biphenyl	ng/L	-	-	-	0.0010 to 0.0012	0.0009 to 0.0012	0.0027 to 0.0037
Dibenzothiophene	ng/L	-	-	0.00025 to 0.00034	0.0006 to 0.0007	0.0006 to 0.0007	0.0006 to 0.0007
Fluoranthene	ng/L	-	40	0.0017 to 0.021	0.14 to 0.31	0.16 to 0.40	0.25 to 0.30
Fluorene	ng/L	-	-	0.0027 to 0.0096	0.028 to 0.056	0.033 to 0.096	0.054 to 0.090
Naphthalene	ng/L	-	1,100	0.0096 to 0.019	0.14 to 0.26	0.16 to 0.42	0.26 to 0.43
Phenanthrene	ng/L	-	400	0.0059 to 0.012	0.077 to 0.16	0.090 to 0.22	0.097 to 0.16
Pyrene	ng/L	-	25	0.052 to 0.13	0.86 to 1.90	0.99 to 2.52	0.99 to 1.66

[a]   - = No guideline.

[b]   From (AENV 1999, CCME 1999, U.S. EPA 2002) using median pH of 7.7, median temperature of 4.2°C and median hardness of 172 mg/L (reflective of on-site conditions).

Note: Numbers in bold identifies concentrations above guidelines.

3.3   Sediment Within the Local Study Area

Sediment concentrations resulting from aerial deposition in the LSA are predicted to be below interim sediment quality guidelines and probable effect levels (CCME 1999) as shown in Table 3.1-3. Sediment concentrations are predicted to increase from existing conditions with each assessment case for all PACs. In the baseline studies for the JME and PRM Project (Golder 2007), naphthalene and pyrene were measured in sediments of the watercourses and waterbodies within the Muskeg River watershed. The observed natural variation based on sediment samples collected in the middle Muskeg River, lower Muskeg River, Jackpine Creek and Kearl Lake was 850 to 26,000 pg/g for naphthalene and 1,000 to 110,000 pg/g for pyrene. The modelled concentrations, which reflect an incremental increase due to aerial emissions, for the 2013 Base Case were 4.6 to 10 pg/g for

naphthalene and 266 to 621 pg/g for pyrene. While it is possible that sediment concentrations of PACs are under-predicted by the model, it is considered more likely that other sources have resulted in baseline concentrations above what this model predicts. As noted by Kurek et al. (2013) in their discussion of sediment concentrations in the Oil Sands Region, PACs may enter fresh waters by additional pathways, including atmospheric deposition from forest fires, localized wind-blown dust from active surface-mining areas, and erosion and transport of bitumen-rich sediments by flowing waters. The Cozmo-POP modelling was not designed to capture all of these sources; rather, it attempts to examine the contribution to sediment from fleet and stationary emissions alone. Thus, predicted concentrations that are lower than measured values can be expected. The overall conclusion from the sediment modelling is that the contribution of these emissions to sediment concentrations results in predicted concentrations that are well below sediment quality guidelines.

Table 3.1-3   Predicted Concentrations of Polycyclic Aromatic Compounds in Sediment in the Local Study Area

Parameter	Units	Guidelines[a]		Existing Conditions	2013 Base Case	2013 PRM Application Case	2013 PDC
		ISQG[b]	PEL[b]				
Polycyclic Aromatic Compounds							
Acenaphthene	pg/g	6,710	88,900	0.03 to 0.08	0.51 to 1.2	0.63 to 6.89	0.92 to 1.19
Anthracene	pg/g	46,900	245,000	0.27 to 0.68	4.46 to 10.1	5.40 to 12.4	7.76 to 9.48
Benzo(a)pyrene	pg/g	31,900	782,000	7.67 to 16.3	107 to 216	115 to 232	169 to 192
Biphenyl	pg/g	-	-	-	0.18 to 0.27	0.14 to 0.20	0.38 to 0.50
Dibenzothiophene	pg/g	-	-	0.08 to 0.12	0.19 to 0.24	0.16 to 0.21	0.16 to 0.19
Fluoranthene	pg/g	111,000	2,355,000	9.37 to 24.3	159 to 373	198 to 509	293 to 410
Fluorene	pg/g	21,100	144,000	0.44 to 7.49	7.24 to 16.5	8.83 to 22.4	13.2 to 18.0
Naphthalene	pg/g	34,600	391,000	0.33 to 0.75	4.64 to 9.98	5.15 to 11.2	7.68 to 8.58
Phenanthrene	pg/g	41,900	515,000	2.36 to 5.58	31.4 to 71.4	37.9 to 85.2	53.9 to 65.0
Pyrene	pg/g	53,000	875,000	15.2 to 33.9	266 to 621	330 to 840	485 to 689

[a]   - = No guideline.

