APPENDIX 3.5

Aerial Deposition Assessment

Table of Contents

TABLES

FIGURES

1.0   INTRODUCTION

This appendix provides technical information regarding the modelling methods used to assess potential impacts of aerial deposition to snowpack and snowmelt water concentrations. The modelling approach described herein was applied to the Jackpine Mine Expansion (JME) under existing conditions, 2012 Base Case, 2012 JME Application Case and 2012 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).

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 Kelly et al. (2009, 2010) studies highlighted this issue as an emerging concern for oil sands developments. The study described herein attempted to quantify the effects of aerial deposition on snowpack and ultimately on receiving watercourses in the Local Study Area (LSA). This study was completed in response to stakeholder and regulator requests to evaluate this pathway as a potential source of metals and PAHs to the receiving environment. It examined potential effects from existing and approved projects, JME, 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.

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).

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:

■ 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 approach was adapted for metals. More detailed information about these models is presented in the following sections.

2.1   Data Sources

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

■ deposition rates and ambient concentrations associated with the existing condition 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); and

■ chemical properties of PACs from a variety of literature sources.

2.2   Models and Assumptions

Polycyclic Aromatic Compounds

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). Prior to the addition of snow, the model had compartments describing the atmosphere, forest canopy, forest soil, agricultural soil, freshwater, freshwater sediment, coastal water and coastal sediment. It allows for seasonally variable temperature, wind speed and hydroxyl radical concentrations.

The model treats water content in soils, snowpack and freshwater as functions of time, dynamically determined by the balance of water flowing in and out of these compartments (Figure 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.

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

Water Balance Equations

snowpack $\mathrm{d}h_{sp}/\mathrm{d}t = (wG_{a-sp} - wG_{sp-a} - wG_{sp-w} - wG_{sp-e})/(A_{sp}vf_{swe-sp})$

soil $\mathrm{d}vf_{we}/\mathrm{d}t = (wG_{ae} + wG_{sp-e})/V_e - (k_{evap-e} + k_{runoff-e})vf_{we}$

freshwater $\mathrm{d}V_w/\mathrm{d}t = wG_{aw} + wG_{sp-w} + wG_{ew} - (k_{evap-w} + k_{runoff-w})V_w$

parameter	equation	description
wG		water fluxes in m^3/h
wG_{a-w}	$U_3 A_w$	air−freshwater (w)
wG_{a-e}	$U_3 A_e$	air−soil (e)
wG_{a-sp}	$U_3 A_{sp}$	air−snow (sp)
wG_{w-a}	$V_w k_{evap-w}$	water−air
wG_{e-a}	$vf_{we} V_e k_{evap-e}$	soil−air
wG_{sp-a}	$vf_{swe-sp} h_{sp} A_{sp} k_{sub}$	snow−air
wG_{sp-w}	$vf_{swe-sp} h_{sp-max} A_w k_{melt}$	snow−freshwater
wG_{sp-e}	$vf_{swe-sp} h_{sp-max} A_e k_{melt}$	snow−soil
wG_{e-w}	$vf_{we} V_e k_{runoff-e}$	soil−freshwater
wG_{w-c}	$V_w k_{runoff-w}$	freshwater−coastal (c)
U_3		precipitation rate in m/h
A_x		surface area of compartment x in m^2
V_x		volume of compartment x in m^3
vf_{we}		volume fraction of water in soil
vf_{swe-sp}		volume fraction snow water equivalent in snowpack
h_{sp}		height of snowpack in m
h_{sp-max}		maximum height of snowpack in m
k_{evap}		evaporation rate in h^{-1}
k_{sub}		sublimation rate in h^{-1}
k_{melt}		melting rate in h^{-1}
$k_{runoff-e}$		soil runoff rate in h^{-1}
$k_{runoff-w}$		freshwater outflow rate in h^{-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 2.2-2. 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 freshwater 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.
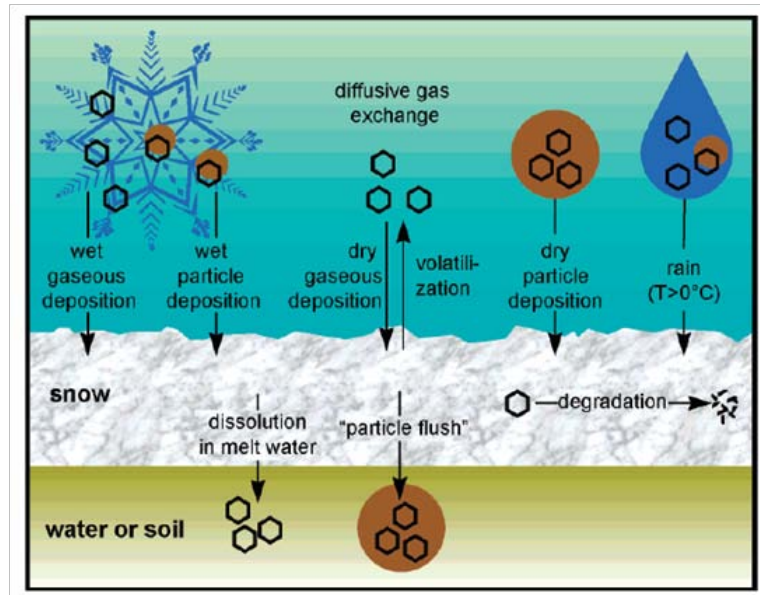
Figure 2.2-2   *Processes Involved in the Delivery and Loss of Organic Contaminants in a Seasonal Snow Cover in the Modified CoZMo-POP Model*

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 Figure 2.2-3. 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.

