

**DEVELOPMENT AND EVALUATION OF A MULTIMEDIA  
ENVIRONMENTAL FATE AND FOOD WEB MODEL FOR  
PHTHALATE ESTERS IN FALSE CREEK, BRITISH  
COLUMBIA**

by

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B.Sc., Western Washington University, 2006

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## **ABSTRACT**

There is limited information on the environmental fate of di-alkyl phthalate esters (DPEs). To better understand the fate of DPEs and their primary metabolites, mono-alkyl phthalates (MPEs), a steady-state multimedia environmental fate and food-web model was developed and tested. The model suggests that the lower log  $K_{ow}$  DPEs mainly flow out of the system and by a smaller extent in the ionized form of MPEs, or further biodegrade into phthalic acid. The higher log  $K_{ow}$  DPEs are mainly bound to sediment that is buried and flow out of the system. The model also predicted that in fish, lower log  $K_{ow}$  DPEs are mainly eliminated through gills whereas the higher log  $K_{ow}$  DPEs undergo fecal route. Biotransformation of DEHP and mixture of C8 isomers are also predicted. This model can be used in preliminary ecological risk assessment to predict exposure concentrations, internal body burdens, and remediation targets in aquatic ecosystems.

**Keywords:** Di-alkyl phthalate ester; mono-alkyl phthalate ester; biotransformation; environmental model; food web.

## DEDICATION

*A graduate degree requires an extensive commitment of time and energy such that normal family obligations and social interactions are abandoned. For dealing with an often tired, forgetful, and dull person, but also for the support I have received during the last four years (and before), I dedicate this thesis especially:*

- *to my mother, Ati, who could not witness this achievement but has been and will always be the backbone and foundation for my thirst of knowledge and love for the path I chose; her encouragement of my dreams and 28 years of support with all her strength, dedication, and love helped me start, continue, and finish this thesis, even in her absence;*
- *to my father, Massoud, for his patience, words of encouragement, sense of humour, his love, and support through the rough ups and downs of my life;*
- *to my grandmother and mentor, Atekeh, my uncle and teacher Mozaffar, my aunt and hero, Soheila, my cousins and prides, Afra and Aryan, my sister and best friend, Katie, and my life partner and soon forever husband, Wasse, who all have loved me unconditionally, and have offered sincere friendship and encouragement throughout my years of studies, and during the darkest and most difficult times of my life.*

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# TABLE OF CONTENTS

Approval.....	ii
Abstract.....	iii
Dedication.....	iv
Acknowledgements.....	v
Table of Contents.....	vi
List of Figures.....	viii
List of Tables.....	xii
List of maps.....	xiii
Glossary.....	xiv
<b>1: Introduction.....</b>	<b>1</b>
1.1 Background.....	1
1.2 Objective.....	10
<b>2: Modeling Theory.....</b>	<b>11</b>
2.1 Steady-State Environmental Fate Sub-Model.....	11
2.2 DPE Steady-State Environmental Fate Sub-Model Theory.....	13
2.3 Non-ionized MPE Steady-State Environmental Fate Sub-Model Theory.....	14
2.4 Ionized MPE Steady-State Environmental Fate Sub-Model Theory.....	17
2.5 Steady-State Food Web Sub-Model Theory.....	19
2.6 Steady-State Environmental Fate & Food Web Model Theory.....	23
2.7 Environmental Fate Sub-Model Assumptions.....	23
2.8 Food Web Sub-Model Assumptions.....	24
<b>3: Methods.....</b>	<b>25</b>
3.1 Modelling Format.....	26
3.2 Parameterization.....	26
3.2.1 Chemical Specific Properties.....	26
3.2.2 System Specific Characteristics.....	32
3.2.3 Simulation Parameters.....	38
3.2.4 Food Web Parameterization.....	39
3.3 Testing the Environmental Fate Sub-Model.....	41
3.3.1 Comparison of Measured and Predicted log K <sub>oc</sub> Values.....	41
3.3.2 Calibration of the Food Web Sub-Model.....	41
3.3.3 Environmental Fate Sub-model Bias.....	44
<b>4: Results &amp; Discussion.....</b>	<b>46</b>
4.1 Environmental Fate Sub-model.....	46
4.1.1 Model Calibration.....	46
4.1.2 Calculated Rate Constants.....	50

4.1.3	MPE log $K_{oc}$ Results .....	52
4.1.4	Environmental Fate Profiles for Each of the DPEs and Their MPE Metabolites .....	54
4.1.5	Overall environmental fate of phthalates.....	67
4.2	Food Web Sub-model .....	68
4.2.1	Model calibration .....	68
4.2.2	Food Web Sub-model Model Performance .....	78
4.2.3	Fate of DPEs in biota.....	82
4.2.4	Overall fate of DPEs in biota.....	87
4.2.5	Model applications.....	89
<b>5: Conclusions and Recommendations.....</b>		<b>92</b>
<b>6: references.....</b>		<b>96</b>
<b>7: Appendices.....</b>		<b>102</b>
Appendix A-1 Chemical specific parameters for DPEs .....		103
Appendix A-2 Chemical specific parameters for MPEs.....		104
Appendix A-3 Environmental fate sub-model parameters and rate constants.....		105
Appendix A-4 Calculated rate constant for DPEs and their corresponding MPE metabolites.....		111
Appendix B-1 Food-web dietary matrix (Mackintosh, et al., 2004).....		112
Appendix B-2 Organism specific parameters.....		113
Appendix B-3 Food web sub-model parameters and rate constants.....		114
Appendix B-4 Calculated organism specific parameters for DPEs.....		123
Appendix B-5 Calculated organism specific parameters for MPEs .....		124
Appendix B-6 Predicted and measured TMF regression analysis results .....		125
Appendix B-7 S-plus statistics for Predicted and Observed TMFs.....		126
Appendix C: CD-ROM Data Appendix.....		127

## LIST OF FIGURES

Figure 1.1-1	General structure of di-alkyl phthalate esters.....	1
Figure 1.1-2	Biodegradation DPEs and MEPs. Figure 1.1-2 A describes the hydrolysis of DPE into MPE and alcohol. Figure 1.1-2 B described the ionization of MPEs and Figure 1.1-2 C describes the hydrolysis of MPEs into phthalic ester and alcohol. ....	2
Figure 2.1-1	Conceptual model of the distribution of DPEs and MPEs in an aquatic ecosystem as described by the environmental fate sub-model. ....	12
Figure 2.5-1	Conceptual diagram representing the major routes of chemical uptake and elimination for an aquatic organism.....	20
Figure 3.2-1	False Creek marine food web and the trophic level of the eighteen marine organisms comprising the food web (reproduced from Mackintosh, <i>et al.</i> , 2004). ....	40
Figure 4.1-1	Comparison of the model predicted log $K_{oc}$ to the empirical log $K_{oc}$ values (Mackintosh, <i>et al.</i> 2006). A, B, C, and D show results of simulations run with an assumption of 100% loading into the water column, 80% loading into water and 20% loading into sediment, 50% loading into the sediment and water, and 20% loading into water and 80% loading into sediment, respectively. The whiskers on the measured mean bars are one standard deviation of the mean.....	47
Figure 4.1-2	Comparison of the laboratory measured and predicted log $K_{oc}$ values of MPEs. Error bars represent 1 standard deviation of the mean. Measured values are adopted from Sura, 2007. ....	52
Figure 4.1-3	Field measured and model predicted log $K_{oc}$ values for MPEs. Log $K_{oc}$ (Sura, 2007) are the mean log $K_{oc}$ obtained from a study conducted by S. Sura (2007) and log $K_{oc}$ (McConnell, 2007) are the mean log $K_{oc}$ values obtained from a separate study conducted by M. McConnell (2007). The error bars represent standard deviation of the mean.....	53
Figure 4.1-4	DMP Environmental fate profile showing the fluxes of DMP (mol/day) between different compartments of the model. ....	56
Figure 4.1-5	DEP Environmental fate profile showing the fluxes of DEP (mol/day) between different compartments of the model. ....	57
Figure 4.1-6	DnBP environmental fate profile showing the fluxes of DnBP (mol/day) between different compartments of the model. ....	57

Figure 4.1-7	BBP environmental fate profile showing the fluxes of BBP (mol/day) between different compartments of the model. ....	58
Figure 4.1-8	MMP Environmental fate profile showing the fluxes of MMP (mol/day) between the compartments. The ionized (the top bold values) and non-ionized MMP fluxes (the lower values) are shown in each box.....	59
Figure 4.1-9	MEP Environmental fate profile showing the fluxes of MEP (mol/day) between the compartments. The ionized (the top bold values) and non-ionized MEP fluxes (the lower values) are shown in each box.....	61
Figure 4.1-10	MnBP Environmental fate profile showing the fluxes of MnBP (mol/day) between the compartments. The ionized (the top bold values) and non-ionized MnBP fluxes (the lower values) are shown in each box.....	61
Figure 4.1-11	MBzP Environmental fate profile showing the fluxes of MBzP (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MBzP fluxes (the lower values) are shown in each box. ....	62
Figure 4.1-12	DEHP environmental fate profile showing the fluxes of DEHP (mol/day) between different compartments of the model. ....	63
Figure 4.1-13	C8 environmental fate profile showing the fluxes of C8 (mol/day) between different compartment of the model. ....	63
Figure 4.1-14	C9 environmental fate profile showing the fluxes of C9 (mol/day) between different compartment of the model. ....	64
Figure 4.1-15	C10 environmental fate profile showing the fluxes of C10 (mol/day) between different compartments of the model. ....	64
Figure 4.1-16	MEHP Environmental fate profile showing the fluxes of MEHP (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MEHP fluxes (the lower values) are shown in each box. ....	65
Figure 4.1-17	MoC8 Environmental fate profile showing the fluxes of MoC8 (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MoC8 fluxes (the lower values) are shown in each box. ....	66
Figure 4.1-18	MoC9 environmental fate profile showing the fluxes of MoC9 (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MoC9 fluxes (the lower values) are shown in each box. ....	66
Figure 4.1-19	MoC10 environmental fate profile showing the fluxes of MoC10 (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MoC10 fluxes (the lower values) are shown in each box.....	67
Figure 4.1-20	Environmental fate pathways of phthalate esters.....	68

Figure 4.2-1	Model predicted and empirical log BAF values for low log $K_{ow}$ DPEs prior to model calibration, when $k_m = 0$ . ....	69
Figure 4.2-2	Model predicted and empirical log BAF values for high log $K_{ow}$ DPEs prior to model calibration, when $k_m = 0$ . ....	70
Figure 4.2-3	Log lipid normalized concentration versus trophic level for the lower log $K_{ow}$ DPEs, DMP, DEP, DnBP, and BBP. The blue diamonds represent measured concentrations (Mackintosh, <i>et al.</i> , 2004) and the red circles represent the model predicted concentrations. ....	72
Figure 4.2-4	Log lipid normalized concentration versus trophic level for the higher log $K_{ow}$ DPEs, DEHP, C8, C9, and C10. The blue diamonds represent measured concentrations (Mackintosh, <i>et al.</i> , 2004) and the red circles represent the model predicted concentrations. ....	73
Figure 4.2-5	Model predicted and empirical Log BAF values for low log $K_{ow}$ DPEs after the estimation and inclusion of a universal biotransformation rate constant. ....	77
Figure 4.2-6	Model predicted and empirical log BAF values for higher log $K_{ow}$ DPEs after the estimation and inclusion of a universal biotransformation rate constant. ....	78
Figure 4.2-7	Overall log model bias of the individual DPEs. Values above the dashed red line (log MB=0) are over predicted by the model and values below the dashed red line are under predicted. The error bars represent one standard deviation from the mean. ....	79
Figure 4.2-8	Model bias calculated from the ratios of model predicted and empirical BAFs for individual DPEs in various biota. ....	81
Figure 4.2-9	DMP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish. ....	83
Figure 4.2-10	DEP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish. ....	84
Figure 4.2-11	DnBP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish. ....	84
Figure 4.2-12	BBP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish. ....	85
Figure 4.2-13	DEHP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish. ....	85
Figure 4.2-14	C8 fluxes (mol/day) in and out of blue mussel, Dugeness crab, staghorn sculpin, and spiny dogfish. ....	86
Figure 4.2-15	C9 fluxes (mol/day) in and out of blue mussel, Dugeness crab, staghorn sculpin, and spiny dogfish. ....	86
Figure 4.2-16	C10 fluxes (mol/day) in and out of blue mussel, Dugeness crab, staghorn sculpin, and spiny dogfish. ....	87

Figure 4.2-17 Overall percentage of elimination fluxes of DPEs (%) in four organisms, blue mussels, Dungeness crabs, staghorn sculpin, and spiny dogfish;  $D_2$  is gill elimination flux (mol/day),  $D_e$  is fecal egestion rate constant (mol/day),  $D_g$  is growth dilution rate constant (mol/day), and  $D_m$  is metabolic transformation rate constant (mol /day)..... 88