[b]   Interim Sediment Quality Guidelines (ISQG) and Probable Effects Levels (PEL) from CCME (1999).

4.0   DISCUSSION

A critical factor in determining the extent of contaminant delivery to surface water in the Oil Sands Region is the proportion of contaminant mass (delivered to the watershed via aerial deposition) that is retained by the watershed vs. the proportion that is exported to surface water. In studies of contaminant delivery to surface water in northern Sweden, Bergknut et al. (2011) defined a retention factor (R) as:

$$R(\%) = \frac{(F_{input} - F_{output}) \times 100}{F_{input}}$$

Where: F_{input} = Input flux delivered to the watershed by atmospheric deposition; and

F_{output} = Output flux delivered to surface water.

Based on mass balance calculations using measured deposition rates, surface water concentrations and water discharge rates, Bergknut et al. (2011) found retention factors of 96.0% to 99.9% for polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Although differences can be expected between results derived for PCBs and PCDD/Fs and the PACs evaluated in the current oil sands modelling, some similarity is expected because they are both classes of organic contaminants

with comparable ranges of volatility, water-solubility and hydrophobicity. Also, the study was carried out in Northern Sweden, an area with a mean annual precipitation and temperature of 612 mm and 1.7^{o}C, which is similar to the modelled meteorological conditions for the PRM study areas in Alberta.

Evaluating retention factors for the different chemicals and zones modelled herein provides a greater understanding of the chemical fate processes controlling contaminant delivery to surface water. The zones in the PRM have a range of environmental properties, which will affect retention. Retention factors were calculated for all zones in the 2013 Base Case, which have the following properties:

- Zone 1: Total watershed area 1.34 x 10^8 m^2, 22% surface water, 69% forested;

- Zone 2: Total watershed area 3.34 x 10^8 m^2, 21% surface water, 64% forested;

- Zone 3: Total watershed area 3.26 x 10^8 m^2, 11% surface water, 63% forested; and

- Zone 4: Total watershed area 2.43 x 10^8 m^2, 18% surface water, 44% forested.

The physical-chemical properties of the modelled chemicals will also affect the retention factor, as chemicals will be exported to surface water to varying degrees depending on their tendency to partition to soil, volatilize, degrade and dissolve in melt water, for example. Retention factors were calculated for phenanthrene, pyrene and benzo(a)pyrene, because these chemicals represent a range in physical-chemical properties (Tables 2.2-5 and 2.2-6). In the CoZMo-POP model, the retention factor was calculated based on the following:

- F_{input} = Cumulative flux of contaminant transferred from air to snow (kg) minus cumulative flux of contaminant transferred from snow to air (kg); and

- F_{output} = Cumulative flux of contaminant delivered from non-forested soil, forested soil and snow to surface water (kg).

During the snow cover and snow melt periods, it was assumed in CoZMo-POP that snow covers the entire forested, non-forested and surface water compartments; therefore all contaminant delivery to the underlying surfaces occurs by transfer from snow. Contaminants that volatilize or degrade in soil are not exported to surface water, and are effectively "retained" by the watershed for the purposes of this calculation. While F_{input} reflects contaminant transfer during the snow cover and snow melt periods in the model, F_{output} considers contaminant transfer only during snow melt. This method provides an overall estimate of the percentage of contaminant that is deposited to the watershed and ends up in surface water. The calculated retention factors are shown in Figure 4.1-1. The results reflect the modelling completed for half the year (snow accumulation and snow melt), consistent with the surface water modelling.