Figure 2.2-3   Model Equations Related to Contaminant in the Snowpack

Mass Balance Equation for Contaminant in Snowpack

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

M_{sp}	amount of contaminant in snowpack in mol
t	time in h
f_A, f_{sp}	fugacity in air and snowpack in Pa

parameter	equation	description
		D Values in mol/Pa·h
D_R	$k_{sp}V_{sp}Z_{sp}$	reaction in snowpack
D_{sp-e}	$wG_{sp-e}Z_w$	meltwater runoff to soil
D_{sp-w}	$wG_{sp-w}Z_w$	meltwater runoff to freshwater
D_{pf-e}	$G_{pf}Z_w + A_e/A_{sp}M_{o-max}Z_o/\rho_o$	particle flush to soil
D_{pf-w}	$G_{pf}Z_w + A_w/A_{sp}M_{o-max}Z_o/\rho_o$	particle flush to freshwater
D_{sp-a}	$A_{sp}/(1/U_{S/A-bl}Z_A) + 1/(wpfU_{S/A-ps}Z_A))$	snow to air transfer
D_{a-sp}	$D_{sp-a} + A_{sp}DDV_{sp}vf_AZ_Q + wG_{a-sp}BZ_x$	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	$1/(RT)$	air
Z_w	$K_{WA}Z_a$	water
Z_I	$K_{IA}Z_a$	interface
Z_o	$K_{OA}(\rho_{part}/\rho_{oct})Z_a$	organic matter
Z_{sp}	$Z_av_a + Z_wv_w + Z_IA_{snow}\rho_{mw} + Z_ov_o$	snowpack
BZ_{rain}	$Z_w + W_{p1}vf_AZ_o\,f_{oa}$	rain
BZ_{snow}	$Z_IA_{snow}\rho_{mw} + W_{p2}vf_AZ_o\,f_{oa}$	falling snow
k_{sp}		reaction rate of contaminant in snowpack in h⁻¹
V_{sp}		volume of snowpack in m³
wpf		wind-pumping factor
M_{o-max}		maximum mass of organic carbon in snowpack in g
ρ_o		density of organic matter in g/m³
$U_{S/A-ps}$	$B_a(v_a^{10/3}/v_a + v_w)^2/(\ln(2)h_{sp})$	mass transfer coefficient for air-filled pore space in m/h
$U_{S/A-bl}$		mass transfer coefficient for air boundary layer above snow in m/h
B_a		molecular diffusivity in air in m²/h
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_{SA}		partition coefficient between snow surface and air in m
K_{IA}		partition coefficient between liquid water surface and air in m
R		gas constant in J/(mol·K)
T		absolute temperature in K
$\rho_{part}, \rho_{oct}, \rho_{mw}$		density of atmospheric particles, octanol, and snowmelt water in g/m³
v_a, v_w, v_o		volume fraction of air, liquid water, and organic matter in snowpack
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
G_{pf}		water remaining in snowpack when particle flush occurs in m³

Source: Daly and Wania 2004.

