APPENDIX D

Environmental Fate and Weathering Models for Hydrocarbons in Intertidal and Subtidal Sediments, and Bioaccumulation of Hydrocarbons by Marine Biota

Table of Contents

APPENDIX D ENVIRONMENTAL FATE AND WEATHERING MODELS FOR HYDROCARBONS IN INTERTIDAL AND SUBTIDAL SEDIMENTS, AND BIOACCUMULATION OF HYDROCARBONS BY MARINE BIOTA

List of Tables

List of Figures

D.1 Introduction

Environmental fate models are often used to simulate the distribution of contaminants of potential concern (COPC) in environmental media (*e.g.,* water, sediment), and can be useful tools in extending available scientific knowledge to predictions of future conditions.

Crude oils are mixtures of many different hydrocarbon compounds. Upon release to the environment, they undergo weathering processes. Weathering refers to the cumulative changes in the composition and characteristics of the hydrocarbon mixtures that result from differential rates of volatilization, solubility, and tendencies to sorb to solids, as well as biodegradation. It includes dispersion in the environment and distribution between environmental media such as air, soil, water and sediment.

As part of the risk assessment for chronic exposure to hydrocarbons, mass balance compartment models were constructed to evaluate the likely fate and weathering of COPC found in crude oil over a period of days to years following a hypothetical release to the marine environment. Mass balance models are based on the fundamental principle that mass can neither be created nor destroyed. They are termed compartment models because they consist of compartments configured to represent COPC in environmental media (*e.g.,* the atmosphere, water, intertidal sediment, and subtidal sediment). The models simulate the transfer of COPC between various environmental compartments, as well as processes of degradation.

Two long-term mass balance compartment models, representing subtidal and intertidal sediment respectively, were developed to provide information required for environmental assessment purposes. The models were designed to use information generated using the SPILLCALC 3-D model (Tetra Tech EBA 2015), which describes the fate and weathering of hydrocarbons as slicks on the surface of the water, as well as the stranding of crude oil on shorelines, and the dissolution or mixing of crude oil as droplets in the upper layers of the water column. The SPILLCALC model operates over a period of hours to a few weeks following the hypothetical hydrocarbon release.

The Subtidal Sediment Quality Model (SSQM) simulates the fate of COPC that are assumed to be deposited to marine sediment below the low tide mark, following a hypothetical oil release. The Intertidal Sediment Quality Model (ISQM) simulates the fate of COPC stranded on intertidal sediment beginning days following a hypothetical release, and extending forward in time for up to two years.

The SSQM and ISQM are used to calculate concentrations of 17 pseudocomponents and 83 individual compounds, including 49 polycyclic aromatic hydrocarbons (PAHs) (including both parents and alkylated species) in subtidal and intertidal sediment, as a function of time. These data are used directly and through subsequent calculations to estimate the concentrations of COPC in the tissues of marine biota. These calculated tissue concentrations support the EHHRA for chronic exposure of humans as well as marine birds and mammals to the COPC. By simulating the relative volatility, solubility, sorption potential and biodegradation of the individual COPC, the models also account for the weathering of the hydrocarbon mixtures. Both models were implemented using the commercially available software Stella® version 8.1.1.

The Stella® modelling framework offers a mass balance modelling system that allows the construction of models using four basic components:

- *Stocks*, compartments that hold and account for mass (COPC);
- *Flows*, links between compartments that act as valves, and allow mass (COPC) to be transferred between compartments at rates that are specified by controlling equations;
- *Converters*, generally parameters or variables that are entered into the model in order to support equations, and calculate flows between stocks; and
- *Connecters*, arrows that provide links between stocks, flows and converters, and allow equations describing the transfer of mass or other calculations to be implemented and performed.

The individual Subtidal and Intertidal Sediment Quality Models were based on published models and concepts describing the behavior and fate of environmental contaminants, as documented in the following sections.

D.2 Subtidal Sediment Quality Model (SSQM) for Hydrocarbon Spills

A simple conceptual model was developed to describe the fate of hydrocarbons deposited to subtidal sediments in the Bay of Fundy.

D.2.1 Conceptual Model of Hydrocarbon Fate and Bioaccumulation in Subtidal Sediments of the Bay of Fundy

Miller (1966) studied the suspended sediment system of the Bay of Fundy. He wrote that:

> "*The bottom sediments [of the Bay of Fundy] may be divided into three types: reworked sand and gravel; intact glacial sediments; and recently deposited sand, silt, and clay. The mineralogy of these sediments is very similar to that observed in the suspended sediments.*
>
> *The coastal morphology is the result of marine erosion in an area of bedrock control. Basalt and other well-lithified rock units form the coastline in the main portion of the Bay, while moderately and poorly consolidated sediments make up much of the coastline in the upper portions of the Bay.*
>
> *Coastal erosion, which proceeds at a rate of more than 6 feet (1.8 m) per year in some parts of the Bay, is the main source for the detrital suspended sediments, with most of the sediment originating in Chignecto Bay and in the Minas Basin. Bottom erosion and fluvial discharge contribute minor quantities of material to the system.*
>
> *Highly turbid water from Chignecto Bay and the Minas Basin mixes with less turbid water in the main Bay, and is gradually moved along the New Brunswick shore toward the mouth of the Bay. Much of the material settles to the bottom during periods of slack water, but most if it is resuspended during ensuing periods of wave and/or tidal action.*

> *A certain percentage of the suspended sediment load is permanently deposited in the Minas Basin, Chignecto Bay, and along the New Brunswick side of the main Bay. Shallow seismic work has shown that more than 40 meters (131.2 ft) of post Pleistocene sediment is present in parts of Chignecto Bay and along much of the New Brunswick side of the main Bay. Similar thicknesses of post Pleistocene sediment are also present at the mouth of the main Bay and in portions of the Gulf of Maine.*
>
> *Suspended sediment concentrations, temperature and salinity distributions, residual current patterns, drift bottle data, bottom (sea bed) drifter data, heavy mineral assemblages, bottom sediment colour, and the pattern of post Pleistocene deposition, indicate that there is a slight net movement of sediment out of the Bay of Fundy and into the Gulf of Maine*".