## LIST OF TABLES

Table 1.1-1	Physiochemical properties of selected phthalate di-esters and their mono-ester metabolites. ....	3
Table 3.2-1	Chemical specific characteristics of DEHP and its metabolite, MEHP. ....	32
Table 3.2-2	System Specific Characteristics of False Creek. ....	37
Table 4.1-1	Empirical concentrations of DPE in bottom sediment (mol/kg) and in the freely dissolved water fraction (mol/L), were used to obtain empirical log $K_{oc}$ values (Mackintosh <i>et al.</i> , 2006). The model predicted log $K_{oc}$ values are based on the 80% loading into water and 20% loading into sediment. ....	46
Table 4.1-2	Measured and predicted log $K_{oc}$ values of DPEs (unitless) and the calculated Mean Model Bias $\pm$ 1 standard deviation, using the 100% loading into water and 0% into sediment. ....	48
Table 4.1-3	Measured and predicted log $K_{oc}$ values of DPEs (unitless) and the calculated Mean Model Bias $\pm$ 1 standard deviation, using the 80% loading into water and 20% into sediment. ....	49
Table 4.1-4	Measured and predicted log $K_{oc}$ values of DPEs (unitless) and the calculated Mean Model Bias $\pm$ 1 standard deviation, using the 50% loading into water and 50% into sediment. ....	49
Table 4.1-5	Measured and predicted log $K_{oc}$ values of DPEs (unitless) and the calculated Mean Model Bias $\pm$ 1 standard deviation, using the 0% loading into water and 100% into sediment. ....	49
Table 4.1-6	Calculated rate constants ( $day^{-1}$ ) of DEHP and its metabolite, MEHP, in its non-ionized and ionized forms. ....	51
Table 4.1-7	Measured (McConnell, 2007) and predicted log $K_{oc}$ values of MPEs (unitless) and calculated Mean Model Bias $\pm$ 1 standard deviation of the mean. ....	54
Table 4.2-1	Measured and predicted Trophic Magnification Factors (TMF) for DPEs, the Solver Solution for Minimizing the Difference between the Two Slopes and the Estimated Universal Biotransformation Rate Constant. Values in the parenthesis are the 95% Confidence Limit range. ....	75
Table 4.2-2	Chemical based log Mean Model Bias and the associated standard deviation of the mean. ....	79

## LIST OF MAPS

Map 1-1	False Creek in Vancouver, BC, is a part of the Strait of Georgia and separates downtown Vancouver from the rest of the city.....	8
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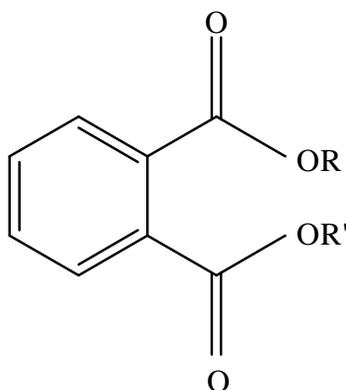
## GLOSSARY

ANOVA	Analysis of variance
BAF	Bioaccumulation factor
BBP	Benzyl butyl phthalate
BCF	Bioconcentration factor
C8	Di-iso-octyl phthalate
C9	Di-iso-nonyl phthalate
C10	Di-iso-decyl phthalate
DEP	Di-ethyl phthalate
DEHP	Di-2-ethylhexyl phthalate
DPE	Di-alkyl phthalate ester
DMP	Di-methyl phthalate
DnBP	Di-n-butyl phthalate
DOC	Dissolved organic carbon
ERA	Ecological risk assessment
$K_{ow}$	Octanol-water partition coefficient
$K_{oc}$	Organic carbon-water partition coefficient
pKa	Negative logarithm of the Acid dissociation constant
TL	Trophic level
MBuP	Mono-butyl phthalate
MEHP	Mono-2-ethylhexyl phthalate
MEP	Mono-ethyl phthalate
MMP	Mono-methyl phthalate
MnBP	Mono-n-butyl phthalate
MoC8	Mono-nonyl phthalate isomer mixture
MoC9	Mono-nonyl phthalate isomer mixture
MoC10	Mon-decyl phthalate isomer mixture
MPE	Mono-alkyl phthalate ester
OC	Organic carbon
TMF	Trophic magnification factor
TOC	Total organic carbon

# 1: INTRODUCTION

## 1.1 Background

Di-alkyl phthalate esters (DPEs) are branched or unbranched alkyl esters which are produced on an industrial scale by the esterification of phthalic acid. They are used as plasticizers in flexible polyvinyl chloride (PVC) and have many other applications, e.g. in paints, adhesives and cosmetics (SCCNFP, 2003). Figure 1.1-1 shows the general chemical structure of DPEs.

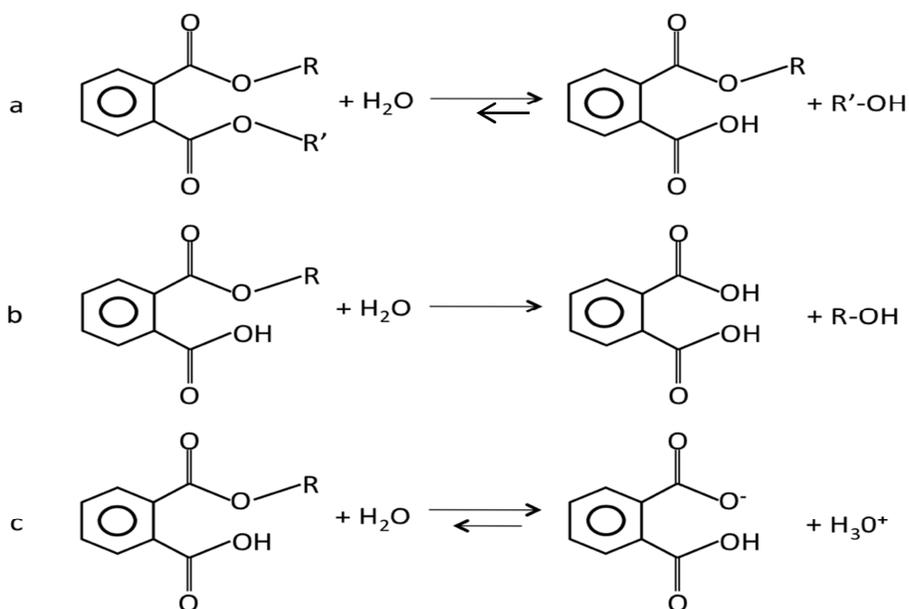


**Figure 1.1-1 General structure of di-alkyl phthalate esters.**

For most DPEs, the two alkyl side chains (-R and -R') are the same, and range in length from one carbon (dimethyl phthalate, DMP) to ten carbons (di-*iso*-decyl phthalate, C10). Phthalate esters also include other phthalates such as benzyl butyl phthalate (BBP) which is an asymmetrical DPE with a benzyl ring on one side and a butyl group on the other side. The length and extent of branching of the side chains determine the physicochemical properties of individual DPEs. DMP is the most water-

soluble DPE and has a log  $K_{ow}$  of 1.61, whereas C10 is the least water soluble and has an approximate log  $K_{ow}$  of 9.46 (Cousins and Mackay, 2000).

DPEs are metabolized by microbes in water and sediment and by enzymes in various other biota via a hydrolysis reaction that results in the formation of the corresponding mono-alkyl phthalate ester (MPE) (Otton, *et al.*, 2008). MPEs can also be hydrolyzed to phthalic acid, which can be further degraded. Figure 1.1-2 illustrates the biodegradation pathway of DPEs to MPEs.



**Figure 1.1-2 Biodegradation DPEs and MPEs. Figure 1.1-2 A describes the hydrolysis of DPE into MPE and alcohol. Figure 1.1-2 B described the ionization of MPEs and Figure 1.1-2 C describes the hydrolysis of MPEs into phthalic ester and alcohol.**

Like DPEs, MPEs range widely in their molecular weights and log  $K_{ow}$  values, but the neutral (non-ionized) form of an MPE is less hydrophobic than the parent compound. MPEs are weak acids with pKa values estimated to be 4.2 (Peterson and Parkerton, 1999), and so exist predominantly in their ionized form at neutral pH values. For ionizable chemicals, log D is a better measure of partitioning than  $K_{ow}$  because it includes

the ionized species and accounts for pH levels. Log D is the ratio of concentrations of the neutral plus ionized forms in octanol in comparison to water at a specified pH value (Kickham *et al.*, 2012). The following equation describes the above relationship:

$$\log D = \log K_{ow} - \log(1 + 10^{(pH-pKa)})$$

Table 1.1-1 gives the physicochemical properties of several DPEs and their corresponding MPE metabolites. The DPE log Kow values given in Table 1.1-1 are corrected for salinity (Mackintosh, 2002). The log D values of the MPEs were calculated using ChemSilico software (ChemSilico, 2009, [www.chemsilico.com](http://www.chemsilico.com)) at pH 8, which is the measured pH of False Creek water.

**Table 1.1-1 Physiochemical properties of selected phthalate di-esters and their mono-ester metabolites.**

<i>Di-ester</i>	<i>Molecular Weight (g/mol)</i>	<sup>2</sup> <i>Log K<sub>ow</sub></i>	<i>Monoester metabolite</i>	<i>Molecular Weight (g/mol)</i>	<sup>3</sup> <i>Log K<sub>ow</sub></i>	<sup>4</sup> <i>Log D (pH=8)</i>
<b>DMP</b>	194.2	1.80	<b>MMP</b>	180.2	1.71	-1.97
<b>DEP</b>	222.2	2.77	<b>MEP</b>	194.2	1.71	-1.63
<b>DnBP</b>	278.4	4.58	<b>MnBP</b>	222.2	3.39	-0.29
<b>BBP</b>	312.4	5.03	<b>MBzP</b>	256.3	3.39	-0.76
<b>DEHP</b>	390.6	8.20	<b>MEHP</b>	278.3	4.51	0.83
<b>C8</b>	390.6	8.20	<b>MoC8</b>	278.3	3.39	0.83
<b>C9</b>	418.6	9.11	<b>MoC9</b>	292.4	4.90	1.22
<b>C10</b>	446.7	10.6	<b>MoC10</b>	306.4	5.29	1.61

<sup>1</sup> di-ester abbreviations are explained in the Glossary.

<sup>2</sup> salinity-corrected values taken from Mackintosh, 2002.

<sup>3</sup> calculated by Peterson & Parkerton (1999) using EPIWIN.

<sup>4</sup> calculated using ChemSilico (<http://www.chemsilico.com>)

Because of the overall very high global production volumes, which are estimated to be greater than 5 million tons per year (ref, 2008), there have been concerns over the potential impacts of both DPEs and MPEs in the environment and on human health

(Parkerton & Konkel, 2000, Staples, *et al.*, 2011). There have been many studies linking chronic and acute DPE exposure to a variety of toxic effects such as endocrine disruptive effects, developmental toxicity, and carcinogenesis (Staples, *et al.*, 1997, Hoppin, *et al.*, 2002; Howdeshell, *et al.*, 2008; Saillenfait, *et al.*, 2009) of phthalate esters. Specifically, the main metabolites of DPEs, i.e. MPEs, are suspected to be endocrine disrupting chemicals (Jobling, *et al.*, 1995; Soto, *et al.*, 1995; Harris, *et al.*, 1997; Sohoni and Sumber, 1998; Paganetto, *et al.*, 2000).

Under the Canadian Environmental Protection Act, DPEs are currently being evaluated for Persistence (P), Bioaccumulation (B), and Toxicity (T) (UNEP, 2001). If they are found to have any one of these characteristics, a screening level risk assessment is conducted. DPEs are also undergoing regulatory evaluations elsewhere in the world.

Due to the ubiquitous presence globally and the possible endocrine toxicity of these chemicals, there have been a few regulatory actions in North America, Europe, and Japan (Staples, *et al.*, 2011). For example, Health Canada has limited the allowable concentrations of DEHP, DBP, and BBP into soft children's toys as well as DINP, DIDP, and DNOP if it is an article that the children could potentially put in their mouth (Health Canada, 2011).

As noted, phthalate esters are produced in large quantities globally and are present in all environmental media. In False Creek sediment, 68% of total PE sediment concentrations were comprised of C8, specifically DEHP (Lin, *et al.*, 2003). C9 and C10 were 14 and 10% of the total PE sediment concentrations while the lower log Kow PE comprised less than 5% of the total PE (Lin, *et al.*, 2003). Estrogenic activity of DEP, BBP, DnBP, and DINP has been reported to be much lower than 17 $\beta$ -estradiol (Harris, *et al.*, 1997). When compared to the activity of the naturally occurring 17 $\beta$ -

estrodol, DEHP and monoesters were inactive (Harris, *et al.*, 1997). Exposure to some PEs exhibit effects similar to substances with anti-androgenic-like effects (David and Gans, 2003) although no direct interference with androgenic receptors have been observed (Staple, *et al.*, 2011; Sultan, *et al.* 2001, Paganetto, *et al.*, 2000).

A variety of other toxicological effects are associated with PEs that has been gathered in a previous review study (Staples, *et al.*, 2001). Among others, induction of vitellogenin and changes in metabolic enzymes (Brase, *et al.*, 2007), changes in developmental rate of embryo, and cleavage in embryo were effected after exposure to DMP and DEP (Kuhn, *et al.* 1989; Rhodes, *et al.*, 1995). For DnBP decreases of survival and growth of fish (Rhodes, *et al.*, 1995), altered feeding behavior (Rhodes, *et al.*, 1995; Wibe, *et al.*, 2004), embryo viability (David, 1988) have been reported. Some studies have shown no induction of vitellogenin after exposure to DnBP (Ortiz-Zarragoitia, *et al.*, 2006). Chronic BBP exposure showed no effects on hatchability, fry survival, or physical characteristic of the fish at any of the tested concentrations (McAllister, 1986; Gledhill, *et al.*, 1980; Harris, *et al.*, 2000). Effects on developmental rate on *Daphnia magna* however was detected with exposure to BBP (Liu, *et al.*, 2009).