Figure 4.1-1   Retention Factors for Selected Chemicals in all Zones of the 2013 Base Case
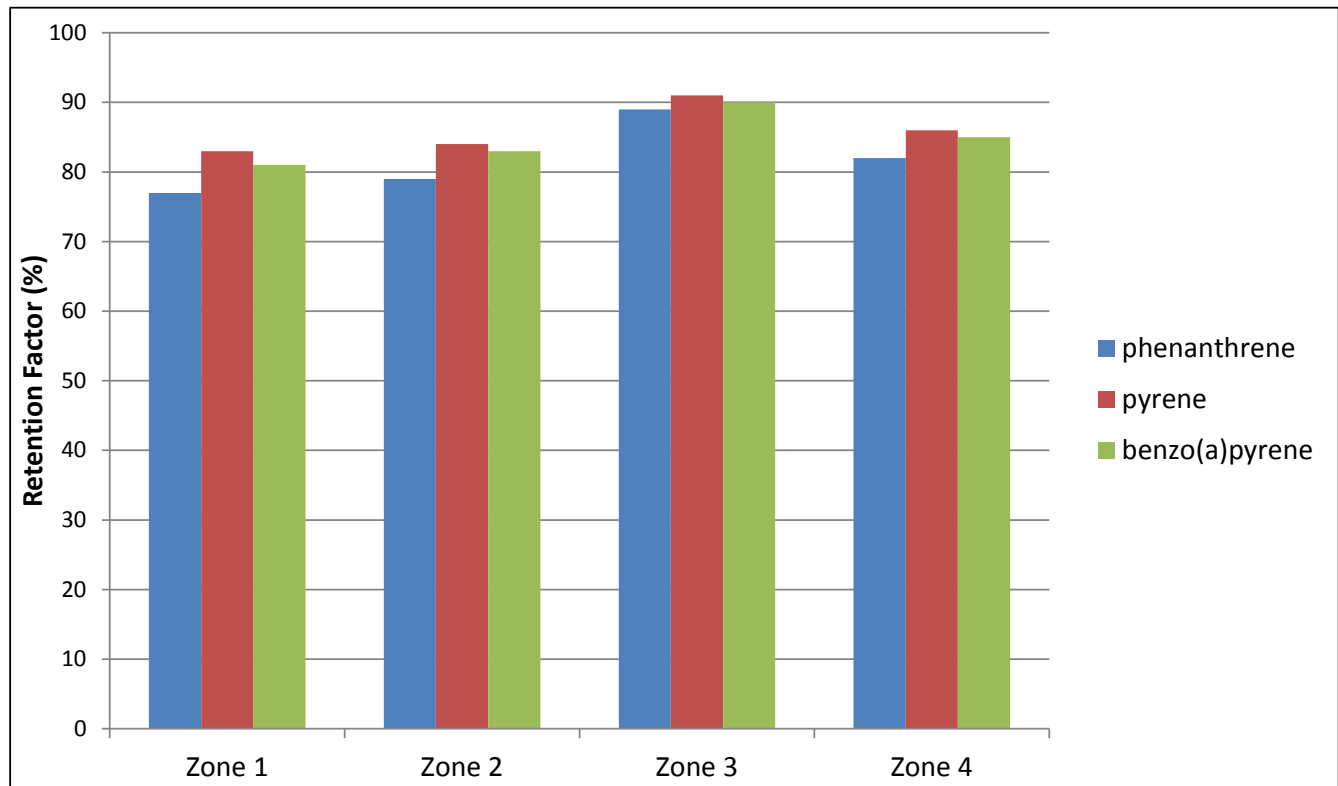
The zone with the highest percentage surface water (Zone 1) has the lowest retention factors, because a greater amount of contaminants deposit directly on to surface water. Zone 2 and Zone 4 have similar retention factors, despite differences in the percentage forest in each zone (64% for Zone 2 and 44% for Zone 4). This indicates that although there are differences in deposition to forested and non-forested areas, termed the "forest filter effect" by Nizzetto et al. (2006), the extent of contaminant export to surface water from these areas may be similar. Phenanthrene, which is the most water soluble of the modelled chemicals, had the lowest retention factors, likely a result of more efficient transfer to surface water via melt water. Pyrene and benzo(a)pyrene had similar retention factors, although benzo(a)pyrene is primarily transferred to surface water in the model via the particulates in snow melt water, while pyrene is also transferred via the dissolved phase in melt water. Overall, retention factors modelled in CoZMo-POP for the PRM ranged from 77% to 91%. These values are generally lower than those listed in the Bergknut et al. (2011) study, but variation can be expected given the differences in environmental parameters and physical-chemical properties used in the model. Using lower retention factors results in predicting higher water concentrations from aerial deposition, which maintains a conservative approach when estimating water concentrations for the purposes of environmental assessment.

5.0   PREDICTION CONFIDENCE

The results presented in this appendix should be viewed as preliminary and developing, representing efforts to better understand the impacts of aerial deposition to snowpack and consequently snowmelt water and receiving waterbody sediment concentrations. The assessment employed the most appropriate modelling framework for the type and amount of data available, and it advanced the state of modelling by completing a preliminary calibration to an existing waterbody (Isadore's Lake).