Miller (1966) also wrote that:

> "*Suspended sediment concentration had an average about 6.6 mg per liter, with values ranging from 0.2 to 30.4 mg per liter. Sediment concentration increased from the mouth to the head of the Bay, from the Nova Scotia side to the New Brunswick side of the Bay, and generally with increasing depth in the water column.*
>
> *The suspended load was composed of sand, silt, clay, micro-fauna, and organic film and debris, with silt and organic debris being the major constituents. Organic carbon made up 0.3 – 2.65 percent of the suspended materials*".

Fader (2005) wrote that

> "*Miller characterized the suspended sediment system in the Bay of Fundy as an open system. He interpreted 4 components of the system: 1) an oscillating body of turbid water, 2) a seabed that exchanges sediment with the overlying water, 3) minor fresh turbid water input and, 4) minor turbid water release to the Gulf of Maine. He expressed the northwest nearshore zone as a mud facies in a state of short-term equilibrium with the overlying water. Seabed sampling at slack water revealed thin layers of fluid mud that appeared to have settled out on the seabed.*

The potential for hydrocarbon residues to contaminate bottom sediments in the Bay of Fundy are therefore conceptualized as follows.

1. Any crude oil remaining in the water column (as dissolved, entrained or submerged oil), or on the surface of the water at the end of the model simulation, is conservatively assumed to be deposited directly to the bottom sediment below.
2. The deposited hydrocarbons are assumed to be associated with mobile sediment that is predominantly silty with high water content (90% by volume). The sediment solid fraction has an assumed dry bulk density of 2.65 g/cm^3, and has a detrital organic carbon content of approximately 2 percent of sediment dry weight. Assuming a salinity value for the sediment pore water of about 32 parts per thousand (typical of coastal seawater), the density of the wet bulk sediment is estimated to be approximately 1.1938 g/cm^3.
3. Hydrocarbons associated with the mobile sediment are subject to re-suspension and dispersion with tidal water movements, and do not become buried by subsequently deposited sediments.

4. Contact between crude oil or hydrocarbon residues, and sediment in the presence of oxygen is known to facilitate microbial degradation of the hydrocarbons, and therefore the long-term fate of such hydrocarbons is to be degraded. Residual hydrocarbons that are not readily degraded (*e.g.,* asphaltenes) are considered to have negligible bioavailability or toxicity.
5. Bioaccumulation of hydrocarbon residues from sediment to sediment-associated biota (*e.g.,* demersal fish, mollusks and crustaceans) about four weeks following a hypothetical crude oil spill is conservatively simulated by assuming steady-state accumulation based upon a Biota-Sediment Accumulation Factor (BSAF). As a result of biodegradation of bioavailable hydrocarbon residues in contact with sediment, as well as dispersion and dilution of such residues into the broader Gulf of Maine, bioaccumulation of hydrocarbon residues by sediment-associated biota is assumed to be negligible within one to two years of the hypothetical oil spill accident.

D.2.2 Predicted Hydrocarbon Concentrations in Subtidal Sediments of the Bay of Fundy

Based upon the conceptual model described in the previous section, the model to predict the hydrocarbon concentrations in the subtidal sediments of the Bay of Fundy is very simple. The bioavailable hydrocarbons are assumed to be those represented by the following pseudocomponents: VOL, AR1 to AR7 and AL1 to AL3. The remaining pseudocomponents are assumed to have negligible bioavailability and toxicity.

The mass of bioavailable hydrocarbons (as 11 of the 17 pseudocomponents and including up to 83 individual compounds, of which about 50 are parent or alkylated PAH compounds) is calculated by summing the mass (g) of hydrocarbon constituents (as total hydrocarbons and as total PAHs) present within each water grid cell of the oil spill fate and transport model (SPILLCALC 3-D, Tetra Tech EBA 2015) at the end of the simulation period. Specifically, this includes hydrocarbons present on the surface of the water, and in any of the water layers represented that lie beneath the surface of the water. This mass of hydrocarbons is transformed into a depositional flux (g/m^2) by dividing the mass by the area of the grid cell (m^2).

The bottom sediment is represented as a thin (1-cm) layer of silt having a high water content (90% water content with a salinity of 32 parts per thousand) that is temporarily deposited during periods of slack tide. This sediment layer is assumed to have a bulk (wet) density of 1.1938 g/cm^3, and a dry mass of 0.265 g/cm^2. Therefore, the sediment dry mass can also be defined as being equal to 2.65 kg/m^2.

The hydrocarbon concentration in the mobile sediment layer (g/kg dry weight) is therefore equal to the assumed downward flux (g/m^2) divided by the mass of dry sediment on the bottom (2.65 kg/m^2).

D.3 Intertidal Sediment Quality Model for Hydrocarbon Spills

The ISQM simulates the fate of COPC in intertidal sediment over a period of days to years following a hypothetical hydrocarbon release. The key input to the ISQM, from the SPILLCALC 3-D model (Tetra Tech EBA 2015) is the loading (g/m^2) of hydrocarbons onto intertidal sediment. This hydrocarbon is represented as a slightly weathered version of the fresh crude oil released during the hypothetical spill scenarios.

The SPILLCALC 3-D model provides estimated hydrocarbon deposition to intertidal sediment for each shoreline segment within the study area. The shoreline segment information includes site-specific details of substrate type, from which the total crude oil holding capacity (i.e., what mass of crude oil can be retained per square metre of intertidal habitat) can be estimated. The average loading of slightly weathered hydrocarbon (g/m^2), as predicted by the SPILLCALC 3-D model, was assumed to be stranded on intertidal sediments within each segment.