Chronic exposure of medaka to DEHP with a variety of nominal concentrations as high as 5000 µg/L resulted in no effects on the fish (DeFoe, *et al.*, 1990; Metcalfe, *et al.*, 2001). *Chironomus riparius* exposure to DEHP exhibited expression of stress related proteins at concentrations that exceeded the solubility of DEHP on dose response manner (Park and Kwak, 2008a,b).

Through exposure of fish to DINP and DIDP via food, no consistent treatment-related effects were reported for the exposed eggs, hatching success, post-hatch survival, delay in gonad differentiation, development, or fecundity in any of the generations (Patyna, *et al.*, 2006). No effects were observed after exposure to DINP and

DIDP to *D. magna* and blue mussels after exposure to DINP and DIDP (Brown and Thompson, 1982; Rhodes, *et al*, 1995).

Based on the extensive review of literature by Staples and colleagues, there are some toxic effects associated with the exposure to lower log  $K_{ow}$  PEs such as DMP, DEP, Dinp, and BBP to fish and invertebrates (Staples, *et al*, 2011). However, higher log  $K_{ow}$  PEs such as DEHP, C8, C9, and C10 seem not to have toxic effects on fish and aquatic invertebrate even when exposure was conducted via dietary route. Many authors have hypothesized that the lack of such effects could be due to the presence of biotransformation mechanism (Staples, *et al*, 1997b; Parkerton and Konekel, 2000; Mackintosh, *et al*, 2004).

Some toxicity tests for MPEs performed with *D. magna* reported  $LC_{50}$  values much higher than DPEs due to the much higher solubility of these compounds (Staples, *et al.*, 2011). In general, lower log  $K_{ow}$  MPEs were less toxic than the parent DPEs, while the higher log  $K_{ow}$  MPEs were more potent than the parent DPE metabolites (Staples, *et al*, 2011). This again was due to the low bioavailability of the higher Low  $K_{ow}$  DPEs and high solubility and hence higher bioavailability of the corresponding MPE metabolites (Adams, *et al*, 1995; Staples, *et al*, 2011).

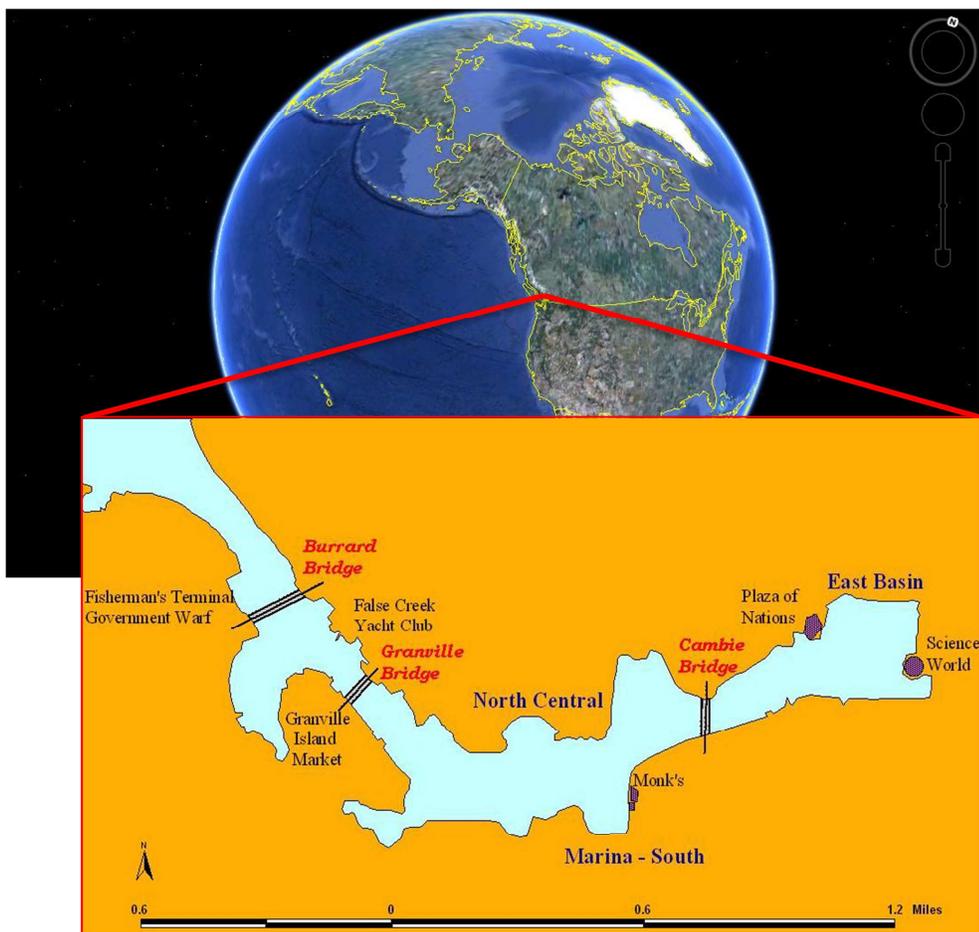
Previously, the biodegradation, bioaccumulative properties, and food web distribution of DPEs and MPEs have been investigated by researchers in the laboratory of Frank Gobas at Simon Fraser University (Mackintosh, *et al.*, 2004; McConnell, 2007; Mackintosh, *et al.*, 2006; Sura, 2007; Otton, *et al.*, 2008; Kickham, 2010). A study investigating the bioaccumulative nature of DPEs in a food web that included many organisms from different trophic levels (Mackintosh, *et al.*, 2004) concluded that none of the DPEs examined had a potential for biomagnification. In fact, lipid-normalized DPE concentrations in biota decreased with increasing trophic level, suggesting trophic

dilution of DPE in the food-web due to biotransformation. However, there is very little information available regarding the biotransformation of DPEs by biota, and the overall fate of DPEs and MPEs in the environment and biota. As a result, there is no way to determine whether current inputs of DPEs into the environment are causing exposures to wildlife that may be harmful to the health of wildlife species.

The work done in this thesis is an effort to generate a model of the environmental fate of MPEs and DPEs on an ecosystem level. It is the final phase of an on-going research program and aims to develop a more integrated understanding of the fate of DPEs in the marine environment.

This study focused on DPEs in False Creek Harbour, a marine inlet of English Bay located in downtown Vancouver and surrounded by residential/industrial land use areas (Map 1-1). False Creek has a mean depth of about 6 meters and is approximately 2.4 kilometers long. By using a multimedia mass balance environmental fate model in conjunction with a food web model (see Chapter 2), a better understanding of the distribution and biotransformation of DPEs in False Creek can be acquired. These models have the potential to be applied in other aquatic locations as well.

There are many factors that can affect the behaviour of DPEs in the environment. As noted above, physicochemical properties of DPEs are largely determined by the length of the alkyl side chains (the -R and -R' groups in Figure 1.1-1). In general, as the alkyl side chain lengthens, the molecular weight and the hydrophobicity of the chemical increase (Table 1.1-1).



**Map 1-1** False Creek in Vancouver (Latitude 49° 16' 29"; Longitude -123° 8' 13"), BC, is a part of the Pacific Ocean Strait of Georgia and separates downtown Vancouver from the rest of the city.

The smallest and least hydrophobic DPE studied here is di-methyl phthalate ester (DMP) while C10 has the longest alkyl group, the highest molecular weight, and is highly hydrophobic. Despite the highly hydrophobic nature of several DPEs, the bioaccumulation factors measured in the biota were much lower than expected (Staples, *et al.*, 1997; Mackintosh, *et al.*, 2004). The ability of biota to biotransform the ingested DPEs and/or the limited bioavailability of these compounds for uptake have been two

possible explanations offered to explain this phenomenon (Mackintosh, *et al.*, 2004, Webster, 2003).

In addition to the physicochemical characteristics of DPEs, other physical parameters can affect the behaviour of these chemicals in the environment. Temperature affects the vapour pressure and therefore the volatility of these chemicals (Guckel, *et al.*, 1982; Staples, *et al.*, 1997). Salinity also could affect the biodegradation and sorptive behaviour of the phthalate esters. For example, the sorption of BBP to sediments increased with a decrease in temperature and an increase in salinity (Xu, *et al.*, 2009).

Organic carbon (OC) content of sediment is also expected to have a significant effect on the bioavailability of hydrophobic chemicals (Park and Erstfeld, 1998). Since hydrophobic organic chemicals have a high tendency to bind to organic matter (McCarthy, 1983), the presence of high concentrations of sediment OC is expected to result in low free fractions of the chemical. Therefore, for highly sorbed chemicals, there is only a small portion of the chemical that is available for biodegradation reactions or uptake into organisms. In the case of DPEs, this was recently demonstrated by Kickham and colleagues (2012) who showed that highly hydrophobic DPEs were not biodegraded by microbes in natural sediments obtained from False Creek likely because they were predominantly bound to sediment OC. Less hydrophobic DPEs (e.g. DMP) were not bound to sediment OC and were biodegraded at approximately the same rate as the more hydrophilic MPEs (Kickham, *et al.*, 2012).

Biodegradation rates of DPE also can be affected by the temperature, nutrient addition, and their concentration (Staples, *et al.*, 1997). Environmental conditions such as temperature, pH, the fraction of OC dissolved or suspended in the water column

could also affect the overall fate of DPEs (Staples, *et al.*, 1997, Mackintosh, *et al.*, 2006, Liang, *et al.*, 2008).

As noted above, DPE biodegradation results in the formation of MPEs. Monoesters exist primarily as ionized forms, in water at neutral pH. Ionization of MPEs adds another level of complexity to understanding the overall fate of phthalate esters in the environment and biota. Last but not least, MPEs can further biodegrade into phthalic acid which can be ultimately be broken down to carbon dioxide (Otton, *et al.*, 2008).

## **1.2 Objective**

The objective of this project is to develop and evaluate a multi-media mass balance model of the fate of DPEs and MPEs in a marine ecosystem located in Vancouver, BC, Canada. The aim of this project is to use the model as a tool to assess the degree of DPE exposure to fish and wildlife in False Creek.

The environmental fate of five DPEs, dimethyl (DMP), diethyl (DEP), di-n-butyl (DnBP), butyl benzyl (BBP), di 2-ethylhexyl (DEHP), and three isomeric mixtures, di-isooctyl (C8), di-isononyl (C9), and di-isodecyl (C10), as well as the fate of their primary metabolites were investigated in this study. The model is tested against previously measured concentrations from False Creek.

## **2: MODELING THEORY**

Two separate sub-models were built: an environmental fate sub-model and a food web bioaccumulation sub-model. Once the sub-models were built, the environmental fate sub-model outputs were used as input parameters for the food web bioaccumulation sub-model, thus connecting the two sub-models together.

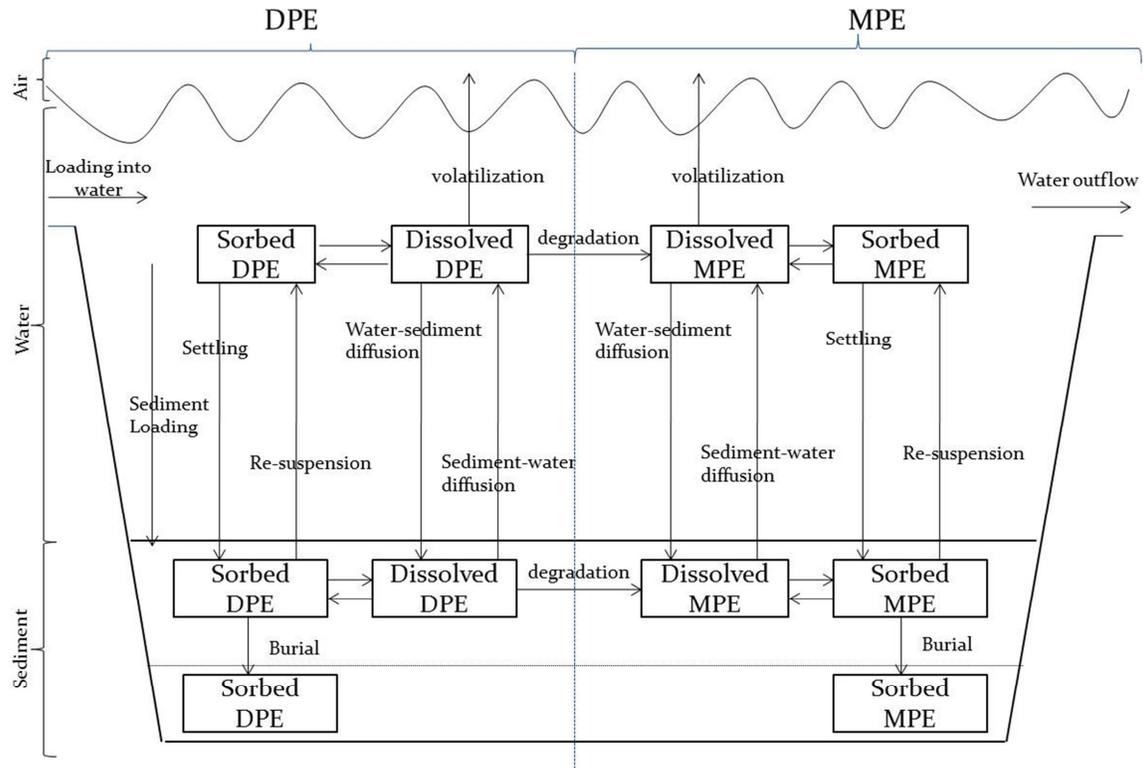
### **2.1 Steady-State Environmental Fate Sub-Model**

This section of the model is described by an open system under the steady-state condition, which allows for input of DPEs and MPEs into the system as well as parameters describing the degradation of DPEs, and the formation of MPEs. The model is built so that it is possible to track concentrations of DEPs and both ionized and non-ionized forms of MPEs. Presently, there are other models that used similar principles for determining environmental concentrations of chemicals (Fugacity level III, Mackay, 1991; EcoFate Model, Gobas, *et al.*, 1998; QWASI model, Mackay, 2002; Lake Ontario model, Gobas, 1993). However, these models do not incorporate the relationship between a parent and metabolite compounds, and only track neutral molecules.