The surface area accessible to gases for a given mass of snow (specific snow surface area, A_{snow} in m²/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 m²/g) and for the snowmelt period (a linear decrease from 0.1 to 0.01 m²/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.
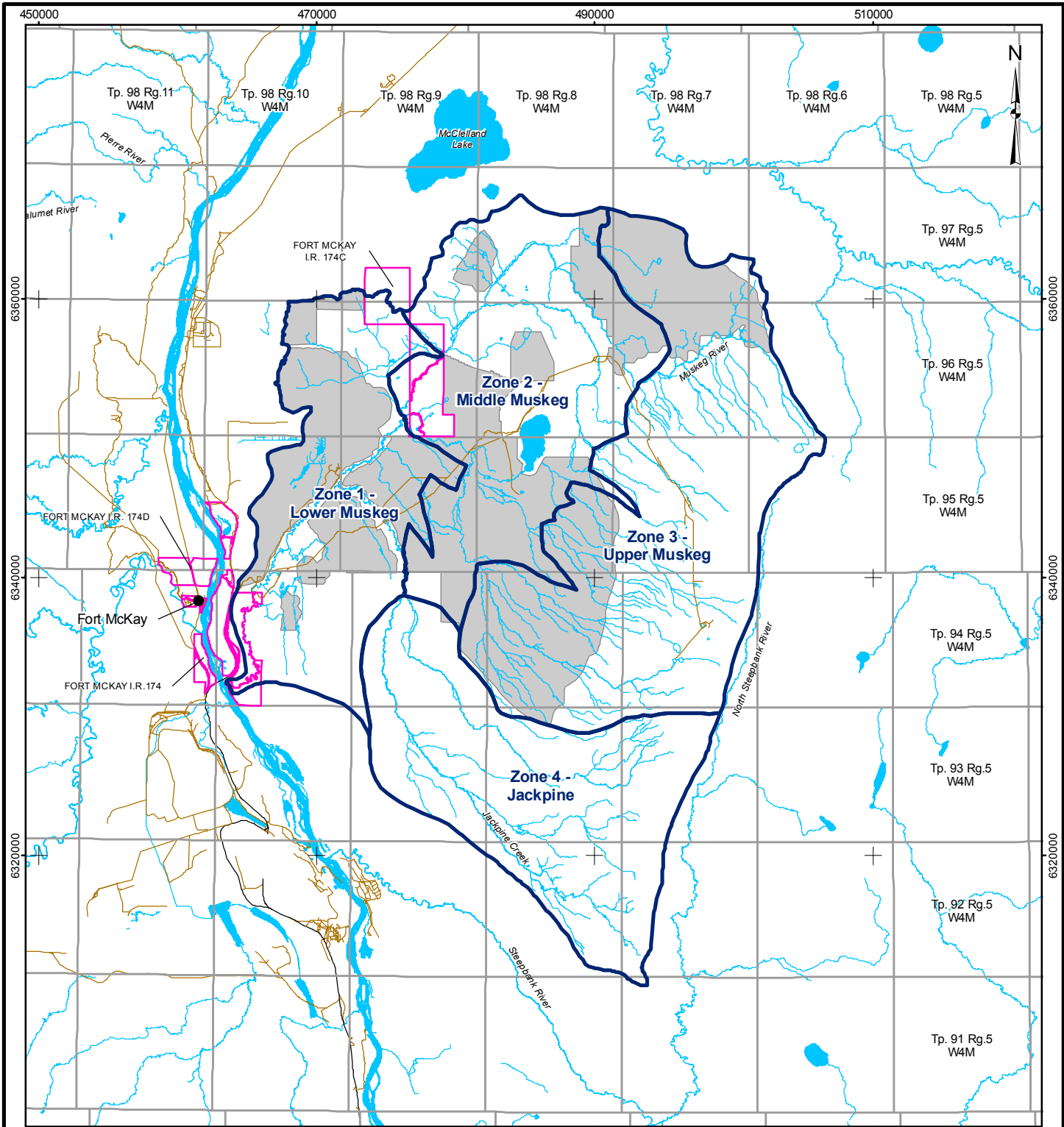
2.3   Model Application

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. The model predicted incremental concentrations of substances in snowmelt water, averaged over the snowmelt period. The model was applied to the LSA, because that is where the 'worst-case' effects were expected to be observed. The LSA is expected to be 'worst-case' because the Muskeg River watershed 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.

To apply the model to the small streams in the LSA, four zones were defined as discrete model segments: Lower Muskeg – zone 1; Middle Muskeg – zone 2; Upper Muskeg– zone 3; and Jackpine – zone 4 (Figure 2.3-1). 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, 2012 Base Case, 2012 JME Application Case and 2012 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. It represents development conditions as of the period of 2006 to 2012, which is the period of record for the various inputs to the model. It differs from the 2012 Base Case in that air modelling for the existing case incorporates emissions from this period, whereas the 2012 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).

450000 470000 490000 510000

N

Tp. 98 Rg.11 W4M
Tp. 98 Rg.10 W4M
Tp. 98 Rg.9 W4M
Tp. 98 Rg.8 W4M
Tp. 98 Rg.7 W4M
Tp. 98 Rg.6 W4M
Tp. 98 Rg.5 W4M

Pierre River
alumet River
McClelland Lake

Tp. 97 Rg.5 W4M

6360000

FORT MCKAY I.R. 174C

Zone 2 - Middle Muskeg

Muskeg River

Tp. 96 Rg.5 W4M

Zone 1 - Lower Muskeg

FORT MCKAY I.R. 174D

Zone 3 - Upper Muskeg

Tp. 95 Rg.5 W4M

6340000

Fort McKay

FORT MCKAY I.R.174

North Steepbank River

Tp. 94 Rg.5 W4M

Tp. 93 Rg.5 W4M

Zone 4 - Jackpine

Jackpine Creek

6320000

Tp. 92 Rg.5 W4M

Steepbank River

Tp. 91 Rg.5 W4M

LEGEND

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

10   0   10
SCALE 1:400,000   KILOMETRES

REFERENCE
ALBERTA DIGITAL DATA OBTAINED FROM ALTALIS LTD. © GOVERNMENT OF ALBERTA 2004.
DATUM: NAD83 PROJECTION: UTM ZONE 12N

I:\CLIENTS\SHELL\10-1346-0001\mapping\mxd\8000\Water Quality\REPORT FIGURES\FINAL\1013460001-WQ-001-GIS_FINAL.mxd

Closed-circuited areas, which were also set to represent each assessment case, were excluded from the areas contributing to surface water concentrations. The 2012 Base Case, 2012 JME Application Case and 2012 PDC closed-circuited areas were based on the 2029 snapshot, representing the mid-life of operations. This snapshot does not correspond with the maximum closed-circuited area, which is anticipated to occur in 2049. 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 potentially affected snowmelt to surface waters.