The ISQM was used to predict the fate and chemical fingerprint of the stranded hydrocarbon at time points of four weeks and one to two years following the deposition event, using a time step (dt) of 30 minutes. The ISQM is a single-compartment mass balance model, simultaneously representing the mass of 17 pseudocomponents and up to 83 individual compounds (of which 49 are PAH compounds) in the intertidal sediment. The concentration of each COPC in the intertidal sediment is calculated by dividing the mass of COPC incorporated into the intertidal sediment by the mass of the affected intertidal sediment.

A conceptual ISQM representing the intertidal sediment compartment and fluxes of COPC is presented in Figure D-1. Note that the majority of model converters and connecters are not shown in Figure D-1 in order to reduce visual complexity.

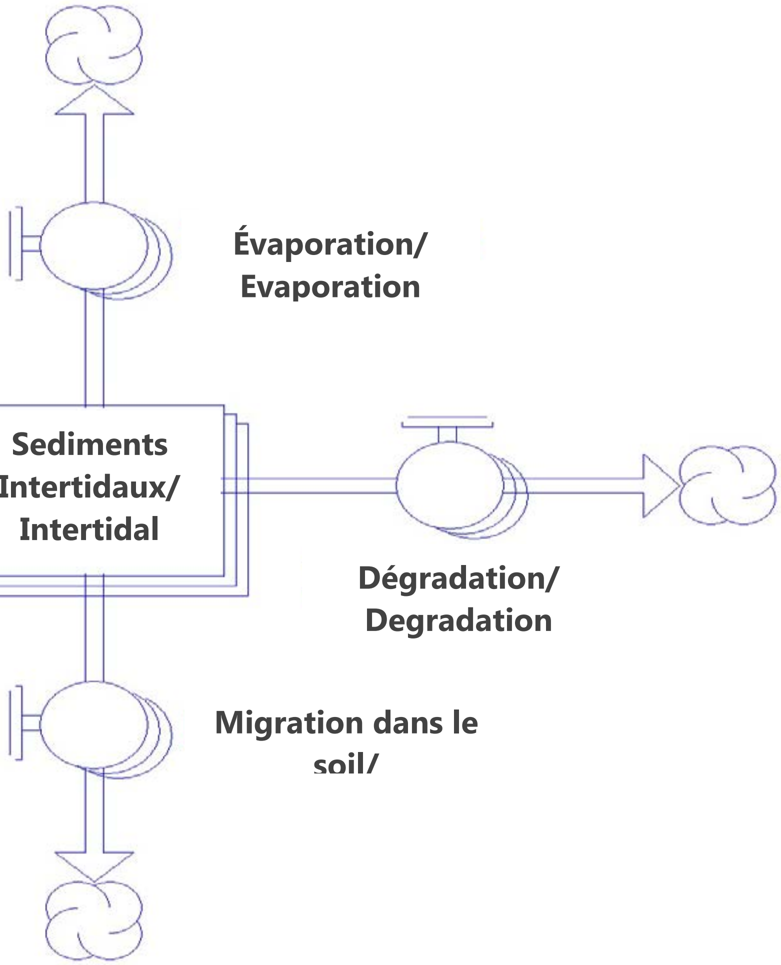

Figure D-1 Intertidal Sediment Quality Model Conceptual Diagram

D.3.1 Principal Model Processes

Three primary processes are responsible for driving the flow of mass (weathering of COPC) in the ISQM:

1. evaporation of individual COPC to the atmosphere;
2. dissolution and downward transport (flushing) of individual COPC stranded on intertidal sediment; and
3. microbial degradation of individual COPC stranded on intertidal sediment.

The physical, chemical and toxicological properties of the spilled hydrocarbon mixture evolve over time, in response to the weathering of the spilled mixture (*i.e.,* loss of volatile or soluble hydrocarbon fractions from the original mixture).

The ISQM was developed based upon an assumption that substrate temperatures are moderate (10°C, representing a typical annual average daily temperature for coastal areas of the Bay of Fundy) throughout the model run. It was assumed that the intertidal zone of the Bay of Fundy will rarely be exposed to freezing. As a result of this assumption, and considering that an accidental oil spill could occur at any time of the year, the characteristics of the residual oil on intertidal sediment after 52 weeks of weathering in the model are in reality more representative of the likely characteristics of the oil after two summers of weathering, or one to two years following a hypothetical spill.

EVAPORATION OF HYDROCARBON STRANDED ON INTERTIDAL SEDIMENT TO THE ATMOSPHERE

The evaporation rate of a mixture of hydrocarbons to the atmosphere is due to the evaporation of its individual components as dictated by their respective volatility, typically expressed using vapour pressure values. The stranded hydrocarbon mixture considered here is composed of many individual components, possessing a wide range of physicochemical properties including volatility. For example, benzene is highly volatile (vapour pressure = 12,700 Pa; Mackay *et al.* 2000) whereas the higher TPH fractions (*e.g.,* the higher aliphatic pseudocomponents, resins and asphaltenes) are typically considered non-volatile. Relatively volatile components may be expected to readily evaporate, whereas components with low vapour pressures are not expected to evaporate in appreciable amounts.

The evaporation rate of individual COPC was determined using equations provided by Schwarzenbach *et al.* (2002) to estimate the evaporation rates of pure organic liquids. These equations were adapted to units used in the ISQM and adjusted according to the partial vapour pressure of each COPC within the stranded hydrocarbon. As such, the evaporation rate (g/d) of each COPC was calculated as:

$$\text{Evaporation rate} = A \cdot v_a \cdot C_{ia}$$

where for component i:

A = unitized area of intertidal sediment containing the stranded hydrocarbon (1 m^2);

v_a = vertical evaporation velocity (m/d); and

C_{ia} = equilibrium air phase concentration (g/m^3) immediately above the stranded hydrocarbon.