The conceptual model describing the fate of the DPEs and MPEs is provided in Figure 2.1-1. The conceptual model consists of three compartments: air, water, and sediment. Loading into the water compartment consists of water-soluble chemicals as well as those sorbed to suspended particulate matter.

DPEs bound to heavier particles quickly settle and these are represented as loading to the sediments. Equilibrium is assumed between sorbed and dissolved DPEs in the water column and sediment compartments; the dissolved portion of the DPEs can

break down into MPEs. Again, equilibrium is assumed between the dissolved and sorbed MPEs in the water column and in sediment. The sorbed portion of DPEs and MPEs in the water column enter the sediment compartment via the settling process, and the dissolved portion of DPEs and MPEs in the water column can move into the sediment compartment by the water-to-sediment diffusion process.



**Figure 2.1-1 Conceptual model of the distribution of DPEs and MPEs in an aquatic ecosystem as described by the environmental fate sub-model.**

Conversely, the sorbed and dissolved chemicals in the sediment compartment can enter the water column by re-suspension or sediment-to-water diffusion, respectively.

This conceptual model also includes the ionization of monoesters which is not depicted in Figure 2.1-1. Sections 2.2 to 2.4 describe the equations defining the processes described in the above conceptual model for each type of chemical (DPEs, and ionized and non-ionized MPEs) in the water and sediment compartments.

## 2.2 DPE Steady-State Environmental Fate Sub-Model Theory

Processes contributing to the total DPE input into the water compartment of the model include direct DPE release into the water, diffusion of DPEs from sediment into water, as well as re-suspension of sediment which results in releasing of DPE into water. Evaporation to atmosphere, outflow from the system, degradation of DPE into monoesters, diffusion from water-to-sediment, and settling of sediment are the processes contributing to DPE output from water compartment. The total mass of DPE in the water compartment (mol) is given by

$$M_{W,D} = \frac{\left[ \left( \frac{L_{W,D}}{k_{WW,D}} \right) + \left( \frac{k_{SW,D} \cdot L_{S,D}}{k_{WW,D} \cdot k_{SS,D}} \right) \right]}{\left[ 1 - \frac{k_{SW,D} \cdot k_{WS,D}}{k_{WW,D} \cdot k_{SS,D}} \right]} \quad [1]$$

where:

$M_{W,D}$  = total mass of DPE in water (mol)

$L_{W,D}$  = total external loading of DPE in water (mol/day)

$k_{WW,D}$  = total DPE water loss rate constant ( $\text{day}^{-1}$ )

$k_{SS,D}$  = total DPE sediment loss rate constant ( $\text{day}^{-1}$ )

$k_{sw,D}$  = overall DPE sediment to water transport rate constant ( $\text{day}^{-1}$ )

$k_{ws,D}$  = overall DPE water to sediment transport rate constant ( $\text{day}^{-1}$ )

For the calculations of the constant rates, please refer to Appendix 3-A.

The input of chemicals into the sediment compartment of the environmental fate model is satisfied through direct DPE inputs into sediment, sediment settling, as well as diffusion of DPEs from water into sediment. Processes responsible for the output of DPEs from the sediment compartment include sediment burial, settling of suspended solids, DPE diffusion from sediment into water column, and degradation of DPEs in sediment. The total mass of DPE in the sediment compartment (mol) is given by

$$M_{S,D} = (L_{S,D} + K_{WS,D} \cdot M_{W,D}) / K_{SS,D} \quad [2]$$

where:

$M_{S,D}$  = Total mass of DPE in sediment (mol)

$L_{S,D}$  = Total external loading in sediment (mol/day)

$K_{WS,D}$  = Overall DPE water to sediment transport rate constant ( $\text{day}^{-1}$ )

$M_{W,D}$  = Total mass of DPE in water (mol)

$K_{SS,D}$  = Total sediment loss rate constant ( $\text{day}^{-1}$ )

### **2.3 Non-ionized MPE Steady-State Environmental Fate Sub-Model Theory**

MPE loading is the result of MPE formation from its parent DPE. No external MPE loadings are considered. It is worth noting that the formation rates of MPEs are likely over-estimated as the biodegradation rates used are in fact depletion rates of DPEs; therefore, in reality the biodegradation process encompasses the combined breakdown to all the possible metabolites of DPEs and not just the MPEs.

The following equation describes the calculation of the loading of non-ionized MPEs based on the degradation rates of DPEs.

$$L_{W,MPE,ni} = k_{WR,DPE} \cdot M_{W,DPE} \cdot \phi_{MPE,ni} \quad [3]$$

where

$L_{W,MPE,ni}$  = total loading off non-ionized MPE into water (mol/day)

$k_{WR,DPE}$  = degradation rate constant of parent DPE in water ( $\text{day}^{-1}$ )

$M_{W,DPE}$  = total mass of parent DPE in water (mol)

$\phi_{MPE,ni}$  = fraction of non-ionized MPE

Equation [4] describes the calculation of the fraction of non-ionized MPE:

$$\phi_{MPE,ni} = 1 - \left( \frac{1}{1 + 10^{pKa - pH}} \right) \quad [4]$$

where

$\phi_{MPE,ni}$  = percent non-ionized MPE

pKa = negative logarithm of the acid dissociation constant (unitless)

Once the loading of non-ionized MPE into water is determined, the total mass of the non-ionized MPE in water (mol) is calculated according to equation [5]:

$$M_{W,MPE,ni} = \left( \frac{L_{W,MPE,ni}}{k_{WW,MPE,ni}} \right) + \left( \frac{k_{SW,MPE,ni} \cdot L_{S,MPE,ni}}{k_{WW,MPE,ni} \cdot k_{SS,MPE,ni}} \right) / \left( 1 - \frac{k_{SW,MPE,ni} \cdot k_{WS,MPE,ni}}{k_{WW,MPE,ni} \cdot k_{SS,MPE,ni}} \right) \quad [5]$$

where:

$M_{W,MPE,ni}$  = total mass of non-ionized MPE in water (mol)

$L_{W,MPE,ni}$  = total loading of non-ionized MPE in water (mol/day)

$k_{WW,MPE,ni}$  = non-ionized MPE total water loss rate constant ( $\text{day}^{-1}$ )

$k_{SW, MPE,ni}$  = non-ionized MPE overall sediment to water transport rate constant ( $\text{day}^{-1}$ )

$L_{S, MPE,ni}$  = total external loading of MPE in sediment (mol/day)

$k_{SS, MPE,ni}$  = non-ionized MPE total sediment loss rate constant ( $\text{day}^{-1}$ )

$k_{WS, MPE,ni}$  = non-ionized MPE overall water to sediment transport rate constant ( $\text{day}^{-1}$ )

Loading of non-ionized MPE as a result of the breakdown of the parent DPE into the non-ionized monoester is described by equation [6]

$$L_{S, MPE,ni} = k_{SR, DPE} \cdot M_{S, DPE} \cdot \phi_{MPE,ni} \quad [6]$$

where

$L_{S, NIM}$  = total loading of non-ionized MPE in sediment (mol/day)

$k_{SR, DPE}$  = degradation rate constant of parent DPE in sediment ( $\text{day}^{-1}$ )

$M_{S, DPE}$  = total mass of parent DPE in sediment (mol)

$\phi_{MPE,ni}$  = percent non-ionized MPE (%)

The calculated loading of non-ionized MPE in the sediment is used to estimate the total mass of non-ionized MPE in the sediment:

$$M_{S, MPE,ni} = (L_{S, MPE,ni}) + \frac{k_{WS, MPE,ni} \cdot M_{W, MPE,ni}}{k_{SS, MPE,ni}} \quad [7]$$

where:

$M_{S, MPE,ni}$  = total mass of non-ionized MPE in sediment (mol)

$L_{S, MPE,ni}$  = total external loading of non-ionized MPE (mol/day)

$k_{WS, MPE,ni}$  = non-ionized MPE overall water to sediment transport rate constant ( $\text{day}^{-1}$ )

$M_{W, MPE,ni}$  = total mass of non-ionized MPE in water (mol)

$k_{SS,MPE,ni}$  = non-ionized MPE total sediment loss rate constant ( $\text{day}^{-1}$ )

## 2.4 Ionized MPE Steady-State Environmental Fate Sub-Model Theory:

Methodology used to calculate the total mass of ionized MPE in water is similar to that used for calculating the total mass of non-ionized MPE:

$$L_{W,MPE,i} = k_{WR,DPE} \cdot M_{W,DPE} \cdot \phi_{MPE,i} \quad [8]$$

where

$L_{W,MPE,i}$  = total loading of ionized MPE into water (mol/day)

$k_{WR,DPE}$  = degradation rate constant of parent DPE in water ( $\text{day}^{-1}$ )

$M_{W,DPE}$  = total mass of parent DPE in water (mol)

$\phi_{MPE,i}$  = fraction of ionized MPE

To calculate the fraction of ionized MPE, which is necessary for the estimation of the total loadings of ionized MPE, equation [9] was used:

$$\phi_{MPE,i} = \frac{1}{1+10^{pKa-pH}} \quad [9]$$

where

$\phi_{MPE,i}$  = percent ionized MPE

pKa = negative logarithm of the acid dissociation constant (unitless),

$$M_{W,IM} = \frac{\left[ \left( \frac{L_{W,MPE,i}}{k_{WW,MPE,i}} \right) + \frac{k_{SW,MPE,i} \cdot L_{S,MPE,i}}{k_{WW,IM} \cdot k_{SS,IM}} \right]}{\left[ 1 - \left( \frac{k_{SW,MPE,i} \cdot k_{WS,MPE,i}}{k_{WW,MPE,i} \cdot k_{SS,MPE,i}} \right) \right]} \quad [10]$$

where:

$M_{W,IM}$  = total mass of ionized MPE in water (mol)

$L_{W,MPE,i}$  = total loading of ionized MPE in water (mol/day)

$k_{WW,MPE,i}$  = ionized MPE total water loss rate constant ( $\text{day}^{-1}$ )

$k_{SW,MPE,i}$  = ionized MPE overall sediment to water transport rate constant ( $\text{day}^{-1}$ )

$L_{S,MPE,i}$  = total external loading of ionized MPE in sediment (mol/day)

$k_{SS,MPE,i}$  = ionized MPE total sediment loss rate constant ( $\text{day}^{-1}$ )

$k_{WS,MPE,i}$  = ionized MPE overall water to sediment transport rate constant ( $\text{day}^{-1}$ )

To calculate the mass of ionized MPE in sediment, again, a similar approach to the mass of non-ionized MPE in sediment was utilized:

$$L_{S,MPE,i} = k_{SR,DPE} \cdot M_{S,DPE} \cdot \phi_{MPE,i} \quad [11]$$

where

$L_{S,MPE,i}$  = total loading of ionized MPE in sediment (mol/day)

$k_{SR,DPE}$  = degradation rate constant of parent DPE in sediment ( $\text{day}^{-1}$ )

$M_{S,DPE}$  = total mass of parent DPE in sediment (mol)

$\phi_{MPE,i}$  = percent non-ionized MPE (%)

Using the estimated total loadings of ionized MPE in the sediment, the total mass of ionized monoesters was calculated according to equation [12]:

$$M_{S,IM} = \frac{L_{S,MPE,i} + k_{WS,MPE,i} \cdot M_{W,MPE,i}}{k_{SS,MPE,i}} \quad [12]$$

where:

$M_{S,MPE,i}$  = total mass of ionized MPE in sediment (mol)

$L_{S,MPE,i}$  = total external loading of ionized MPE (mol/day)

$k_{WS,MPE,i}$  = ionized MPE overall water to sediment transport rate constant ( $\text{day}^{-1}$ )

$M_{W,MPE,i}$  = total mass of ionized MPE in water (mol)

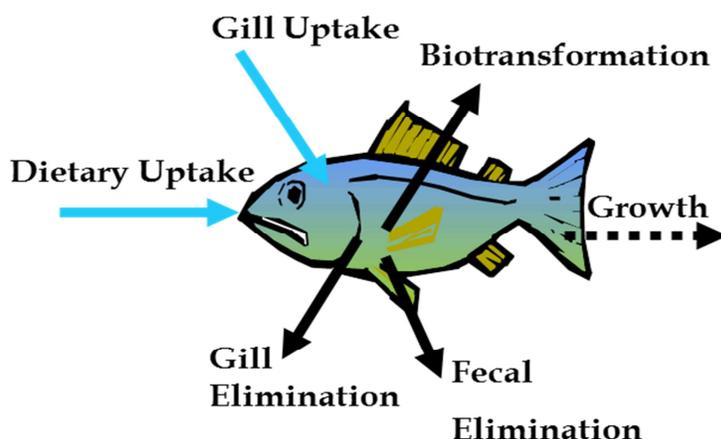
$k_{SS,MPE,i}$  = ionized MPE total sediment loss rate constant ( $\text{day}^{-1}$ )

Chemical concentrations in water and sediment were obtained by dividing the estimated mass of the chemical by the volume of the water or sediment compartments. Equations describing the rate constants in the conceptual model as well as the other parameter formulas used in the fate sub-model are provided in Appendix A-3.