Model Inputs

The model relied on emission data from oil sands facilities and regional meteorological data. Deposition rates and ambient concentrations associated with the existing condition and the assessment cases were predicted using the CALPUFF model (EIA, Volume 3, Appendix 3-8) and entered into CoZMo-POP as 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. Model simulations were carried out for one year, based on meteorological data from 2002. 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 fresh water compartment (k_{runoff}-w) was also set to a negligible level so substances delivered to the freshwater compartment from the snowpack did not exit 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.

i)   CoZMo-POP Environmental Input Parameters

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) were used. Site-specific environmental input parameters for one zone are presented in Table 2.3-1.

Table 2.3-1   Site-Specific Environmental Input Parameters

Parameter	Value	Reference
Fraction of drainage basin covered by forest	0.25	GIS land-use maps
Fraction of forest area covered by coniferous trees	0.33	GIS land-use maps
Deciduous canopy development		
Start of growth	133	
End of growth	144	Downing and Pettapiece (2006)
Start of falling	261	
End of falling	283	
Drainage basin surface area in m^2	129,000,000	GIS maps
Fraction of drainage basin covered by lakes and rivers	0.13	GIS land-use maps

ii)   CoZMo-POP 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.

iii)   CoZMo-POP Physical-Chemical Property Data

The physical-chemical property data selected for the chemicals of interest are shown in Tables 2.3-2 and 2.3-3. 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 2.3-2   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 2.3-3   Selected Physical-Chemical Property Data – Solute Descriptors, Half-Lives and Reaction Rates

Parameter	α	β	L16	Reference	Soil $t_{1/2}$ [hours]	Water $t_{1/2}$ [hours]	Sediment $t_{1/2}$ [hours]	Reference	k_{OH} [cm³/molec/s]	Reference
Acenaphthene	0	0.21	6.68	Lei and Wania (2004)	5,500	550	17,000	Mackay (2001)	6.69E-11	U.S. EPA (2011)
Anthracene	0	0.26	7.73	Lei and Wania (2004)	5,500	550	17,000	Mackay (2001)	4E-11	U.S. EPA (2011)
Phenanthrene	0	0.26	7.73	Lei and Wania (2004)	5,500	550	17,000	Mackay (2001)	1.3E-11	U.S. EPA (2011)
Fluorene	0	0.21	7.0	Lei and Wania (2004)	5,500	550	17,000	Mackay (2001)	8.85E-12	U.S. EPA (2011)
Fluoranthene	0	0.29	8.70	Shunthirasingham et al. (2007)	17,000	1,700	55,000	Mackay (2001)	2.92E-11	U.S. EPA (2011)
Naphthalene	0	0.19	3.35	Lei and Wania (2004)	1,700	170	5,500	Mackay (2001)	2.16E-11	U.S. EPA (2011)
Pyrene	0	0.33	9.42	Lei and Wania (2004)	17,000	1,700	55,000	Mackay (2001)	5E-11	U.S. EPA (2011)
Benzo(a)pyrene	0	0.39	11.8	Lei and Wania (2004)	17,000	1,700	55,000	Mackay (2001)	5E-11	U.S. EPA (2011)
Dibenzothiophene	0	0.16	4.11	Roth et al. (2004)	1,700	550	5,500	Mackay (2001)	8.1E-12	U.S. EPA (2011)
Biphenyl	0	0.13	8.5	Lei and Wania (2004)	550	170	1,700	Mackay (2001)	2.14E-11	U.S. EPA (2011)

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.

2.4   Model Simulations

2.4.1   Polycyclic Aromatic Compounds

The objective of the model simulations was to determine the substance flux to fresh water 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 development scenario, 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 and each development scenario (existing condition, 2012 Base Case, 2012 JME Application Case and 2012 PDC). Where site-specific environmental input parameters were not available, the generic parameters used by Daly and Wania (2004) were used.

2.4.2   Metals

The contribution of snowmelt to freshwater metal concentrations was assessed 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 and each development scenario (existing condition, 2012 Base Case, 2012 JME Application Case and 2012 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 2.4-1). The calculations were completed for one spring melt event, corresponding to the meteorological data for the year 2002, one of the years of data used for the air quality modelling completed for JME. 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, and a value from each zone was used to calculate concentration at the mouth of the Muskeg River.