To account for uncertainties, it was conservatively assumed that the transport of all metals associated with interflow to waterbodies occurred without partitioning or settling from the snowpack. Additionally, the air quality modelling for all assessment cases, except the existing conditions, assumed that all operations will be at full capacity simultaneously. Thus, the uncertainties in this assessment are related to the assumptions made while developing this model, and the estimation of the associated emissions and deposition rates provided by the air modelling (Appendix 3.2), and they are expected to bias the predictions upwards for most constituents.

The modelling indicated that during the snowmelt period, concentrations of cadmium, chromium and silver might exceed the water quality guidelines in the 2013 Base Case, 2013 PRM Application Case and 2013 PDC. To indicate whether snowpack runoff is presently affecting instream concentrations, observed concentrations of these constituents in the Muskeg River and its tributaries are plotted by day of the year in Figures 5-1 to 5-3. Muskeg River was selected because sufficient observed data were available over a 30-year period. These figures display no discernible 'pulse' during the snowmelt period, which would be expected if these constituents were being washed into receiving watercourses during freshet. A more likely fate of these metals is retention in the soil or muskeg, which may be incorporated into these models as further refinements when more data become available. The instream concentrations indicate that the model results are high due to the conservative assumptions mentioned above.

The watershed retention factors calculated using the CoZMo-POP model were less than those that have been measured in the field (Bergknut et al. 2011), for a similar environment (Northern Sweden) and similar chemicals (PCBs and PCDDs/DFs), indicating that the modelling assessment method is more likely to provide an over-estimate of water concentrations than an under-estimate.

The Isadore's Lake modelling indicated that the model was performing well for five PACs, under-predicting two PACs and over-predicting three PACs in both water and sediment. Further refinements to the inputs and processes in the model are anticipated as snowpack data become available. In particular, the Governments of Alberta and Canada have conducted snowpack surveys in the Oil Sands Region. These data could be used to refine the model but to date they have not been made available to the public or industry.