## 2.5 Steady-State Food Web Sub-Model Theory

The food web used for this study consisted of 18 different marine species residing in False Creek (Mackintosh, *et al.*, 2006). Most of the data on ecology, feeding regimes and diet composition of the species were obtained from Mackintosh and colleagues (2004). For the remaining gaps in the data, [www.fishbase.org](http://www.fishbase.org) (Froese and Pauly, 2011) and [www.sealifebase.org](http://www.sealifebase.org) (Palomares and Pauly, 2010) were used. The steady-state food web sub-model is based on the Arnot and Gobas food web bioaccumulation model (2004a).

The food web sub-model is based on the assumption that the exchange of hydrophobic organic chemicals between the organism and its aquatic environment can be described by a single mass balance equation (Arnot and Gobas, 2004b). Figure 2.5-1 describes the major routes of intake and elimination of chemicals in an aquatic, gill-breathing organism. Absorption can be via ingestion and respiration through the gills, while elimination takes place through fecal elimination, growth, metabolism, and gill elimination.



**Figure 2.5-1** Conceptual diagram representing the major routes of chemical uptake and elimination for an aquatic organism.

In order to estimate the concentration of a DPE in biota, the following equation was used:

$$dM_B/dt = W_B \cdot (k_1 \cdot m_O \cdot \varphi \cdot C_{W,DPE} + m_P \cdot C_{WD,DPE,P}) + k_D \cdot \sum(P_i \cdot C_{DPE,j}) - (k_2 + k_E + k_G + k_M) \cdot M_b \quad [13]$$

where

$dM_B/dt$  = net flux of DPE being absorbed at any point in time  $t$  (day)

$W_B$  = weight of the organism at time  $t$  (kg)

$k_1$  = gill uptake rate constant (L/kg.day)

$m_O$  = fraction of the respiratory ventilation that involves the overlaying water

$\varphi$  = bioavailable DPE fraction (unitless)

$C_{W,DPE}$  = total DPE concentration in the water column above the sediment (mol/L)

$m_P$  = fraction of the respiratory ventilation that involves sediment associated pore-water

$C_{WD,DPE,P}$  = freely dissolved DPE concentration in the sediment associated pore water (mol/L)

$k_D$  = dietary uptake rate constant (kg/kg.day)

$P_i$  = fraction of diet consisting of prey item  $i$ ,

$C_{DPE,i}$  = concentration of DPE (mol/kg) in prey item  $i$ ,

$k_2$  = gill elimination rate constant ( $\text{day}^{-1}$ )

$k_E$  = fecal egestion rate constant ( $\text{day}^{-1}$ )

$k_G$  = growth dilution rate constant ( $\text{day}^{-1}$ )

$k_M$  = metabolic transformation rate constant ( $\text{day}^{-1}$ )

Equation [13] can be simplified by dividing both sides of the equation by the weight of the organism ( $W_B$ ) as well as setting the  $dM_B/dt$  equal the value of zero.

$$C_{DPE,B} = \frac{k_1 \cdot (m_O \cdot \varphi \cdot C_{W,DPE} + m_P \cdot C_{WD,DPE,P}) + k_D \cdot (P_i \cdot C_{DPE,i})}{k_2 + k_E + k_G + k_M}$$

[14]

where

$C_{DPE,B}$  = concentration of DPE in the body of the biota (mol/kg ww)

$k_1$  = gill uptake rate constant (L/kg.day)

$m_O$  = fraction of the respiratory ventilation that involves the overlaying water

$\varphi$  = bioavailable DPE fraction (unitless)

$C_{W,DPE}$  = total DPE concentration in the water column above the sediment (mol/L)

$m_P$  = fraction of the respiratory ventilation that involves sediment associated pore-water

$C_{WD,DPE,P}$  = freely dissolved DPE concentration in the sediment associated pore water (mol/L)

$k_D$  = dietary uptake rate constant (kg/kg.day)

$P_i$  = fraction of diet consisting of prey item  $i$ ,

$C_{DPE,i}$  = concentration of DPE (mol/kg) in prey item  $i$ ,

$k_2$  = gill elimination rate constant ( $\text{day}^{-1}$ )

$k_E$  = fecal egestion rate constant ( $\text{day}^{-1}$ )

$k_G$  = growth dilution rate constant ( $\text{day}^{-1}$ )

$k_M$  = metabolic transformation rate constant ( $\text{day}^{-1}$ )

In the case of phytoplankton, due to different means of uptake and elimination in comparison to zooplankton and larger biota such as fish, the following equation was used:

$$C_{DPE,P} = \left( \frac{k_1}{k_2 + k_G} \right) \cdot (m_o \cdot \varphi \cdot C_{DPE,W} + m_p \cdot C_{WD,DPE,P})$$

[15]

where

$C_{DPE,P}$  = concentration of DPE in phytoplankton (mol/kg ww)

$K_1$  = gill uptake rate constant (L/kg.day)

$K_2$  = gill elimination rate constant ( $\text{day}^{-1}$ )

$K_G$  = growth dilution rate constant ( $\text{day}^{-1}$ )

$m_o$  = fraction of the respiratory ventilation that involves the overlaying water

$\varphi$  = bioavailable DPE fraction (unitless)

$C_{DPE,W}$  = total DPE concentration in the water column above the sediment (mol/L)

$m_p$  = fraction of the respiratory ventilation that involves sediment associated pore-water

$C_{WD,DPE,P}$  = freely dissolved DPE concentration in the sediment associated pore water (mol/L)

The appropriate mass balance equations describing the chemical partitioning in the organism were applied for each of the biota. Concentrations of DPEs and MPEs were calculated in each of the organisms in the food web used in previous studies from this lab (Mackintosh, *et al.*, 2004). The food web structure for the feeding interactions and the fraction of the predator's diet consisting of various prey items can be found in

Appendix B-1 (Mackintosh, *et al.*, 2004). In addition, organism-specific parameters and rate constant formulas can be found in Appendix B-2 and Appendix B-3.

## **2.6 Steady-State Environmental Fate & Food Web Model Theory**

The two sub-models are linked together so that the predicted concentrations in the sediment and water compartments are set as inputs for the food web portion of the model, and result in predicted DPE and MPE concentrations in the biota.

## **2.7 Environmental Fate Sub-Model Assumptions**

In order to predict DPE and MPE concentrations in different environmental compartments, a steady-state approach was employed. Such an approach is based on the rationale that the chemicals have been in the system long enough to allow for reaching a dynamic equilibrium whereby the chemical concentrations in each of the compartments remain constant over time. In other words, the ratio between chemical concentrations present in any two compartments of the model and the ratio of loading-to-emission of the different congeners of DPEs and MPEs are assumed to remain constant. The model also assumed a homogeneous distribution of DPEs and MPEs in each of the compartments.

The steady-state approach allows for some simplifications in the model in comparison to a time-dependent approach. DPEs and MPEs have been in the system for a very long time after they were first introduced as plasticizers in the 1920s (Nexant, 2007). As a result of the above reasons, steady-state assumptions are assumed to be reasonable for the model. Abiotic degradation of PEs has been assumed negligible.

## **2.8 Food Web Sub-Model Assumptions**

The steady-state assumptions mentioned in the environmental fate sub-model also apply in the food web sub-model. In addition, each organism is assumed to be a single compartment and the dietary composition for individuals within the species is the same. Biomagnification is assumed not to occur for phytoplankton and algae.

### 3: METHODS

To develop the multi-media mass balance model, the environment was compartmentalized in water, bottom sediments, suspended sediments, algae, sediment dwelling organisms, as well as fish living in the water columns. Some of the data tables and calculations used in the model are provided in an accompanying CD.

First, DPE and MPE concentrations within each compartment of the system were estimated from the inputs of DPE into False Creek, using a mass balance approach (Figure 2.1-1). Once these concentrations were obtained, they were fed into the food-web model in order to estimate the concentrations in aquatic and sediment dwelling organisms. In this manner, estimates of concentrations of phthalate esters in numerous environmental compartments are obtained. These predicted concentrations can be compared to DPE and MPE concentrations that have been measured previously in False Creek and its biota in order to evaluate the performance of the model. In the water compartment of the model, the total mass of chemical in False Creek depends on the total input of the chemical subtracted by the total output of the chemical from False Creek.

The total input of DPE in the water is the sum of the point source discharges into the water, and sediment-to-water partitioning of the chemical through the diffusion process. The total output includes volatilization to the air, outflow from False Creek, degradation of the chemical in the water, and chemical diffusion from the water to sediment. In the sediment compartment of the model, a similar mass balance framework was employed.

### **3.1 Modelling Format**

The steady-state food web bioaccumulation model was developed using Microsoft Excel spread sheets. A master sheet was set that contained the system specific parameters. For each DPE and MPE, a separate Excel file was created that was fed from the original master sheet. For further information on these models please refer to Appendix C and the accompanying CD.

The model parameters and the mass balance equations for each sub-model were calculated within the spread sheet. Once results were obtained, the final outputs were then fed to a new spread sheet to create the necessary graphs and data for analysis.

The Excel spread sheets were used for both testing the model performance and studying different scenarios.

### **3.2 Parameterization**

Parameters for the multimedia environmental fate sub-model were divided into three major groups: chemical specific parameters, system specific characteristics parameters, and simulation parameters. Sections 3.2.1 to 3.2.3 describe how each parameter in each category was obtained and used in the model. The input parameters were obtained from a variety of sources and in cases where the value was not available; the best scientific judgment was used.

#### **3.2.1 Chemical Specific Properties**

The following section provides the sources and rationale for choosing the chemical specific properties. Table 3.2-1 provides an example of the parameters chosen for DEHP and its metabolite mono-2-ethylhexyl phthalate (MEHP). Appendix A-1 and

Appendix A-2 contains the chemical specific properties of the other DPEs and MPEs, respectively.

### **Molecular weight or MolW**

The molecular weight for each DPE was obtained from Cousins and Mackay (2000) and for MPEs from Peterson and Parkerton (1999).

### **Henry's Law Constant or H (Pa.m<sup>3</sup>/mol)**

The Henry's Law Constant for each DPE was obtained from Cousins and Mackay (2000). Henry's Law Constants for ionized MPEs were assumed to be negligible and were given a small value of  $10^{-9}$  Pa.m<sup>3</sup>/mol. For the non-ionized forms of the MPEs, Henry's Law Constants were taken from Peterson and Parkerton (1999) who corrected the Henry's Law Constants of the neutral MPEs for the extent of ionization at pH 7.

### **Log octanol to water partition coefficient or Log K<sub>ow</sub>**

Salinity corrected log K<sub>ow</sub> values for DPEs were obtained from the thesis of C. Mackintosh (2002). For the ionized form of MPEs, log D values were calculated using the MarvinSketch program. This program can be accessed at:

[www.chemaxon.com/products/marvin/marvinsketch/](http://www.chemaxon.com/products/marvin/marvinsketch/)

At low pH values, MPEs exist predominantly in the non-ionized form; log D values calculated at pH=1 by the MarvinSketch program were used as octanol to water partition coefficient for the neutral forms of MPEs. Similarly for ionized forms of the MPEs, log D values calculated at pH=14 by the MarvinSketch program were utilized.

### **Inherent biodegradation rate constant or hlw (day<sup>-1</sup>) and Inherent half lifetime in sediment or hls (day)**

The inherent biodegradation rate for DPEs in sediment was estimated to be 0.29 day<sup>-1</sup> (Kickham *et al.*, 2012). As a result, the inherent half life time in sediment will be

$$t_{\frac{1}{2}} = \frac{\text{Ln}(2)}{0.29} = 2.4 \text{ days}$$

## Biodegradation

There have been a number of studies on the degradation in sediment of DPEs and MPEs (Staples, *et al.*, 1997, Peterson and Staples, 2002, Cousins, *et al.*, 2002; Chang, *et al.*, 2005, Xu, *et al.*, 2009). Among factors affecting the persistence and bioavailability of these chemicals, biodegradation and sorption to sediment particles play key roles (Kickham, *et al.*, 2012). While low biodegradation characteristics for a chemical can result in further persistence in the environment, the chemical's capability to sorb to particles and therefore reduce the bioavailability should also be considered (Kickham, *et al.*, 2012).