Figure 2.4-1   *Meteorological and Flow Conditions Used to Estimate Snowmelt Period*
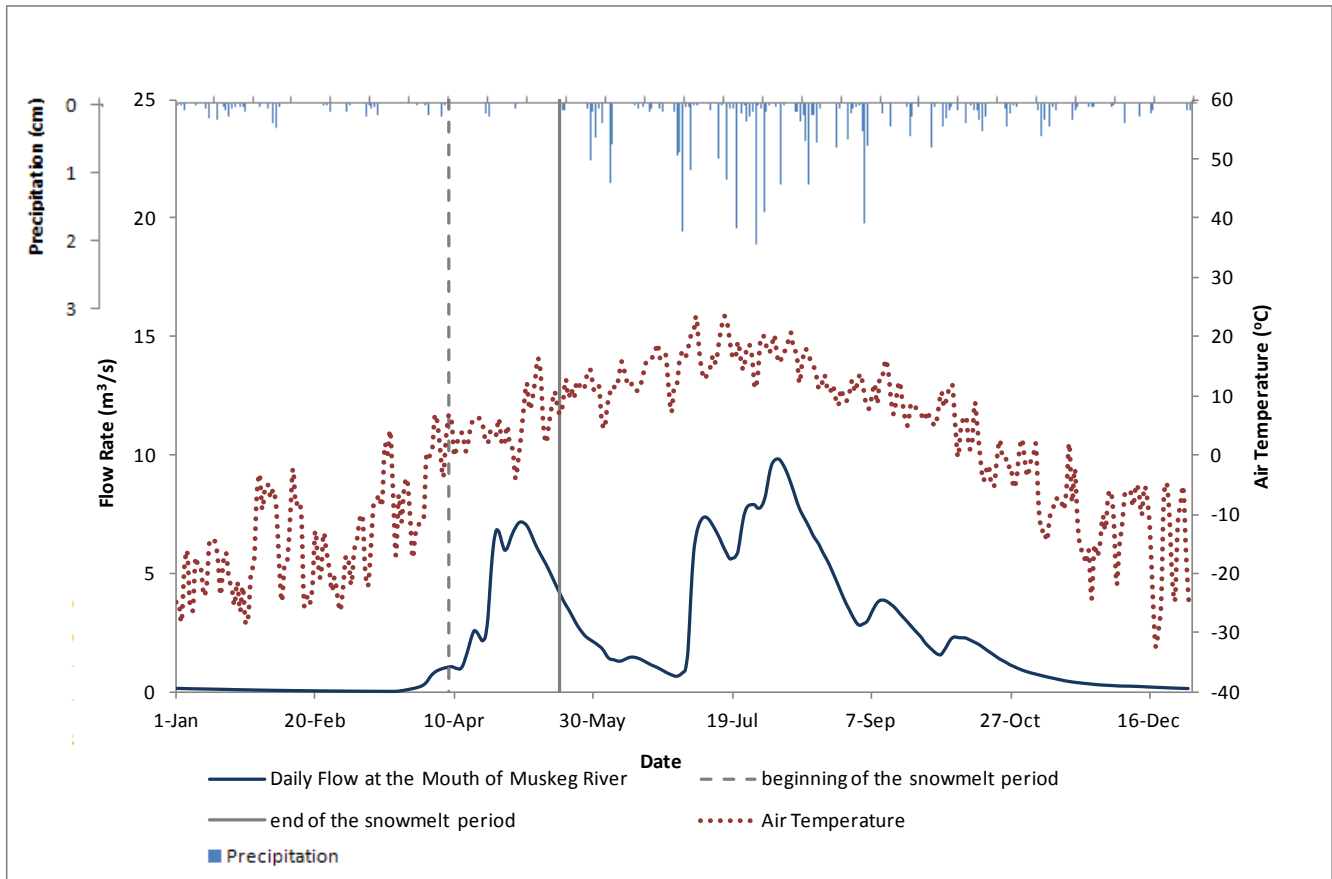
3.0   RESULTS

Under the existing conditions, the incremental concentrations of PACs and metals in snowmelt due to aerial deposition are predicted to be below guidelines, except for cadmium (Table 3-1).

Chromium, cadmium and silver concentrations are predicted to exceed guidelines during the snowmelt period in the 2012 Base Case (Table 3-1). Concentrations of PACs and metals increased from the existing condition to the 2012 Base Case, due to emissions from the approved projects.

The results presented in Table 3-1 for the snowmelt period indicate that the concentrations of metals increased slightly (less than 13%) in the 2012 JME Application Case compared to the 2012 Base Case. The changes in PAC concentrations were negligible. Increases in concentrations were due to the addition of the JME's emissions. The changes in the concentrations were small in this case, because the increased close-circuited area resulted in a smaller depositional area and thus a decreased pathway to receiving waters. In each assessment case, closed-circuited areas were excluded from the areas contributing to surface water concentrations.

The metals and PACs concentrations were generally predicted to increase in the 2012 PDC compared to the 2012 JME Application Case except for manganese, silver, anthracene and fluoranthene. Increases in concentrations were due to addition of planned projects to the 2012 PDC. Decreases in concentrations were most likely due to the combined effects of changes in the different projects' emissions (see Appendix 3.2 of this submission) and an increase in the closed-circuited areas. No additional metals or PAC were predicted to exceed guidelines under the 2012 PDC.