The vertical evaporation velocity was assumed to equal that of water vapour since both transfers are mainly wind driven physical processes. The water vapour velocity (v_a; cm/s) was calculated using an empirical relationship between wind velocity and the air-phase transfer velocity as provided by Schwarzenbach *et al.* (2002, Table 20.1):

$$v_a = 0.15\ u_{10}$$

where u_{10} is the wind speed (m/s) measured 10 m above the water surface.

The equilibrium air phase concentration of each COPC at the interface immediately above the intertidal sediment was determined using the ideal gas law as:

$$C_{ia} = (MW_i \cdot P_{ia}) / RT$$

where for component i:

MW_i = molecular weight of hydrocarbon fraction i (g/mol);

P_{ia} = partial vapour pressure of hydrocarbon fraction i (Pa);

R = universal gas constant (8.31451 $Pa \cdot m^3/mol \cdot K$); and

T = temperature (K).

As the vapour pressure of an organic compound is affected by the presence of other components within a mixture, the partial vapour pressure of each COPC was used, as described by Raoult's law (Schwarzenbach *et al.* 2002):

$$P_i = x_i \cdot P_L$$

where for component i:

P_i = partial vapour pressure (Pa);

x_i = molar fraction (# moles within the hydrocarbon / total moles of all components in the hydrocarbon); and

P_L = pure liquid vapour pressure (Pa).

Liquid vapour pressure is needed for this approach because Raoult's law is applied to a liquid mixture. Additionally, as required by Raoult's law, the hydrocarbon mixture described is assumed to follow ideal behavior (Peters *et al.* 1999; Schwarzenbach *et al.* 2002; Sterling *et al.* 2003; Di Toro *et al.* 2007). When COPC-specific liquid vapour pressure was not available, liquid vapour pressure for a similar (surrogate) compound was used.

DISSOLUTION AND FLUSHING OF HYDROCARBON STRANDED ON INTERTIDAL SEDIMENT

The dissolution of a mixture in water is controlled by the dissolution of its individual components as dictated by their respective aqueous solubility. The stranded crude oil considered here is composed of many individual components, each having its own physicochemical properties including aqueous solubility. Aqueous solubility values define the maximum dissolved concentrations in water (Schwarzenbach *et al.* 2002). If the concentration of an organic COPC in water is higher than the reported solubility, then dissolved and undissolved forms may be present.

The aqueous solubility of each individual component of the hydrocarbon mixture has important implications for its environmental behavior. Hydrocarbons that are truly dissolved demonstrate higher mobility and bioavailability than hydrocarbons that are present in droplet form, or sorbed to particles (Schwarzenbach *et al.* 2002). Furthermore, a compound demonstrating high aqueous solubility may also exhibit higher toxic potential as the toxicity potential can be linked not only to its inherent toxicity, but also to the dissolved aqueous concentration (Peters *et al.* 1999; Di Toro *et al.* 2007).

Flushing is linked to the characteristics of the environmental medium and in general, flow through a coarse porous medium (*e.g.,* gravel) is expected to be higher than flow through a finer porous medium (*e.g.,* sand or silt). For marine and estuarine environments, tidal flushing is an important process. Other processes that potentially affect flushing, such as snow cover or frozen ground conditions which would limit water infiltration and flushing, are not considered as part of this evaluation. Dissolution and flushing of hydrocarbons stranded on intertidal sediment were considered simultaneously and termed leaching. The leaching rate (g/d) of hydrocarbon stranded on intertidal sediment was calculated as:

$$\text{Leaching rate} = C_{Fi} \cdot V_{flushing}$$

where for component i:

C_{Fi} = concentration (g/m^3) of COPC dissolved in water flushing out of intertidal sediment; and

$V_{flushing}$ = daily flushing volume (m^3/d).

The concentration of COPC dissolved in water flushing out intertidal sediment was calculated according to the equation:

$$C_{Fi} = C_{Ei} \cdot e^{K \cdot tw}$$

where for component i:

C_{Ei} = effective aqueous solubility (g/m^3);

K = mass transfer rate coefficient (1/d); and

t_w = water residence time (d) through the affected intertidal sediment.

The solubility of an organic compound depends on its presence either in pure form or within a mixture. When present in pure form, the maximum dissolved concentration will be that of its aqueous solubility. However, when present within a mixture (as is the case for the oil types under consideration in the EHHRA) the effective aqueous solubility (C_{Ei}) of each organic component is modified by the presence of other components as described by Raoult's law (Peters *et al.* 1999; Schwarzenbach *et al.* 2002; Sterling *et al.* 2003; Di Toro *et al.* 2007):

$$C_{Ei} = MW_i \cdot x_i \cdot C_{Li}$$

where for component i:

MW_i = molecular weight (g/mol);

x_i = molar fraction (# moles within the hydrocarbon / total moles of all components in the hydrocarbon); and

C_{Li} = subcooled liquid solubility (mol/m^3).

The effective aqueous solubility (expressed in g/m^3 through a molecular weight conversion) is related to the aqueous solubility of the pure organic compound (C_L) and the amount found within the mixture on a molar basis (x_i). If a constituent is present in pure form, then its molar fraction is 1 and its effective aqueous solubility equals the reported solubility. As compounds are mixed together, the molar fraction of each constituent decreases, and the effective solubility of individual constituents also decreases. As a result, a compound with a relatively high aqueous solubility may have a low effective solubility if present in very small amount within the mixture (Peters *et al.* 1999; Sterling *et al.* 2003; Di Toro *et al.* 2007). The subcooled liquid solubility is needed for this approach because the components found within the mixture are liquids. As before, the application of Raoult's law requires the assumption of ideal behavior within the mixture (Peters *et al.* 1999; Sterling *et al.* 2003; Di Toro *et al.* 2007).