### Biodegradation in sediment

The DPE degradation rate constant in sediment was calculated using equation [16] with the following conditions: if the calculated sediment degradation rate constant is below the inherent rate of degradation (0.29 day<sup>-1</sup>), then the calculated rate constant is used. Otherwise, the inherent degradation rate constant is used. It was assumed that the DPE degradation rate in water was zero.

$$\text{Sediment degradation rate constant} = \frac{hls}{1 + \alpha_{soc} * d_{ss} * OC_{ss} * \frac{C_{ss}}{d_{ss}} * K_{ow}} \quad [16]$$

### Biodegradation in Water

Use of the following formula [17] for the water degradation rate constant with the following condition: If the calculated water degradation rate constant is below the

inherent rate of degradation ( $0.29 \text{ day}^{-1}$ ), the calculated rate constant was used.

Otherwise, the inherent degradation rate constant was employed. It was assumed that the DPE degradation rate in sediment was zero.

$$\text{Water degradation rate constant} = \frac{hls}{1 + \alpha_{soc} * d_{pw} * OC_{pw} * \frac{C_{pw}}{d_{pw}} * K_{ow}} \quad [17]$$

### Log transformed organic carbon-to-water partition coefficient (log $K_{oc}$ )

In case of DPEs,  $K_{oc}$  was calculated using the following equation (Seth and Mackay, 1999):

$$K_{oc} = 0.35 * 10^{\text{Log } K_{ow}} \quad [18]$$

In order to calculate log  $K_{oc}$  for the non-ionized fraction of the MPEs,  $K_{oc}$  was obtained using equation [19]:

$$K_{oc} = 0.35 * 10^{\log K_{ow}} \quad [19]$$

In order to calculate  $K_{oc}$  for the ionized fraction of the MPEs the following equation was used:

$$K_{oc} = (\alpha_{soc} * 10^{\log K_{ow}}) + ((1 + O_{css}) * \beta) / O_{css} \quad [20]$$

where

$\alpha_{soc}$  = sediment OC to octanol proportionality constant (0.35),

$O_{css}$  = OC content of bottom sediment (0.028)

$\beta$  = sorption coefficient of ionized MPE to inorganic fraction of particles

The value of  $\alpha_{soc}$  was set to 0.35,  $O_{css}$  was 0.028 and  $\beta$  was 2.9. The value of  $\beta$  was obtained from a model examining the relation of log  $K_{ow}$  of unionized MPEs and log  $K_{ew}$  (EVA-water partition coefficient) where 2.9 is estimated to be the baseline for the

sorption coefficient  $K_{sw}$  of MPEs in sediment regardless of the pH of the media (Gobas, *et al.*, 2010, SETAC 2010 Portland, RP153).

### **Acid dissociation constant (pKa) of the MPEs (unitless)**

The pKa was obtained using the MarvinSketch program. The program was run for each of the monoesters studied. The pKa was estimated to be between 3.06 to 3.08 at the pH of 8 (False Creek pH), lower than the estimated pKa of 4.2 at the pH of 7 by Peterson and Parkerton study (Peterson and Parkerton, 1999).

### **Percentage MPE ionized**

In order to estimate the fraction of MPE in the ionized form, the following rearrangement of the Henderson-Hassel Balch equation was used:

$$\phi_{MPE,i} = \left( \frac{1}{1+10^{pKa-pH}} \right) \quad [21]$$

At the pH of False Creek (pH = 8), more than 99.99% of an MPE is in the ionized form.

### **Percentage MPE non-ionized**

Since 99.99% of an MPE is in the ionized form at the pH of water in False Creek, the remainder, about 0.001%, is in the non-ionized form.

$$\phi_{MPE,ni} = 1 - p\phi_{MPE,i} \quad [22]$$

### **Total $K_{oc}$ for MPEs**

Since MPEs can exist in two forms (ionized and non-ionized), the total  $K_{oc}$  for each MPE is calculated by taking the weighted average of the Koc of the ionized and non-ionized forms, according to equation [23]:

$$Total\ MPE\ K_{oc} = \frac{(K_{oc\ of\ non-ionized\ fraction} * \phi_{MPE,ni})}{100} + \frac{(K_{oc\ of\ ionized\ fraction} * \phi_{MPE,i})}{100} \quad [23]$$

### **Sorption coefficient of ionized MPE to inorganic fraction of particle $\beta$**

$\beta$  was set to a value of 2.9 since previous studies suggest  $\beta$  to be the baseline for the sorption coefficient  $k_{sw}$  of MPEs in sediment regardless of the pH of the media (Gobas, *et al.*, SETAC 2010 Portland, RP153). For further information please refer to “Log transformed organic carbon water partition coefficient (log  $K_{oc}$ ) and  $K_{ocS}$ ” parameterization section in this document.

**Table 3.2-1 Chemical specific characteristics of DEHP and its metabolite, MEHP.**

Chemical Specific Characteristics	DEHP Value	Source	MEHP (non-ionized)	Source	MEHP (ionized)	Source
Molecular weight	390.6	Cousins & Mackay, 2000	278.3	Peterson & Parkerton, 1999	278.3	Peterson & Parkerton, 1999
Henry's Law Constant (pa.m <sup>3</sup> /mol)	3.95	Cousins & Mackay, 2000	3.26E-06	Peterson & Parkerton, 1999	1.00E-09	Estimated
Log Kow of the chemical	8.20	Mackintosh, 2002	4.51	Calculated	0.83	Calculated
Inherent biodegradation half-life (day)	100.76	Kickham, 2010	100.76	Kickham, 2010	100.76	Kickham, 2010
Chemical half life in sediment (day)	0.29	Kickham, 2010	0.29	Kickham, 2010	0.29	Kickham, 2010
Log K <sub>oc</sub>	5.55E+7	Calculated	1.13E+4	Calculated	1.03E+2	Calculated
K <sub>oc</sub>	7.74	Calculated	4.05	Calculated	2.01	Calculated
pKa	---	---		3.08		Calculated
Fraction ionized monoester	---	---		99.998798		Calculated
Fraction non-ionized monoester	---	---		0.001202		Calculated
Total K <sub>oc</sub> for monoesters	---	---		103.1726		Calculated
Sorption coefficient for ionized MPE to inorganic fraction of particle		---		2.9		Calculated

### 3.2.2 System Specific Characteristics

The following section provides the sources and rationale used for obtaining the system specific characteristics necessary for the model. Table 3.2-2 provides a summary of these values.

#### Water body surface area or S<sub>aw</sub> (m<sup>2</sup>)

The water body surface area was estimated to be 6.37E+05 m<sup>2</sup> by obtaining the False Creeks map from Google Earth and breaking down the surface of the water body in smaller geometric shapes and adding the surface area of each of the shapes together.

**Sediment surface area or  $S_{as}$  ( $m^2$ )**

Surface area of the sediment was assumed to be the same as the water surface area.

**Average water depth or  $D_w$  (m)**

The average depth of False Creek water was obtained from previous studies and was set to 20 ft or 6.1 m (Mackintosh, 2002 thesis).

**Depth of active sediment layer or  $D_s$  (m)**

This value was set to be the top 1.5 m of the sediment.

**Water inflow and outflow or  $F$  (L/day)**

This value was estimated from the tide tables for False Creek in 2010 (<http://www.waterlevels.gc.ca>). The maximum fluctuation in each month was calculated by using the highest and lowest tidal flux for each month. Then the average for each season was calculated. The flux was divided by two for each season in order to distinguish between the water entering and leaving False Creek. Finally, these values were averaged for the year and a flux of  $1.40E+09$  L/day was obtained as an annual average of water entering and leaving False Creek.

**Concentration of particles in water or  $C_{PW}$  (kg/L)**

This value was  $1.47E-06$  kg/L and was taken from the thesis of C. Mackintosh (2002).

**Concentration of DOC in water or  $C_{doc}$** 

This value was  $6.60E-07$  kg/L and was taken from the thesis of C. Mackintosh (2002).

**Concentration of solids in sediment  $C_{SS}$** 

Value of 0.2 kg/L was chosen for this parameter.

**Density of suspended solids or  $d_{pw}$** 

This value was 2.4 kg/L and was taken from the thesis of C. Mackintosh (2002).

**Density of sediment solids or  $d_{SS}$** 

This value was 1.9 kg/L and was taken from the thesis of C. Mackintosh (2002).

**Organic carbon content of suspended solids or  $OC_{pw}$  (unitless)**

This value was 0.4 and was taken from the thesis of C. Mackintosh (2002).

**Organic carbon content of bottom sediment or  $OC_{SS}$  (unitless)**

This value was 2.80E-02 and was taken from the thesis of C. Mackintosh (2002).

**Density of organic carbon or  $D_{oc}$  (kg/L)**

A value of 1 kg/L was used which was obtained from EFED, 2007.

**Water side evaporation mass transfer coefficient or  $v_{ew}$  (m/day)**

This value was 2.40E-01 m/day which was obtained from EFED, 2007.

**Air side evaporation mass transfer coefficient or  $v_{ea}$  (m/day)**

This value was 2.40E+01 which was obtained from EFED, 2007.

**Water to sediment diffusion mass transfer coefficient  $v_d$  (m/day)**

This value 9.60 based on EFED, 2007.

**Solid settling rate or  $v_{SS}$  (mol/m<sup>2</sup>/day)**

A solid settling rate of  $9.97 \text{ g/m}^2/\text{day}$  was obtained from a study in Port Moody Arm of Burrard Inlet, Vancouver (Johannessen, *et al.*, 2005). Like False Creek, Port Moody Arm is a narrow inlet, secluded from the rest of the waters of the Strait of Georgia. These similar topographical characteristics and its nearby location to False Creek support using this settling rate value for False Creek.

### **Sediment burial mass transfer coefficient or $v_b$ ( $\text{mol/m}^2/\text{day}$ )**

A value of  $2.01 \text{ g/m}^2/\text{day}$  was chosen based on a previous study (Johannessen, *et al.*, 2005) conducted in Port Moody Arm. According to previous studies, sediment accumulation rates are highest in the deeper waters of the southern Strait than the northern end. The shallower coastal waters and inlets sedimentation rates are between the extreme sedimentation rates. Both due to the sediments released from the drainage of the Fraser River as well as the tidal action at False creek, the highest value measured by Johannessen and colleagues (2005) was selected for use in the False Creek model.

### **Sediment re-suspension rate or $v_{rs}$ ( $\text{mol/m}^2/\text{day}$ )**

The sediment re-suspension rate was calculated by subtracting the sediment burial mass transfer coefficient from the solid settling rate.

### **Dissolved oxygen saturation or $S$ (%)**

The average measured oxygen saturation of False Creek water during summer conditions was measured to be 80% (Kickham, 2010).

### **Disequilibrium factor for particulate organic carbon or $D_{poc}$ (unitless)**

DPEs and MPEs in particulate organic carbon and water were assumed to be at equilibrium, resulting in  $D_{poc}$  of 1.

### **Disequilibrium factor for dissolved organic carbon or $D_{doc}$ (unitless)**

DPEs and MPEs in dissolved organic carbon and water were assumed to be at equilibrium, resulting in  $D_{doc}$  of 1.

### **POC octanol proportionality constant or $\alpha_{poc}$ (unitless)**

In an analysis of compiled sediment water partition coefficient data, Seth and colleagues determined that the sediment and suspended solids relationship is comparable with that of between water and octanol when multiplied by proportionally constant of 0.35 (Seth, *et al.*, 1999). In other words,  $K_{oc} = 0.35 K_{ow} \pm 2.5$  (Seth, *et al.*, 1999).

### **DOC- octanol proportionality constant or $\alpha_{doc}$ (unitless)**

The dissolved organic carbon partition coefficient for non-ionic organic chemicals was set as 0.08 based on a study by Burkhard, 2000.

### **pH of water (pH units)**

A pH value of 8 was used based on previous measurements (P. Kickham thesis, 2010).

### **Water temperature or $T_w$ (°C)**

Temperature of 11° C was used based on previous measurements (Kickham, 2010).

### **Sediment OC-to-octanol proportionality constant or $\alpha_{soc}$ (L/kg)**

Value of 3.50E-01 was chosen as  $\alpha_{soc}$  (Seth and Mackay, 1999).