Figure 5-1   Observed Concentrations of Cadmium (mg/L) in the Muskeg River Watershed (1981 to 2012)
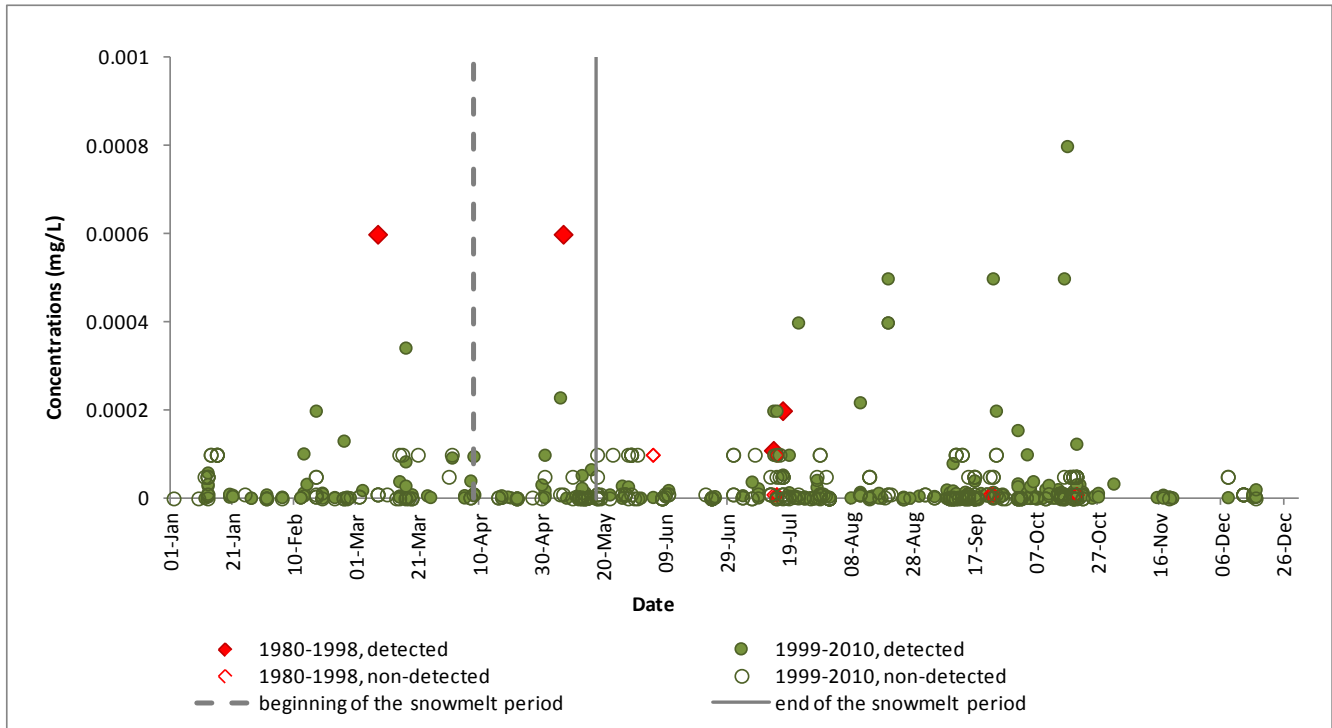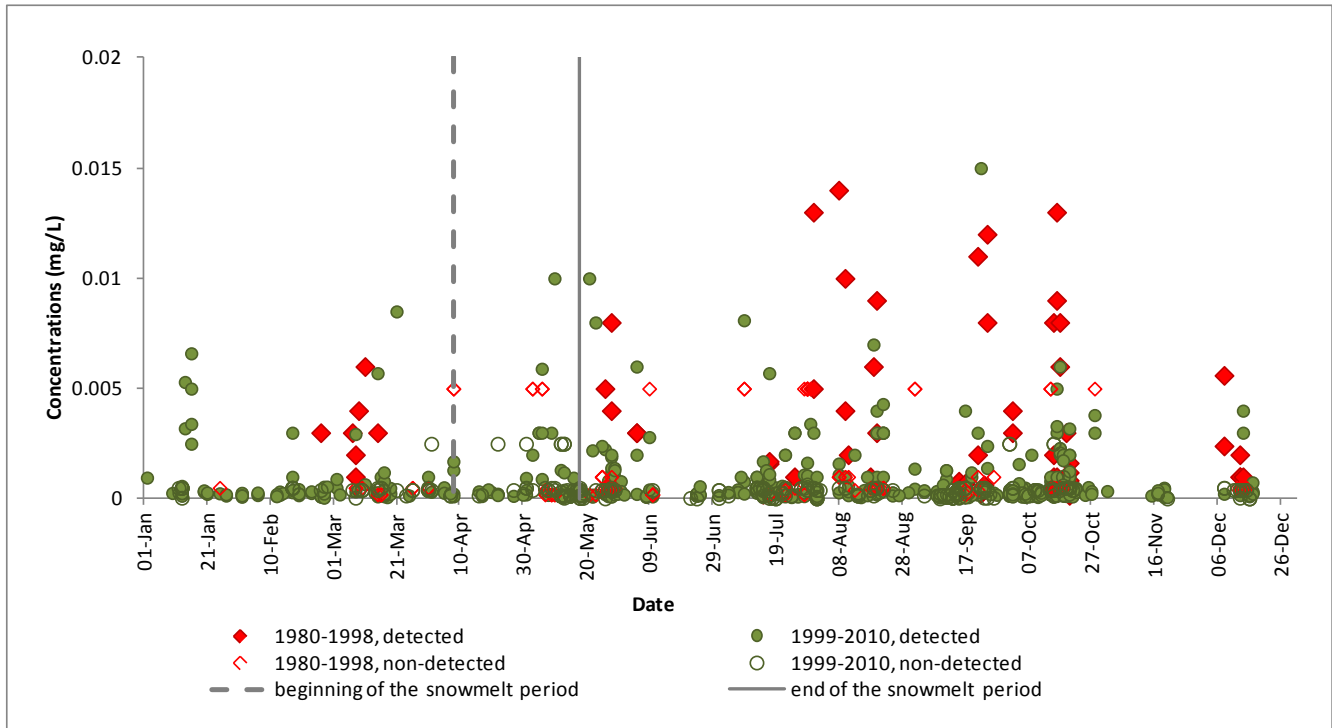