Table 3-1 **Mean Predicted Concentrations of Metals and Polycyclic Aromatic Compounds in Muskeg River Watershed Over the Snowmelt Period, for Existing Condition, 2012 Base Case, 2012 JME Application Case and 2012 PDC**

Parameter	Units	Aquatic Life Guidelines [a, b]		Existing Condition	2012 Base Case	2012 JME Application Case	2012 PDC
		Acute	Chronic				
Metals							
Antimony	µg/L	-	-	0.0086	0.008	0.009	0.0091
Arsenic	µg/L	340	5	0.03	0.049	0.052	0.067
Cadmium	µg/L	3.7	0.4	**0.46**	**2.5**	**2.9**	**2.9**
Chromium	µg/L	16	1	0.92	**1.3**	**1.5**	**1.5**
Copper	µg/L	23	3	0.2	0.6	0.66	0.71
Lead	µg/L	163	6.3	0.19	0.55	0.62	0.64
Manganese	µg/L	-	-	0.37	0.71	0.79	0.78
Molybdenum	µg/L	-	73	0.23	0.33	0.35	0.42
Nickel	µg/L	742	83	1.4	1.5	1.7	1.8
Silver	µg/L	10.3	0.1	0.077	**0.4**	**0.46**	**0.44**
Vanadium	µg/L	-	-	0.72	0.9	1.0	1.1
Zinc	µg/L	190	30	6.5	11.3	12.3	14.1
PACs							
Acenaphthene	µg/L	-	5.8	0.000003	0.000013	0.000014	0.000024
Anthracene	µg/L	-	0.012	0.0000045	0.000044	0.000047	0.000038
Benzo(a)pyrene	µg/L	-	0.015	0.00016	0.00096	0.001	0.0012
Biphenyl	µg/L	-	-	-	0.0000015	0.0000015	0.0000041
Dibenzothiophene	µg/L	-	-	0.0000012	0.0000011	0.0000011	0.0000012
Fluoranthene	µg/L	-	0.04	0.000073	0.0009	0.00097	0.00062
Fluorene	µg/L	-	-	0.000017	0.000058	0.000063	0.00014
Naphthalene	µg/L	-	1.1	0.000086	0.00049	0.00053	0.00062
Phenanthrene	µg/L	-	0.4	0.000045	0.0002	0.00029	0.00034
Pyrene	µg/L	-	0.025	0.00047	0.003	0.0033	0.0039

[a]   - = No guideline / no data.

[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.

4.0   PREDICTION CONFIDENCE

The results presented in this section should be viewed as preliminary, representing an attempt to better understand the impacts of aerial deposition to snowpack and consequently snowmelt water concentrations. The assessment employed the most appropriate modelling framework for the type and amount of data available. The Governments of Alberta and Canada recently conducted snowpack surveys in the Oil Sands Region. Shell will consider aerial deposition when designing detailed aquatic monitoring plans with input from stakeholders and regulators.

Thus, the approach used here to assess PAC and metal deposition is viewed as "developing", given the uncertainties involved. To account for uncertainties, it was conservatively assumed that the transport of all metals associated with interflow to the river occurred without partitioning or settling from the snowpack.

Additionally, the air quality modelling for all assessment cases, except the existing condition, 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 (see Appendix 3.2 of this submission), and they are expected to bias the predictions upwards.

The modelling presented herein indicated that during the snowmelt period, concentrations of cadmium, chromium and silver might exceed the water quality guidelines in the 2012 Base Case, 2012 JME Application Case and 2012 PDC. Cadmium concentrations were predicted to exceed guidelines under existing conditions. 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 4-1 to 4-3. These figures display no discernable '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 as more data become available.   The instream concentrations indicate that the model results are high due to the conservative assumptions mentioned above.