**Table 3.2-2 System Specific Characteristics of False Creek**

<b>System-Specific Characteristics</b>	<b>Symbol</b>	<b>Value</b>	<b>Source</b>
water body surface area (m <sup>2</sup> )	S <sub>aw</sub>	6.37E+5	Calculated from geographical maps
sediment surface area (m <sup>2</sup> )	S <sub>as</sub>	6.37E+5	Calculated from geographical maps
average water depth (m)	D <sub>w</sub>	6.10E+0	Mackintosh, 2002
depth of active sediment layer (m)	D <sub>s</sub>	1.50E-1	Dalziel, <i>et al.</i> , 2006
water in- and out-flow (L/day)	F	1.40E+9	Calculated
Concentration of particles in water (kg/L)	C <sub>pw</sub>	1.47E-6	Mackintosh, 2002
Concentration of DOC in water (kg/L)	C <sub>doc</sub>	6.60E-7	Mackintosh, 2002
concentration of solids in sediment (kg/L)	C <sub>ss</sub>	2.00E-1	Estimated
density of suspended solids (kg/L)	d <sub>pw</sub>	2.40E+0	Mackintosh, 2002
density of sediment solids (kg/L)	d <sub>ss</sub>	1.90E+0	Mackintosh, 2002
organic carbon content of suspended solids (unitless)	OC <sub>pw</sub>	4.00E-1	Mackintosh, 2002
organic carbon content of bottom sediment (unitless)	OC <sub>ss</sub>	2.80E-2	Mackintosh, 2002
density of organic carbon (kg/L)	d <sub>oc</sub>	1.00E+0	EFED, 1997
water-side evaporation mass transfer coefficient (m/day)	V <sub>ew</sub>	2.40E-1	EFED, 1997
air-side evaporation mass transfer coefficient (m/day)	V <sub>ea</sub>	2.40E+1	EFED, 1997
water-to-sediment diffusion mass transfer coefficient (m/day)	V <sub>d</sub>	9.60E-3	EFED, 1997
solids settling rate (mol/m <sup>2</sup> /day)	V <sub>ss</sub>	9.97E+0	Johanessen, <i>et al.</i> , 2005
sediment burial mass transfer coefficient (mol/m <sup>2</sup> /day)	V <sub>b</sub>	6.16E+0	Johanessen, <i>et al.</i> , 2005
sediment resuspension rate (mol/m <sup>2</sup> /day)	V <sub>rs</sub>	3.81E+0	Calculated
dissolved oxygen saturation (%)	S	9.00E-1	Kickham, 2010
Disequilibrium factor POC (unitless)	D <sub>poc</sub>	1.00E+0	Assumed
Disequilibrium factor DOC (unitless)	D <sub>doc</sub>	1.00E+0	Assumed
POC-octanol proportionality constant (unitless)	α <sub>poc</sub>	3.50E-1	Seth, <i>et al.</i> , 1999

DOC-octanol proportionality constant (unitless)	$\alpha_{\text{doc}}$	8.00E-2	Burkhard, 2000
pH of water	pH	8.00E+0	Kickham, 2010
water temperature (°C)	TW	1.10E+1	Kickham, 2010
Sediment OC octanol proportionality constant (unitless)	$\alpha_{\text{soc}}$	3.50E-1	Seth <i>et al.</i> , 1999

### 3.2.3 Simulation Parameters

The following parameters can be used for simulation purposes. Please refer to Appendix A-3 in the accompanying CD for formulas through which the rate constants were calculated for each of the phthalate esters and their metabolites, based on the system specific input parameters provided in Table 3.2-2.

#### Total loading or $L_t$ (mol/day)

To date, there have been no measured or estimated loading values for DPEs in False Creek. For simulation purposes, each DPE was given an arbitrary  $L_t$  value of 1 mol/day.

#### Loading into water or $L_w$ (mol/day)

It was assumed that 80% of the total loading of DPEs (i.e., 0.8 mol/day) was into the water column. Some of the DPE sources include waster from boats, combined sewer outflows during heavy rainfall events, storm water outfalls, or leaky septic tanks.

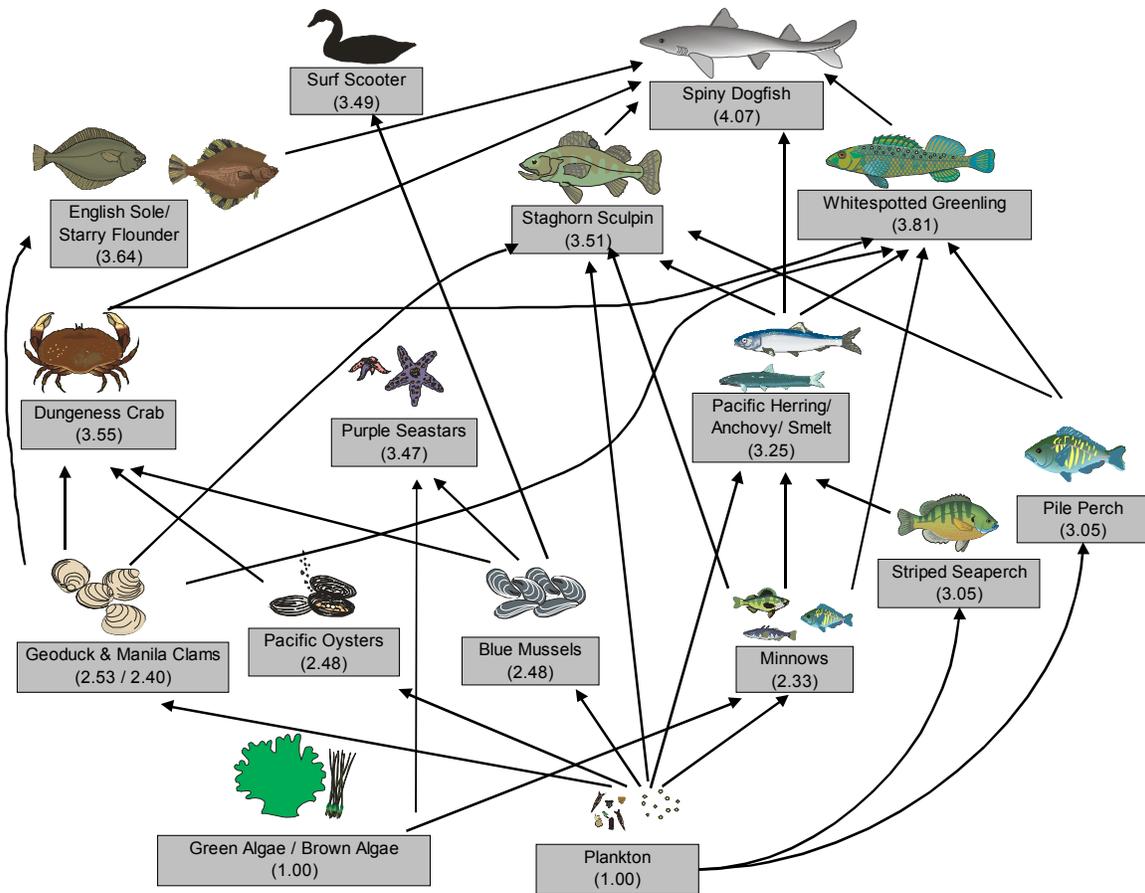
#### Loading into sediment or $L_s$ (mol/day)

Some of the DPE loadings can be directly into the sediment compartment. DPE-containing waste on the surface of the sediment or buried in the sediment could act as a possible source of DPEs being released into the sediment over time. Another possible source of loading of phthalate esters into sediment could be heavier material entering False Creek from boats, combined sewer outfalls, or storm water outfalls. It was

assumed that 20% of the total loading of DPEs enters the sediment compartment (i.e., 0.2 mol/day).

### **3.2.4 Food Web Parameterization**

In this section of the model, the concentrations of DPE, and ionized and unionized MPE in a series of aquatic organisms were estimated using the outputs of the environmental fate portion of the model. Figure 3.2-1 shows the food web of eighteen marine organisms residing in False Creek and their trophic positions (Mackintosh, *et al.*, 2004). Please refer to Appendix B-1 in the accompanying CD for food web structure and the trophic positions used in this study. The trophic position of each organism in the food web was determined using on equation [24] (Adams, *et al.*, 1983 and Vander Zanden, *et al.*, 1996). Appendix B-2 provides the organism specific parameters used in this model.



**Figure 3.2-1 False Creek marine food web and the trophic level of the eighteen marine organisms comprising the food web (reproduced from Mackintosh, *et al.*, 2004).**

$$TP_{predator} = \sum_{n=1}^N TP_{prey,n} \cdot P_{prey,n} + 1 \quad [24]$$

where

$TP_{predator}$  = trophic position of the organism of question

$TP_{prey,n}$  = trophic position of the prey item  $n$

$P_{prey,n}$  = fraction of food, consumed by the predator consisting in prey

$N$  = total number of prey items consumed by the predator

Primary producers were given a trophic level 1 and zooplankton and zoo-benthos were assumed to represent trophic level of 2 (Adams, *et al.*, 1983 and Vander Zanden, *et al.*, 1996).

The feeding preferences ( $P_{\text{prey},n}$ ) for each species were obtained from Mackintosh (2002) and are provided in Appendix B-1. The trophic levels used in this study were confirmed through stable nitrogen and carbon isotope ratio analyses by Mackintosh and colleagues (2004). Calculated organism specific parameters for DPEs and MPEs are provided in Appendix B-4 and Appendix B-5, respectively.

### **3.3 Testing the Environmental Fate Sub-Model**

#### **3.3.1 Comparison of Measured and Predicted log $K_{oc}$ Values**

Once the model was parameterized, it was important to check the model's performance. To examine the model performance and its ability to predict partitioning of the chemicals between sediment and water, the predicted organic carbon normalized sediment-water partition coefficient ( $K_{oc}$ ) for each DPE were compared to empirical  $K_{oc}$  values measured in False Creek by Mackintosh (2006).

#### **3.3.2 Calibration of the Food Web Sub-Model**

Although it is possible that 100% of the loading of PE could be into the water column alone, it is expected that a portion of the DPEs entering False Creek settle directly into the sediment and hence, provide a source of DPEs into the sediment directly.

To estimate the loading allocations of DPEs into False Creek, four scenarios were considered to estimate what the proper ratio of DPE loading into water and sediment compartments is:

1. 100% of the loading allocated to the water column.
2. 80% of the loading allocated to water and 20% to sediment.
3. 50% of the loading allocated to water and 50% to sediment.
4. 20% of the loading allocated to water and 80% to sediment.

In initial model runs, the biotransformation rate constant was given a value of zero. However, this led to large discrepancies between the measured and empirical BAF values for DPEs. Because DPE and MPE biotransformation rate constants in biota are not known, the model was calibrated to obtain estimates of the biotransformation rate constants. Model predicted trophic magnification factor (TMF) in conjunction with the solver function in Excel was used to estimate a universal biotransformation rate constant for each of the DPEs.

Once the biotransformation rate constants ( $k_m$ ) were obtained for each of the DPEs, the new universal  $k_m$  values were used to re-parameterized the model. Finally, after the inclusion of the model predicted universal biotransformation rate constants in the model, the model predicted BAFs were once again compared with the empirical data to test the model performance.

To evaluate the proper performance of the food web sub-model, independent on the performance of the environmental fate sub-model, the empirical concentrations of DPEs and MPEs in sediment, pore-water, total water, and dissolved water concentrations were used as input parameters of the food web sub-model. Then, log BAF of each biota were calculated and compared to the empirical log BAF values.

To quantitatively determine the model performance for the food web sub-model, the chemical and species specific model bias was determined for the food web sub-model according to equation [27].

$$\log \text{ mean } MB_n = \frac{\sum_{n=1}^N (\log BAF_{p,n} - \log BAF_{o,n})}{N} \quad [27]$$

where

$\log \text{ mean } MB_n$  = logarithmic mean model bias specific for biota species ( $n$ )

$\log BAF_{p,n}$  = predicted species specific logarithmic bioaccumulation factor

$\log BAF_{o,n}$  = observed species specific logarithmic bioaccumulation factor

$N$  = number of phthalate esters used

In addition, the all combined mean model bias for each species was calculated as it is shown in equation [28].

$$\log \text{ mean } MB_m = \frac{\sum_m^M (\log MB_m)}{M} \quad [28]$$

where

$\log \text{ mean } MB_m$  = logarithmic mean model bias specific for individual phthalate esters ( $m$ )

$\log MB_m$  = logarithmic model bias for individual phthalate esters

$M$  = number of biota species used

In order to calculate the logarithmic model bias for individual phthalate esters, equation [29] is used:

$$\log MB_m = \log BAF_{p,n} - \log BAF_{o,n} \quad [29]$$

where

$\log MB_m$  = logarithmic model bias calculated for individual phthalate esters

$\log \text{BAF}_{p,n}$  = predicted phthalate ester specific logarithmic bioaccumulation factor

$\log \text{BAF}_{o,n}$  = observed phthalate ester specific logarithmic bioaccumulation factor

### 3.3.3 Environmental Fate Sub-model Bias

Model bias (MB) was calculated for each of the DPE as shown in equation [25]. MB was also calculated for all combined DPEs [26]. Log MB of 0 indicates perfect agreement between the observed and predicted Log  $K_{oc}$ . Values below 0 indicate under-prediction of the model while values above 0 indicate over-prediction of the model.

$$\log MB_{\text{individual PE}} = \log K_{oc,p} - \log K_{oc,o} \quad [25]$$

where

$\log MB_{\text{individual PE}}$  = logarithmic model bias for individual phthalate esters

$\log K_{oc,p}$  = predicted logarithmic organic carbon to water partition coefficient

$\log K_{oc,o}$  = observed logarithmic organic carbon to water partition coefficient

$$\log \text{mean } MB_{PE} = \frac{\sum \log MB_{\text{individual,PE}}}{N} \quad [26]$$

Where

Log mean  $MB_{PE}$  = logarithmic mean model bias for encompassing all phthalate esters

Log  $MB_{\text{individual PE}}$  = logarithmic model bias for individual phthalate esters

N = total number of phthalate esters used

Similarly, model-predicted  $\log K_{oc}$  values for the total MPEs were obtained and compared to independent empirical values from False Creek. Two independent studies have measured field concentrations of MPEs in False Creek water and sediment and calculated  $\log K_{oc}$  values based on these measurements. One study measured the MPE  $\log K_{oc}$  values in 2004 and 2006 (Sura, 2007) and the other study was conducted in 2005 (McConnell, 2007).  $\log K_{oc}$  values for the MPEs from these two studies were compared with the model-predicted  $\log K_{oc}$  values. Individual MPE model bias and the overall MPE model bias were also calculated as described in equations [23] and [24].