Note: Data presented on the graph are split into two periods to show differences in analytical methods, consistent with the Lower Athabasca Region Surface Water Quality Management Framework (AENV 2011).
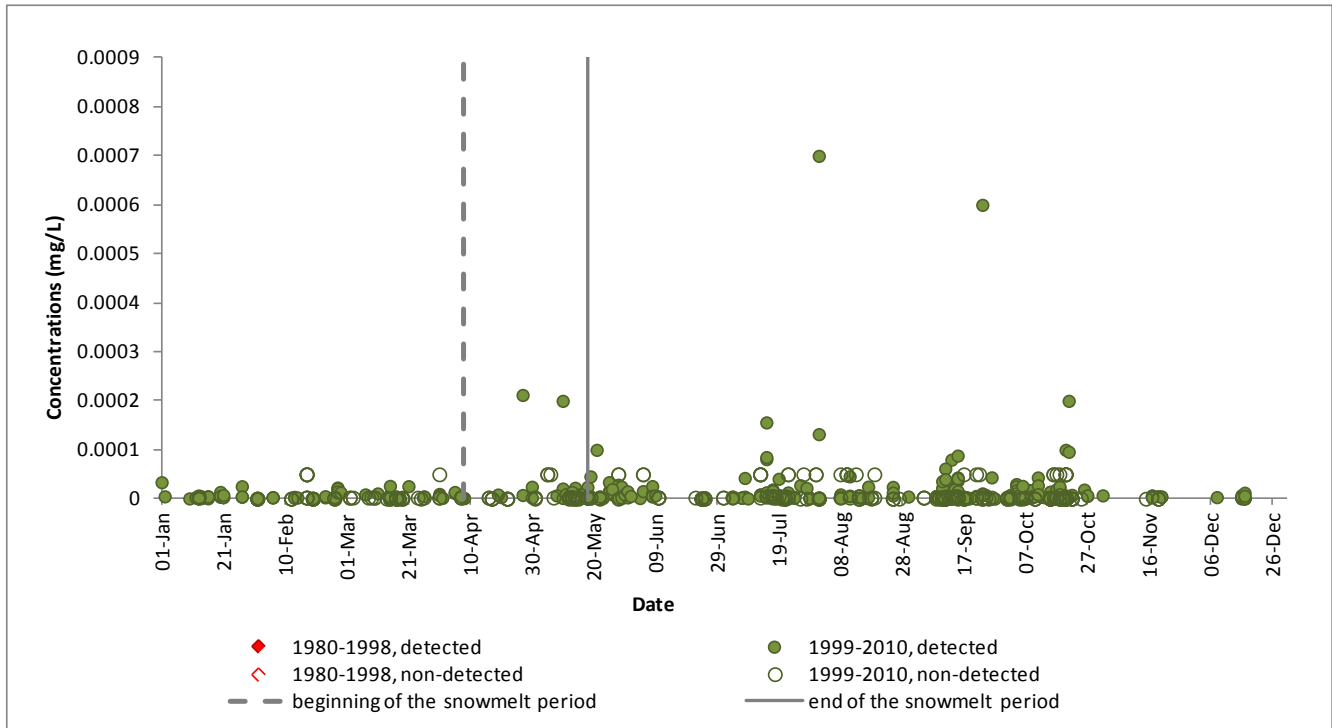
Figure 5-2   Observed Concentrations of Chromium (mg/L) in the Muskeg River Watershed (1981 to 2012)

Note: Data presented on the graph are split into two periods to show differences in analytical methods, consistent with the Lower Athabasca Region Surface Water Quality Management Framework (AENV 2011).

Figure 5-3   *Observed Concentrations of Silver (mg/L) in the Muskeg River Watershed (1981 to 2012)*

Note: Data presented on the graph are split into two periods to show differences in analytical methods, consistent with the Lower Athabasca Region Surface Water Quality Management Framework (AENV 2011).

6.0   SUMMARY

Concentrations of PACs and metals were predicted in surface water and sediment, using the modified CoZMo-POP model for PACs and a conservative mass-balance approach for metals. Deposition rates and ambient air concentrations used in these models were estimated by the CALPUFF model. The results indicated that while some concentrations increased from the 2013 Base Case to the 2013 PRM Application Case, predicted surface water and sediment concentrations for PACs in all zones would be less than guidelines. Similarly, concentrations of all metals except cadmium, chromium and silver were predicted to remain below guidelines in snowmelt. These three metals were predicted to exceed guidelines under the 2013 Base Case, and increase by up to 54% under the 2013 PRM Application Case, although instream monitoring indicated that the model may be over-estimating these concentrations.

Additional modelling simulations were carried out for Isadore's Lake to evaluate whether the CoZMo-POP model could replicate measured concentrations. The results showed reasonable agreement between the modelled and measured surface water and sediment concentrations for 5 of the 10 modelled PACs. Thus, the results presented in this appendix should be viewed as preliminary, representing efforts to better understand the impacts of aerial deposition to snowpack and consequently snowmelt water concentrations and sediment concentrations. Future modelling will be refined as additional data become available.

7.0 REFERENCES

ACD Labs. 2013. *Result of prediction module to calculate Abraham solvation parameters for dibenzothiophene*. Personal Communication from Wania Lab, University of Toronto.