The organic phase (*i.e.,* mixture) to aqueous phase mass transfer rate coefficient (K; 1/d) is calculated according to Clement *et al.* (2004):

$$K = Sh \cdot D_{mi} / (d_{50}^2)$$

where for component i:

Sh = Sherwood number (dimensionless);

D_{mi} = molecular diffusivity (m^2/d); and

d_{50} = median grain diameter (m) of intertidal sediment.

For this model the relationship developed by Powers *et al.* (1994) is used to calculate the Sherwood number. The relationship is (Equation 5a – Powers *et al.* 1994):

$$Sh = 77.6 \cdot Re^{0.658}$$

where:

Re = Reynolds number (dimensionless).

The Reynolds number was calculated according to Clement *et al.* (2004) as:

$$Re = v_{inf} \cdot \rho_W \cdot d_{50} / \mu_W$$

where:

v_{inf} = infiltration velocity of water (m/d);

ρ_W = density of water (g/m^3); and

μ_W = dynamic viscosity of water (g/m·d).

The water residence time (t_w; d) through the affected intertidal sediment was calculated according to:

$$t_w = D / v_{inf}$$

where:

D = depth of impacted intertidal sediment (m); and

v_{inf} = infiltration velocity of water (m/d).

The depth of the affected intertidal sediment was based upon a sand and gravel beach type, and was assumed to be 0.05 m (5 cm). The water infiltration velocity was 20 cm/d, based on the assumption that the affected layer would be flooded or drained by the rising and falling tide four times each day.

DEGRADATION

Hydrocarbons degrade over time in the environment due to physical, chemical and microbial processes (Leahy and Colwell 1990). Certain COPC (*e.g.,* high molecular weight PAHs) may persist for long periods of time, whereas others (*e.g.,* low molecular weight hydrocarbons such as benzene) degrade more rapidly.

The degradation rate of a compound in an environmental medium is typically expressed as the chemical's half-life, which is the time required for 50% of the initial mass of COPC to degrade. Values expressed in units of days were used so as to maintain unit consistency within the model.

Half-lives can be converted to decay constants (k, 1/d) to evaluate the residual concentrations of COPC in intertidal sediment. Assuming that the degradation follows first-order kinetics (typical for degradation reactions), then the half-life may be converted to a decay constant using the equation:

$$k = 0.693 / \text{half-life}.$$

The decay constant is used in the following exponential decay function to model the remaining mass of chemical over time:

$$M(t) = M \cdot e^{-kt}$$

where:

M(t) = the amount (mass) of COPC at time t;

M = the initial mass of COPC at time 0;

e = the base of natural logarithms (approximately 2.71828);

k = the decay constant (1/d); and

t = the amount of time elapsed (days).

D.3.2 Additional Parameter Values Used in the Intertidal Sediment Quality Model

VAPOUR PRESSURE

Vapour pressures of individual COPC were generally obtained from Mackay *et al.* (2000), Gustafson *et al.* (1997), USNLM (n.d.), and RCS (2015) in order of preference. Petroleum hydrocarbon fraction F4 ($>C_{34}$-C_{50}), polars/resins, and asphaltenes were assumed to exhibit negligible vapour pressure. Vapour pressures of individual COPC are presented in Table D-1.

SUB-COOLED LIQUID SOLUBILITY

Sub-cooled liquid solubilities of individual COPC were calculated according to Di Toro (2007) and are presented in Table D-1.

LEBAS MOLAR VOLUME AND MOLECULAR DIFFUSIVITY

The LeBas molar volume was generally obtained from Mackay *et al.* (2000). When a LeBas molar volume could not be found, it was calculated as described in Mackay *et al.* (2000). LeBas molar volumes and molecular diffusivity values of individual COPC are presented in Table D-1.

The molecular diffusivity (D_m), expressed in m^2/d, is a constant relating a concentration gradient to a diffusive flux. The molecular diffusivity of each COPC was calculated according to (USEPA 2015):

$$D_m = \quad [\ 13.26 \times 10^{-5} / \mu_w\ 1.14\ V_B\ ^{0.589}\ ] \cdot [\ 60 \cdot 60 \cdot 24 / 100 \cdot 100\ ]$$

where:

μ_w = dynamic viscosity of water (g/m-s) assumed 1.308 g/m-s for water temperature of 10°C (ThermExcel 2003); and

V_B = LeBas molar volume (cm^3/mol).

***D*EGRADATION *H*ALF-*L*IVES**

Half-lives of individual COPC in soil were assumed to be representative of half-lives in intertidal sediment. When COPC-specific half-lives could not be found, half-lives for a similar (surrogate) compound were used. Half-lives of individual COPC were generally obtained from Mackay *et al.* (2000). Half-lives used in the ISQM are presented in Table D-1. Following the approaches described here, the hydrocarbon concentrations in intertidal sediments are predicted for times of four weeks and one to two years following a hypothetical crude oil spill.