Figure 4-1   *Observed Concentrations of Cadmium (mg/L) in the Muskeg River Watershed (1981 to 2012)*
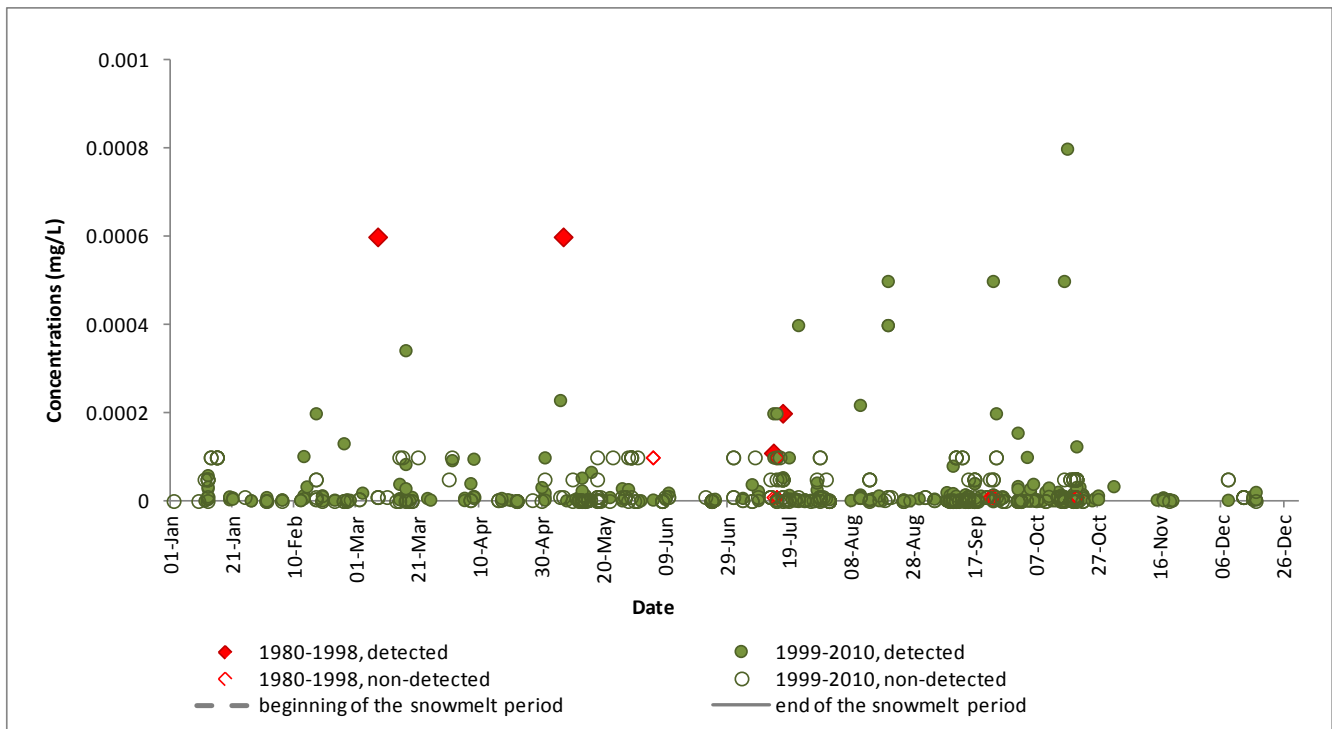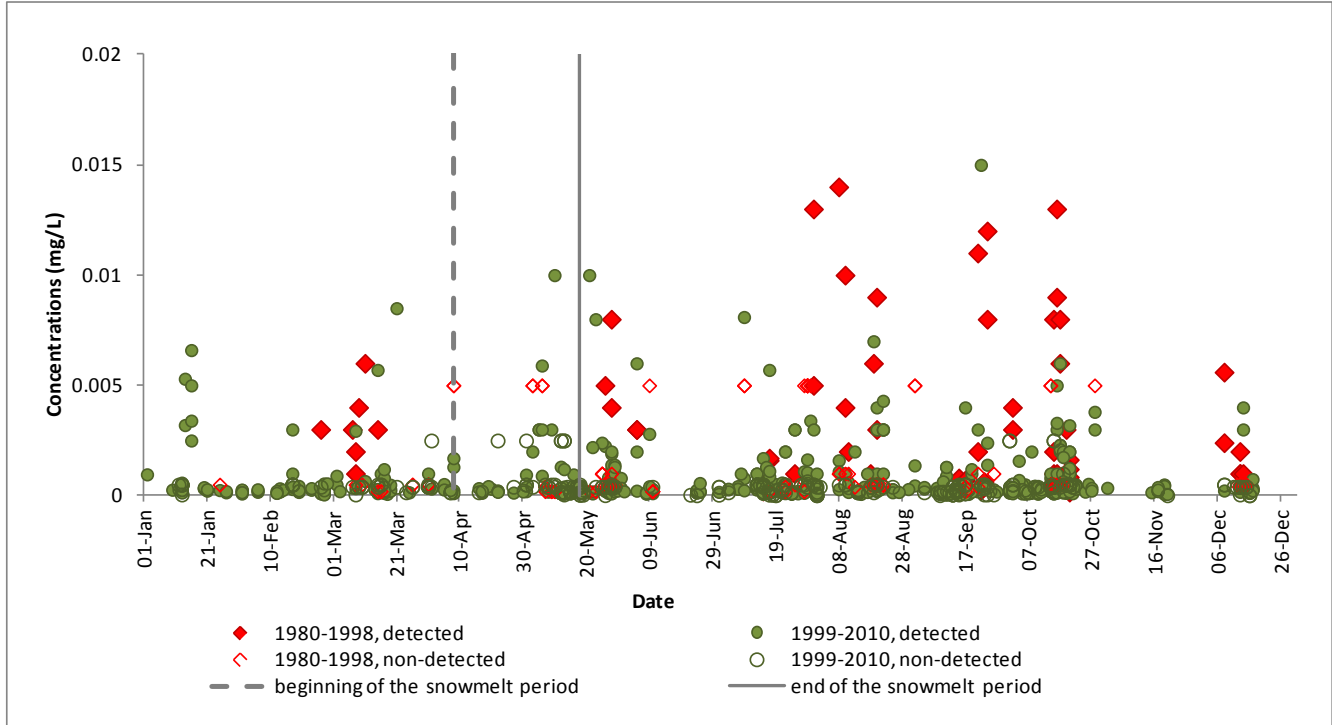