AENV (Alberta Environment). 1999. *Surface Water Quality Guidelines for Use in Alberta*. November 1999. Environmental Service, Environmental Sciences Division. Edmonton, AB. 25 pp.

AENV. 2011. *Lower Athabasca Region Surface Water Quality Management Framework; For the Athabasca River Downstream of Grand Rapids to the Athabasca River Delta.* March 2011. Available at: http://environment.alberta.ca/documents/LAR_SWMF_Mar_31_Final_Draft.pdf

Albert, M.R., E.F. Shultz and F.E. Perron, Jr. 2000. *Snow and firn permeability at Siple Dome, Antarctica*. Ann. Glaciol., 31: 353–356.

Albian Sands (Albian Sands Energy Inc.). 2005. *Muskeg River Mine Expansion Project*. Submitted to Shell Canada Energy. Submitted by AXYS Environmental Consulting Ltd. in association with North/South Consultants Inc. and Hydroconsultant.

Bamford, H.A., D.L. Poster and J.E. Baker. 1999. *Temperature Dependence of Henry's Law Constants of Thirteen Polycyclic Aromatic Hydrocarbons Between 48°C and 31°C.* Environmental Toxicology and Chemistry 18(9):1905-1912.

Bergknut, M., H. Laudon, S. Jansson, A. Larsson, T. Gocht and K. Wiberg. 2011. *Atmospheric deposition, retention and stream export of dioxins and PCBs in a pristine boreal catchment*. Environmental Pollution 159:1592-1598.

CCME (Canadian Council of Ministers of the Environment). 1999. (with updates to 2010). *Canadian Environmental Quality Guidelines*. Winnipeg, Manitoba.

Daly, G.L. and F. Wania. 2004. *Simulating the influence of snow on the fate of organic compounds*. Environmental Science and Technology 38: 4176-4186.

Daly, G.L., Y.D. Lei, L.E. Castillo, D.C.G. Muir and F. Wania. 2007. *Polycyclic aromatic hydrocarbons in Costa Rican air and soil: A tropical/temperate comparison.* Atmospheric Environment 41: 7339-7350.

Domine F. and P.B. Shepson. 2002. *Air-snow interactions and atmospheric chemistry*. Science, 297: 1506-1510.

Domine, F, A. Cabanes and L. Legagneux. *Structure, microphysics and surface area of the Arctic snowpack near Alert, during the ALERT 2000 campaign.* Atmospheric Environment *36*: 2753-2765.

Downing, D.J. and W.W. Pettapiece. 2006. *Natural regions and subregions of Alberta.* Compiled by Government of Alberta, Natural Regions Committee. Pub. No. T/852. Edmonton, AB.

Fletcher, N. 1973. *The surface of ice*. In Physics and Chemistry of Ice; Whalley, E., Jones, S., Gold, L., Eds.; Royal Society of Canada: Ottawa, Ontario.

Golder (Golder Associates Ltd.). 2007. *Wildlife Environmental Setting for the Jackpine Mine Expansion & Pierre River Mine Project*. Prepared for Shell Canada Limited. December 2007. Calgary, AB.

Goss, K.U. and R.P. Schwarzenbach. 1999. *Empirical Prediction of Heats of Vaporization and Heats of Adsorption of Organic Compounds*. Environ. Sci. Technol. 1999, 33, 3390-3393.

Harner, T. and T.F. Bidleman. 1998. *Measurement of Octanol-Air Partition Coefficients for Polycyclic Aromatic Hydrocarbons and Polychlorinated Naphthalenes*. Journal of Chemical Engineering Data, 43, 40-46.

Hoff, J.T., Gregor, D., Mackay, D. Wania, F., and Jia, C.Q. *Measurement of the Specific Surface Area of Snow with the Nitrogen Adsorption Technique*. Environ. Sci. Technol. 1998. 32(1), 58–62.

Johannessen, M. and A. Henriksen. 1978. *Chemistry of snow meltwater: Changes in concentration during melting*. Water Resour. Res., 14: 615-619.

Kelly E.N., J.W. Short, D.W. Schindler, P.V. Hodson, M. Ma, A.K. Kwan and B.L. Fortin. 2009. *Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries*. Proc. Nat. Acad. Sciences 106:52. 22346-22351.

Kelly E.N., D.W. Schindler, P.V. Hodson, J.W. Short, R. Radmanovich and C.C. Nielsen. 2010. *Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries*. Proc. Nat. Acad. Sciences 107(37): 16178-16183.