Table D-1 COPC-Specific Properties Used in the Intertidal Sediment Quality Model

COPC	Liquid Vapour Pressure P_L (Pa)	Sub-cooled Liquid Solubility C_L (mol/m³)	LeBas Molar Volume V_B (cm³/mol)	Molecular Diffusivity D_m (m²/d)	Soil Mean Half Life t½ (d)	Representative Surrogate(s) (if applicable)
Benzene	1.3E+04	1.6E+01	9.6E+01	5.7E-05	5.5E+02	---
Toluene	3.8E+03	3.8E+00	1.2E+02	5.1E-05	1.7E+03	---
Ethylbenzene	1.3E+03	1.3E+00	1.4E+02	4.6E-05	1.7E+03	---
Xylenes	1.1E+03	1.1E+00	1.4E+02	4.6E-05	1.7E+03	---
Ethane	4.2E+06	3.5E+01	5.2E+01	8.2E-05	1.7E+03	---
Propane	9.5E+05	8.8E+00	7.4E+01	6.7E-05	1.7E+03	---
Isobutane	3.6E+05	2.9E+00	9.6E+01	5.7E-05	1.7E+03	---
n-Butane	2.4E+05	2.2E+00	9.6E+01	5.7E-05	1.7E+03	---
Isopentane	9.2E+04	1.0E+01	1.2E+02	5.1E-05	1.7E+03	---
n-Pentane	6.8E+04	5.6E-01	1.2E+02	5.1E-05	1.7E+03	---
>C_8-C_{10} Aromatic	6.4E+02	3.9E-01	1.6E+02	4.2E-05	1.7E+03	1,2,4-trimethylbenzene
>C_{10}-C_{12} Aromatic	6.4E+01	2.3E-01	1.7E+02	4.2E-05	5.5E+03	Acenaphthylene
>C_{12}-C_{16} Aromatic	4.9E+00	1.1E-01	2.0E+02	3.7E-05	5.5E+03	Phenanthrene
>C_{16}-C_{21} Aromatic	1.1E-01	3.1E-02	2.5E+02	3.3E-05	1.7E+04	Benzo(a)anthracene
>C_{21}-C_{34} Aromatic	4.5E-05	3.2E-03	3.0E+02	2.9E-05	1.7E+04	Dibenzo(a,h)anthracene
C_6-C_8 Aliphatic	6.4E+03	1.4E-01	1.9E+02	3.9E-05	1.7E+03	n-octane
>C_8-C_{10} Aliphatic	6.4E+02	1.4E-02	2.3E+02	3.4E-05	1.7E+03	n-decane
>C_{10}-C_{12} Aliphatic	6.4E+01	1.5E-03	2.7E+02	3.1E-05	1.7E+03	n-dodecane

Table D-1 COPC-Specific Properties Used in the Intertidal Sediment Quality Model

COPC	Liquid Vapour Pressure P_L (Pa)	Sub-cooled Liquid Solubility C_L (mol/m³)	LeBas Molar Volume V_B (cm³/mol)	Molecular Diffusivity D_m (m²/d)	Soil Mean Half Life t½ (d)	Representative Surrogate(s) (if applicable)
$>C_{12}$-C_{16} Aliphatic	4.9E+00	5.5E-05	3.6E+02	2.6E-05	1.7E+03	n-C16
$>C_{16}$-C_{21} Aliphatic	1.1E-01	2.7E-07	4.7E+02	2.2E-05	1.7E+03	n-C21
$>C_{21}$-C_{34} Aliphatic	7.0E-05	6.3E-12	7.2E+02	1.8E-05	5.5E+03	n-C32
F4 (C_{34}-C_{50} Hydrocarbons)	1.0E-10	5.2E-15	6.8E+02	1.8E-05	1.0E+06	n-C40 and circumpyrene
Polars	1.0E-10	9.5E-08	6.2E+02	1.9E-05	1.0E+06	---
Asphaltenes	1.0E-10	3.2E-16	1.5E+03	1.1E-05	1.0E+06	---
Acenaphthene	1.5E+00	1.7E-01	1.7E+02	4.1E-05	5.5E+03	---
C1-Acenaphthene	6.0E-01	3.3E-02	2.0E+02	3.8E-05	5.5E+03	1-methylacenaphthene
Acenaphthylene	4.1E+00	1.4E-01	1.7E+02	4.2E-05	5.5E+03	---
Acridine	4.5E-02	6.3E-01	2.0E+02	3.8E-05	5.5E+03	---
Anthracene	7.8E-02	3.5E-02	2.0E+02	3.8E-05	5.5E+03	---
Benzo(a)anthracene	6.1E-04	1.1E-03	2.5E+02	3.3E-05	1.7E+04	---
Benzo(b&j)fluoranthene	6.7E-05	1.4E-03	2.7E+02	3.1E-05	1.7E+04	---
Benzo(k)fluoranthene	4.1E-06	8.7E-04	2.7E+02	3.1E-05	1.7E+04	---
Benzo(g,h,i)perylene	2.3E-05	2.5E-04	2.8E+02	3.1E-05	1.7E+04	---
Benzo(a)pyrene	2.1E-05	7.9E-04	2.6E+02	3.2E-05	1.7E+04	---
Benzo(e)pyrene	2.4E-05	2.9E-04	2.6E+02	3.2E-05	1.7E+04	---
Chrysene	1.1E-04	2.4E-03	2.5E+02	3.3E-05	1.7E+04	---