Note: Data presented on the graph are split into two periods to show differences in analytical methods, consistent with the Lower Athabasca Region Surface Water Quality Management Framework (AENV 2011).
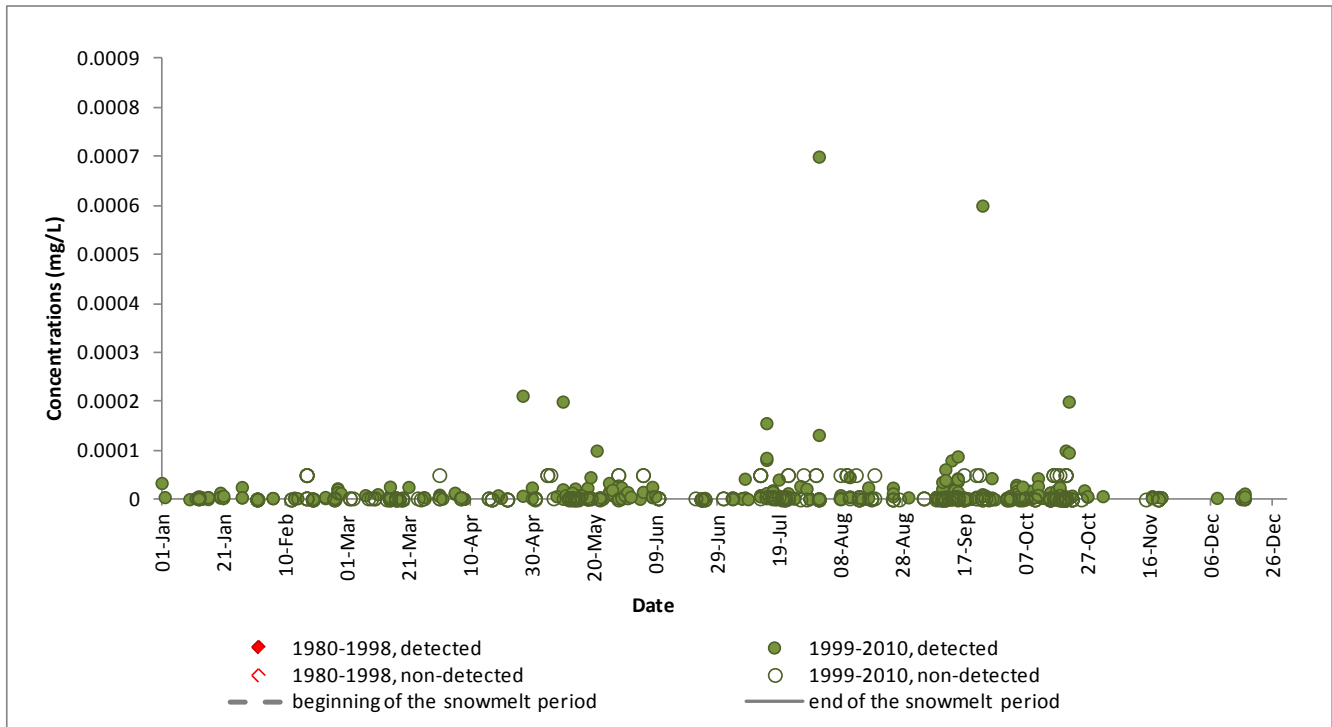
Figure 4-2   *Observed Concentrations of Chromium (mg/L) in the Muskeg River Watershed (1981 to 2012)*

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 4-3   *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).

5.0   SUMMARY

Incremental concentrations of PACs and metals were predicted in receiving surface waters, using the modified CozMo-POP model and a conservative mass-balance approach, respectively. Deposition rates and ambient air concentrations used in these models were estimated by the CALPUFF model (EIA, Volume 3, Appendix 3-8). The results indicated that the concentrations may increase under the 2012 Base Case but are predicted to stay below guidelines for all PACs and metals, except silver, cadmium and chromium. Under the 2012 JME Application Case, concentrations remained the same for PACs but concentrations of metals increased slightly. Under the 2012 PDC, concentrations were generally predicted to increase slightly relative to the 2012 JME Application Case.

The results presented in this appendix should be viewed as preliminary, representing an attempt to better understand the impacts of aerial deposition to snowpack and consequently snowmelt water concentrations. The assessment employed the most appropriate modelling framework for the type and amount of data available. The Governments of Alberta and Canada recently conducted snowpack surveys in the Oil Sands Region. Shell will consider aerial deposition when designing detailed aquatic monitoring plans with input from stakeholders and regulators.

6.0 REFERENCES

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.

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.

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.

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

Domine, F, A. Cabanes, L. Legagneux, Atmos. 2002. *Environ.* 2002, 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.

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., D. Mackay, R. Gillham and W. Y. Shiu.1998. *Environ. Sci. Technol.* 32, 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.

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, Florida.

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, Ontario.

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.

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.Afugacity-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: 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.