Kurek, J., J.L. Kirk, D.C.G. Muir, X. Wang, M.S. Evans and J.P. Smol. 2013. *Legacy of a half century of Athabasca oil sands development recorded by lake ecosystems*. Proceedings of the National Academy of Sciences. January 7, 2013 Early Edition.

Legagneux, L., A. Cabanes and F.J. Domine. 2002. *Measurement of the specific surface area of 176 snow samples using methane adsorption at 77 K*. Geophys. Res.107 (D17), art. no. 4335.

Lei, Y.D. and F. Wania. 2004. *Is rain or snow a more efficient scavenger of organic chemicals?* Atmospheric Environment 38: 3557-3571.

Lei, Y.D., F. Wania, W.Y. Shiu and D.G.B. Boocock. 2000. *HPLC-Based Method for Estimating the Temperature Dependence of n-Octanol-Water Partition Coefficients*. Journal of Chemical Engineering Data 45, 738-742.

Ma, Y-G., Y.D. Lei, H. Xiao, F. Wania and W-H. Wang. 2010. *Critical Review and Recommended Values for the Physical-Chemical Property Data for 15 Polycyclic Aromatic Hydrocarbons at 25°C*. Journal of Chemical Engineering Data 55:819-825.

Mackay, D. 2001. *Multimedia Environmental Models – The Fugacity Approach*. CRC Press. Boca Raton, Florida.

Mackay, D., W.Y. Shiu, K.C. Ma and S.C. Lee. 2006. *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*. SRC Press. Boca Raton, FL.

Meyer, T. and F. Wania. 2008. *Organic contaminant amplification during snowmelt*. Water Res. 42: 1847–1865.

Meyer, T., Y.D. Lei and F. Wania. 2005. *The fate of organic contaminants in melting snow*. 62nd Eastern Snow Conference, Waterloo, ON.

Nizzetto, L., Cassani, C., Di guardo, A. 2006. *Deposition of PCBs in mountains: the forest filter effect of different forest ecosystem types*. Ecotoxicology and Environmental Safety, 63, 75-83.

Odabasi, M., E. Cetin and A. Sofuoglu. 2006. *Determination of octanol-air partition coefficients and supercooled liquid vapour pressures of PAHs as a function of temperature: Application to gas-particle partitioning in an urban atmosphere*. Atmospheric Environment 40: 6615-6625.

RAMP (Regional Aquatics Monitoring Program) 2011. *2011 Technical Report*. Prepared for the RAMP Steering Committee. Prepared by The RAMP 2011 Implementation Team consisting of Hatfield Consultants, Kilgour and Associates Ltd. and Western Resource Solutions.

Roth, C., K-U. Goss and R.P. Schwarzenbach. 2004. *Sorption of Diverse Organic Vapors to Snow*. Environmental Science and Technology 38, 4078-4084.

Schondorf, T. and R. Herrmann. 1987. *Transport and chemodynamics of organic micropollutants and ions during snowmelt*. Nordic Hydrol. 18: 259–278.

Shunthirasingham, S., Y.D. Lei and F. Wania. 2007. *Evidence of Bias in Air-Water Henry's Law Constants for Semivolatile Organic Compounds Measured by Inert Gas Stripping*. Environmental Science and Technology. 41:3807–3814.

Simmleit, N., R. Herrmann and W. Thomas. 1986. *Chemical behavior of hydrophobic micropollutants during the melting of snow*. IAHS Publication 155: 335–346.

U.S. EPA (United States Environmental Protection Agency). 2002. *National Recommended Water Quality Criteria*. Office of Water. U.S. EPA 822–R–02–047. Washington, D.C.

U.S. EPA. 2011. *EPISuite AOPWIN v.1.92*. Available at: http://www.epa.gov/opptintr/exposure/pubs/episuite.htm. Accessed: April 2011.

Wania, F. 1997. *Modelling the Fate of Non-Polar Organic Chemicals in an Ageing Snow Pack*. Chemosphere 35, 2345-2363.

Wania, F. and G.L. Daly. 2002. *Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs*. Atmos. Environ 36:5581-5593.

Wania, F., J. Persson, A. Di Guardo and M.S. McLachlan. 2000. *CoZMo- POP.A fugacity-based multi-compartmental mass balance model of the fate of persistent organic pollutants in the coastal zone; WECC Report 1/2000*. Toronto, Canada. 26 pp. Available at: http://www.utsc.utoronto.ca/~wania/.

Wania, F., R. Semkin, J.T Hoff and D. Mackay.1999. *Modelling the fate of nonpolar organic chemicals during the melting of an Arctic snowpack*. Hydrol. Processes 13:2245-2256.

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