Table D-1 COPC-Specific Properties Used in the Intertidal Sediment Quality Model

COPC	Liquid Vapour Pressure P_L (Pa)	Sub-cooled Liquid Solubility C_L (mol/m³)	LeBas Molar Volume V_B (cm³/mol)	Molecular Diffusivity D_m (m²/d)	Soil Mean Half Life t½ (d)	Representative Surrogate(s) (if applicable)
Dibenzo(a,h)anthracene	9.2E-08	1.3E-04	3.0E+02	2.9E-05	1.7E+04	---
Fluoranthene	8.7E-03	6.3E-03	2.2E+02	3.5E-05	1.7E+04	---
Fluorene	7.2E-01	8.7E-02	1.9E+02	3.9E-05	5.5E+03	---
C1-fluorene	2.0E-01	5.6E-02	2.1E+02	3.6E-05	5.5E+03	2-methylfluorene
C2-fluorene	2.1E-01	1.4E-02	2.3E+02	3.4E-05	5.5E+03	2-ethylfluorene
C3-fluorene	4.5E-02	7.2E-03	2.5E+02	3.2E-05	5.5E+03	3-propylfluorene
Indeno(1,2,3-cd)pyrene	9.2E-08	1.5E-04	2.8E+02	3.0E-05	1.7E+04	---
Naphthalene	3.7E+01	6.8E-01	1.5E+02	4.5E-05	1.7E+03	---
C1-Naphthalene	1.0E+01	1.9E-01	1.7E+02	4.1E-05	1.7E+03	2-methylnaphthalene
C2-Naphthalene	4.2E+00	4.9E-02	1.9E+02	3.8E-05	1.7E+03	2-ethylnaphthalene
C3-Naphthalene	6.4E-01	2.3E-02	2.1E+02	3.6E-05	1.7E+03	2-propylnaphthalene
C4-Naphthalene	2.9E-01	6.4E-03	2.4E+02	3.4E-05	1.7E+03	2-butylnaphthalene
Phenanthrene	1.1E-01	3.3E-02	2.0E+02	3.7E-05	5.5E+03	---
Perylene	2.0E-04	4.6E-04	2.7E+02	3.2E-05	1.7E+04	---
Pyrene	1.2E-02	7.0E-03	2.1E+02	3.6E-05	1.7E+04	---
Biphenyl	3.7E+00	1.8E-01	1.9E+02	3.9E-05	5.5E+02	---
C1-biphenyl	1.4E+00	4.3E-02	2.1E+02	3.6E-05	5.5E+02	4-methylbiphenyl
C2-biphenyl	2.8E-01	1.3E-02	2.3E+02	3.4E-05	5.5E+02	4,4’-dimethylbiphenyl

Table D-1 COPC-Specific Properties Used in the Intertidal Sediment Quality Model

COPC	Liquid Vapour Pressure P_L (Pa)	Sub-cooled Liquid Solubility C_L (mol/m³)	LeBas Molar Volume V_B (cm³/mol)	Molecular Diffusivity D_m (m²/d)	Soil Mean Half Life t½ (d)	Representative Surrogate(s) (if applicable)
Dibenzothiophene	1.0E-01	5.3E-02	1.9E+02	3.8E-05	5.5E+03	---
C1-dibenzothiophene	5.0E-02	1.6E-02	2.1E+02	3.6E-05	5.5E+03	4-methyldibenzothiophene
C2-dibenzothiophene	2.2E-02	4.6E-03	2.4E+02	3.4E-05	5.5E+03	4-ethyldibenzothiophene
C3-dibenzothiophene	1.4E-02	1.2E-03	2.6E+02	3.2E-05	5.5E+03	4-propyldibenzothiophene
C4-dibenzothiophene	5.2E-03	3.0E-04	2.8E+02	3.1E-05	5.5E+03	4-butyldibenzothiophene
C1-phenanthrene/anthracene	2.9E-02	1.1E-02	2.2E+02	3.5E-05	5.5E+03	9-methylphenanthrene 9-methylanthracene
C2-phenanthrene/anthracene	1.6E-02	3.6E-03	2.4E+02	3.3E-05	5.5E+03	9-ethylphenanthrene 9,10-dimethylphenanthrene
C3-phenanthrene/anthracene	8.6E-03	1.0E-03	2.7E+02	3.2E-05	5.5E+03	9-propylphenanthrene 2,9,10-trimethylanthracene
C4-phenanthrene/anthracene	4.0E-03	3.4E-04	2.8E+02	3.0E-05	5.5E+03	9-butylphenanthrene 2,3,9,10-tetramethylanthracene
C1-fluoranthene/pyrene	2.8E-03	3.3E-03	2.4E+02	3.4E-05	1.7E+04	2-methylfluoranthene 1-methlylpyrene
C2-fluoranthene/pyrene	4.7E-03	9.6E-04	2.6E+02	3.2E-05	1.7E+04	2,3-dimethylfluoranthene 1-ethylpyrene
C3-fluoranthene/pyrene	7.6E-04	2.4E-04	2.8E+02	3.0E-05	1.7E+04	1,2,3-trimethylfluoranthene 1-propylpyrene

Table D-1 COPC-Specific Properties Used in the Intertidal Sediment Quality Model

COPC	Liquid Vapour Pressure P_L (Pa)	Sub-cooled Liquid Solubility C_L (mol/m^3)	LeBas Molar Volume V_B (cm^3/mol)	Molecular Diffusivity D_m (m^2/d)	Soil Mean Half Life t½ (d)	Representative Surrogate(s) (if applicable)
C4-fluoranthene/pyrene	4.0E-04	6.3E-05	3.0E+02	2.9E-05	1.7E+04	1,2,3,4-tetramethylfluoranthene n-butylpyrene
C1-benzo(a)anthracene/chrysene	6.1E-04	7.3E-04	2.7E+02	3.1E-05	1.7E+04	7-methylbenzo(a)anthracene 6-methylchrysene
C2-benzo(a)anthracene/chrysene	3.1E-04	1.9E-04	2.9E+02	3.0E-05	1.7E+04	7-ethylbenzo(a)anthracene 6-ethylchrysene
C3-benzo(a)anthracene/chrysene	1.6E-04	5.1E-05	3.2E+02	2.8E-05	1.7E+04	7,9,12-trimethylbenzo(a)anthracene 6-propylchrysene
C4-benzo(a)anthracene/chrysene	1.2E-04	1.9E-05	3.4E+02	2.7E-05	1.7E+04	7-butylbenzo(a)anthracene 6-butylchrysene
C1-benzo(bjk)fluoranthene/ benzo(a)pyrene	7.7E-04	1.8E-04	2.9E+02	3.0E-05	1.7E+04	1-methylbenzo(b)fluoranthene 3-methylbenzo(a)pyrene
C2-benzo(bjk)fluoranthene/ benzo(a)pyrene	2.6E-05	4.2E-05	3.1E+02	2.9E-05	1.7E+04	1,3-dimethylbenzo(b)fluoranthene 3,12-dimethylbenzo(a)pyrene
1,2,4-trimethylbenzene	2.7E+02	3.8E-01	1.6E+02	4.2E-05	1.7E+03	---
1,3,5-trimethylbenzene	3.3E+02	4.0E-01	1.6E+02	4.2E-05	1.7E+03	---
Hydrogen Sulphide	1.8E+06	1.1E+05	3.3E+01	1.1E-04	5.5E+03	---
Carbonyl Sulphide	1.3E+06	1.0E+05	4.7E+01	8.7E-05	1.7E+04	---
Methanethiol	2.0E+05	4.8E+02	5.5E+01	7.9E-05	1.7E+04	---
Ethanethiol	7.1E+04	1.4E+02	7.7E+01	6.5E-05	1.7E+04	---

Table D-1 COPC-Specific Properties Used in the Intertidal Sediment Quality Model

COPC	Liquid Vapour Pressure P_L (Pa)	Sub-cooled Liquid Solubility C_L (mol/m³)	LeBas Molar Volume V_B (cm³/mol)	Molecular Diffusivity D_m (m²/d)	Soil Mean Half Life t½ (d)	Representative Surrogate(s) (if applicable)
Iso-Propanethiol	3.7E+04	4.9E+01	1.0E+02	5.6E-05	1.7E+04	---
n-Propanethiol	2.1E+04	3.5E+01	1.0E+02	5.6E-05	1.7E+04	---
Dimethyl Disulphide	4.0E+03	3.9E+01	1.0E+02	5.5E-05	1.7E+04	---
n-Heptanethiol	1.8E+02	2.8E-01	1.9E+02	3.9E-05	5.5E+03	---

NOTES:

"---" not applicable or not available

Liquid vapour pressures obtained from Mackay *et al.* (2000), Gustafson *et al.* (1997), USNLM (n.d.), and RCS (2015).

Sub-cooled liquid solubilities calculated according to Di Toro (2007).

LeBas molar volumes obtained from or calculated according to Mackay *et al.* (2000).

Molecular diffusivities calculated according to USEPA (2015).

Half-lives obtained from Mackay *et al.* (2000) or using data from RCS (2015) and applying a similar approach as Mackay *et al.* (2000).

D.4 References

Clement, T.P., T.R. Gautam, K.K. Lee, M.J. Truex and G.B. Davis. 2004. Modeling of DNAPL-dissolution, rate-limited sorption and biodegradation reactions in groundwater systems. Bioremediation Journal 8: 47-64.

Di Toro, D.M., J.A. McGrath and W.A. Stubblefield. 2007. Predicting the toxicity of neat and weathered crude oil: toxic potential and the toxicity of saturated mixtures. Environmental Toxicology and Chemistry 26: 24-36.

Fader, G. 2005. Erosion, suspended sediment and sediment transport, Bay of Fundy. Atlantic Marine Geological Consulting Ltd., Halifax, NS, March, 2005.

Gustafson, J.B., J. Griffith Tell and D. Orem. 1997. Selection of Representative TPH Fractions Based on Fate and Transport Considerations. TPHCWG Series, Volume 3.

Leahy, J.G. and R.R. Colwell. 1990. Microbial degradation of hydrocarbons in the environment. Microbiology and Molecular Biology Reviews 54: 305-315.

Mackay, D., W.Y Shiu and K.C. Ma. 2000. Physical-Chemical Properties and Environmental Fate Handbook on CD-ROM. CRC Press. Boca Raton, FL.

Miller, J.A. 1966. The suspended sediment system in the Bay of Fundy. M.Sc. Thesis, Institute of Oceanography, Dalhousie University, Halifax, NS, September, 1966.

Peters, C.A., C.D. Knightes and D.G. Brown. 1999. Long-term composition dynamics of PAH-containing NAPLs and implications for risk assessment. Environmental Science and Technology 33: 4499-4507.

Powers, S.E., L.M. Abriola, J.S. Dunkin and W.J. Weber Jr. 1994. Phenomenological models for transient NAPL – water mass-transfer processes. Journal of Contaminant Hydrology 16: 1-33.

Royal Society of Chemistry (RCS). 2015. Chemspider Online Chemical Structure Database and Properties Generation Service. Available at: http://www.chemspider.com. Accessed: August and September 2015.

Schwarzenbach, R.P., P.M. Gschwend and D.M. Imboden. 2002. Environmental Organic Chemistry. 2nd edition. Wiley-Interscience. Hoboken, NJ.

Sterling, M.C.Jr., J.S. Bonner, C.A. Page, C.B. Fuller, A.N.S. Ernest and R.L. Autenrieth. 2003. Partitioning of crude oil polycyclic aromatic hydrocarbons in aquatic systems. Environmental Science and Technology 37: 4429-4434.

Tetra Tech EBA Inc. 2015. Modelling the Fate and Behaviour of Marine Oil Spills for the Proposed Canaport Energy East Marine Terminal. Prepared for Stantec Consulting Ltd. for the Energy East Project. File: V13203200. November 13, 2015

ThermExcel. 2003. Physical Characteristics of Water. Available at: http://www.thermexcel.com/english/tables/eau_atm.htm. Accessed: October 2015.

United States Environmental Protection Agency (USEPA). 2015. Estimated Diffusion Coefficients in Air and Water. EPA On-line Tools for Site Assessment Calculation. Available at: http://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion.html. Accessed: February 5, 2016.

United States National Library of Medicine. n.d. ChemIDplus – A Toxnet Database. Available at: http://chem.sis.nlm.nih.gov/chemidplus/. Accessed: August and September 2015.