## 4: RESULTS & DISCUSSION

### 4.1 Environmental Fate Sub-model

The result of the environmental fate sub-model is presented and discussed in the following section.

#### 4.1.1 Model Calibration

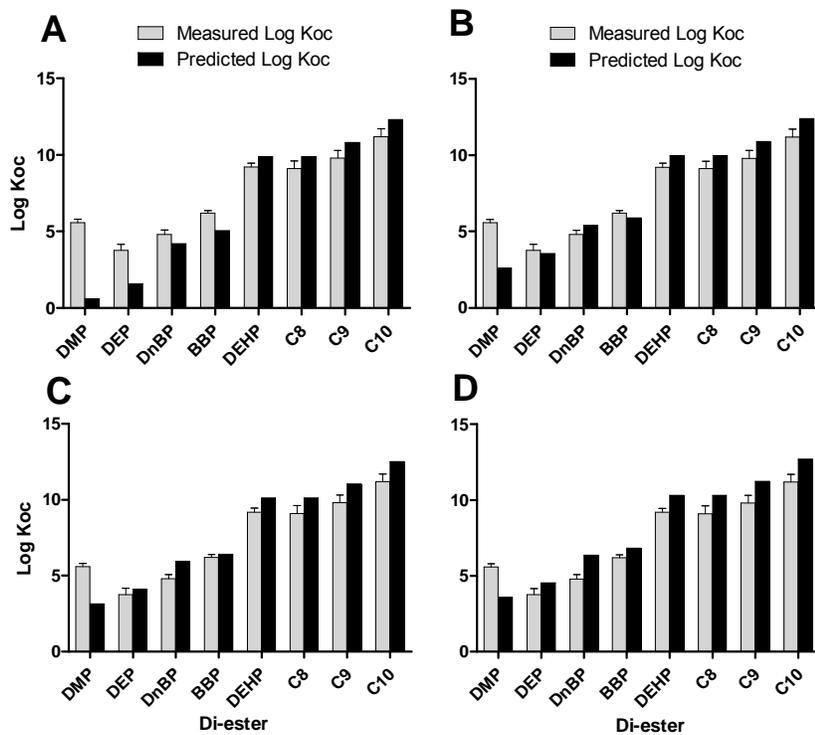
##### 4.1.1.1 Loading Simulation log K<sub>oc</sub> Results and Model Bias

The empirical DPE log K<sub>oc</sub> values in False Creek have been measured in previous studies and are given in Table 4.1-1.

**Table 4.1-1 Empirical concentrations of DPE in bottom sediment (mol/kg) and in the freely dissolved water fraction (mol/L), were used to obtain empirical log K<sub>oc</sub> values (Mackintosh *et al.*, 2006). The model predicted log K<sub>oc</sub> values are based on the 80% loading into water and 20% loading into sediment.**

DPE Chemical	Empirical log K <sub>oc</sub>	Model Predicted log K <sub>oc</sub>
DMP	5.59	2.60
DEP	3.77	3.57
DnBP	4.80	5.40
BBP	6.21	5.90
DEHP	9.20	9.97
C8	8.91	9.97
C9	9.09	10.9
C10	11.2	12.4

Figure 4.1-1 A shows the model-predicted log  $K_{oc}$  results, where all DPE loading takes place from the water phase and sediment loading is negligible, compared to the empirical values (Table 4.1-1). Three other scenarios, where 20% of the loading was allocated to water and 80% to sediment (Figure 4.1-1 B), the loading was allocated equally to the sediment and water compartments (Figure 4.1-1 C), and 80% of the loading was allocated to the water and 20% to sediment (Figure 4.1-1 D) were simulated to see which one fit the empirical values best.



**Figure 4.1-1 Comparison of the model predicted log  $K_{oc}$  to the empirical log  $K_{oc}$  values (Mackintosh, et al. 2006). A, B, C, and D show results of simulations run with an assumption of 100% loading into the water column, 80% loading into water and 20% loading into sediment, 50% loading into the sediment and water, and 20% loading into water and 80% loading into sediment, respectively. The whiskers on the measured mean bars are one standard deviation of the mean.**

To evaluate the accuracy of the environmental fate sub-model under each of the loading scenarios, empirical log  $K_{oc}$  values were used to calculate Model Bias (MB). Log MB = 0 represents perfect agreement between the model's predictions and the empirical data. Model bias values below zero indicates that the model under-predicts while MB values above zero indicates model over-prediction.

Table 4.1-2 contains the predicted and measured log  $K_{oc}$  values and the calculated mean model bias with one standard deviation of the mean, where 100% of the loadings of DPEs enter the water column (Figure 4.1-1 A); Overall, the model under-predicts  $K_{oc}$  by a factor of  $10^{(-0.55 \pm 2.21)}$ . Model under-prediction is greater for low  $K_{ow}$  DPEs. For all other DPEs, the model over-predicted log  $K_{oc}$  values.

**Table 4.1-2 Measured and predicted log Koc values of DPEs (unitless) and the calculated Mean Model Bias  $\pm$  1 standard deviation, using the 100% loading into water and 0% into sediment.**

	<i>DMP</i>	<i>DEP</i>	<i>DnBP</i>	<i>BBP</i>	<i>DEHP</i>	<i>C8</i>	<i>C9</i>	<i>C10</i>	
<b>Measured Log <math>K_{oc}</math></b>	5.59	3.77	4.8	6.21	9.2	8.91	9.09	11.2	
<b>Predicted Log <math>K_{oc}</math></b>	0.61	1.61	4.19	5.04	9.88	9.88	10.80	12.30	
<b>Mean MB <math>K_{oc}</math></b>									<b><math>10^{-0.55 \pm 2.21}</math></b>

Table 4.1-3 shows the log mean model bias of the model when 80% of the DPE loadings are assumed to enter the water and 20% remaining enter the sediment compartment (Figure 4.1-1B). Under this scenario, the overall mean MB shows that the model over-predicts the  $K_{oc}$  values by a factor of  $10^{(0.24 \pm 1.48)}$ .

**Table 4.1-3 Measured and predicted log Koc values of DPEs (unitless) and the calculated Mean Model Bias  $\pm$  1 standard deviation, using the 80% loading into water and 20% into sediment.**

	<i>DMP</i>	<i>DEP</i>	<i>DnBP</i>	<i>BBP</i>	<i>DEHP</i>	<i>C8</i>	<i>C9</i>	<i>C10</i>	
<b>Measured Log K<sub>oc</sub></b>	5.59	3.77	4.8	6.21	9.2	8.91	9.09	11.2	
<b>Predicted Log K<sub>oc</sub></b>	2.60	3.57	5.41	5.90	9.98	9.98	10.90	12.39	
<b>Mean MB K<sub>oc</sub></b>									<b>10<sup>0.24</sup> <math>\pm</math> 1.48</b>

Table 4.1-4 portrays the log mean model bias when the 50% of the DPEs loadings enter the sediment and the remaining 50% enters the water compartments of the model (Figure 4.1-1C). In this case, the model over predicts the K<sub>oc</sub> by a higher factor (10<sup>(0.58 $\pm$ 1.34)</sup>) in comparison to the previous scenario.

**Table 4.1-4 Measured and predicted log Koc values of DPEs (unitless) and the calculated Mean Model Bias  $\pm$  1 standard deviation, using the 50% loading into water and 50% into sediment.**

	<i>DMP</i>	<i>DEP</i>	<i>DnBP</i>	<i>BBP</i>	<i>DEHP</i>	<i>C8</i>	<i>C9</i>	<i>C10</i>	
<b>Measured Log K<sub>oc</sub></b>	5.59	3.77	4.8	6.21	9.2	8.91	9.09	11.2	
<b>Predicted Log K<sub>oc</sub></b>	3.15	4.12	5.94	6.41	10.12	10.12	11.05	12.54	
<b>Mean MB K<sub>oc</sub></b>									<b>10<sup>0.58</sup> <math>\pm</math> 1.34</b>

Table 4.1-5 portrays the log mean model bias when the 80% of the DPEs loadings enter the sediment and the remaining 20% enters the water compartments of the model (Figure 4.1-1D). In this case, the model over-predicts the log Koc by a higher factor (10<sup>(1.15 $\pm$ 1.20)</sup>) in comparison to all of the previous scenarios.

**Table 4.1-5 Measured and predicted log Koc values of DPEs (unitless) and the calculated Mean Model Bias  $\pm$  1 standard deviation, using the 0% loading into water and 100% into sediment.**

	<i>DMP</i>	<i>DEP</i>	<i>DnBP</i>	<i>BBP</i>	<i>DEHP</i>	<i>C8</i>	<i>C9</i>	<i>C10</i>	
<b>Measured Log K<sub>oc</sub></b>	5.59	3.77	4.8	6.21	9.2	8.91	9.09	11.2	
<b>Predicted Log K<sub>oc</sub></b>	3.96	4.93	6.74	7.19	10.46	10.46	11.37	12.86	
<b>Mean MB K<sub>oc</sub></b>									<b>10<sup>1.15</sup> <math>\pm</math> 1.20</b>

Figure 4.1-1 B and C seem to have the best agreement among the results of the four scenarios, with B having a slightly better fit. In addition, the assumption of 80% loading into water and 20% into sediment is a more reasonable assumption in comparison with the equal loading into sediment and water compartments considering the physicochemical properties of phthalates.

After careful examination of the comparison between the mean model bias of the log  $K_{oc}$  values from the four scenarios, the 80% loading into water and 20% sediment loading scenario was selected for use in subsequent model simulations.

#### **4.1.2 Calculated Rate Constants**

Table 4.1-6 provides the calculated rate constants based on the model input parameters provided in Table 3.2-2. Please refer to Appendix A-4 for the calculated rate constant for the remaining phthalate esters and their metabolites.

**Table 4.1-6 Calculated rate constants (day<sup>-1</sup>) of DEHP and its metabolite, MEHP, in its non-ionized and ionized forms.**

Rate Constants (day <sup>-1</sup> )	Symbol	DEHP	MEHP non-ionized	MEHP ionized
<b>outflow</b>	<b>K<sub>O</sub></b>	3.60E-1	3.60E-1	3.60E-01
<b>volatilization</b>	<b>k<sub>V</sub></b>	5.76E-5	1.99E-9	6.17E-13
<b>overall water-to-sediment transport</b>	<b>k<sub>WS</sub></b>	9.11E-1	8.91E-3	1.58E-03
<b>overall sediment-to-water transport</b>	<b>k<sub>SW</sub></b>	1.36E-5	1.01E-3	6.32E-02
<b>solids settling</b>	<b>k<sub>WS1</sub></b>	9.11E-1	7.35E-3	3.24E-06
<b>water-to-sediment diffusion</b>	<b>k<sub>WS2</sub></b>	3.95E-5	1.56E-3	1.57E-03
<b>solids re-suspension</b>	<b>k<sub>SW1</sub></b>	1.34E-5	1.32E-5	1.75E-07
<b>sediment-to-water diffusion</b>	<b>k<sub>SW2</sub></b>	2.06E-7	9.93E-4	6.32E-02
<b>burial</b>	<b>k<sub>B</sub></b>	2.16E-5	2.13E-5	2.83E-07
<b>degradation in water</b>	<b>k<sub>WR</sub></b>	8.63E-3	2.88E-1	2.90E-01
<b>degradation in sediment</b>	<b>k<sub>SR</sub></b>	9.34E-7	4.50E-3	2.86E-01
<b>Total water loss RC</b>	<b>K<sub>WW</sub></b>	1.28E+0	6.57E-1	6.52E-01
<b>Total Sediment loss</b>	<b>K<sub>SS</sub></b>	3.61E-5	5.53E-3	3.49E-01
<b>Pre-cursor of k<sub>wr</sub></b>	<b>pre.k<sub>WR</sub></b>	8.63E-3	2.88E-1	2.90E-01
<b>Pre-cursor of k<sub>sr</sub></b>	<b>pre.k<sub>SR</sub></b>	9.34E-7	4.50E-3	2.86E-01

### 4.1.3 MPE log K<sub>oc</sub> Results

#### 4.1.3.1 Predicted log K<sub>oc</sub> values vs. log K<sub>oc</sub> values measured in the laboratory

Model-predicted MPE log K<sub>oc</sub> values are compared with values measured in the laboratory in Figure 4.1-2. The empirical log K<sub>oc</sub> values were obtained previously in this laboratory by S. Sura (2007); MMP was not examined in that study. With the exception of MEP, where the model under-predicts the log K<sub>oc</sub>, the modelled values are in good agreement with the measured laboratory log K<sub>oc</sub> values with model bias of  $10^{0.25 \pm 0.79}$ , suggesting a reasonable representation of the chemical and environmental processes resulting in the degradation of DPEs and formation of MPEs. At this point, in order to predict the laboratory log K<sub>oc</sub>, no MPE biodegradation was assumed since laboratory tests were conducted with inactive sediments for MPEs (Sura, 2007).

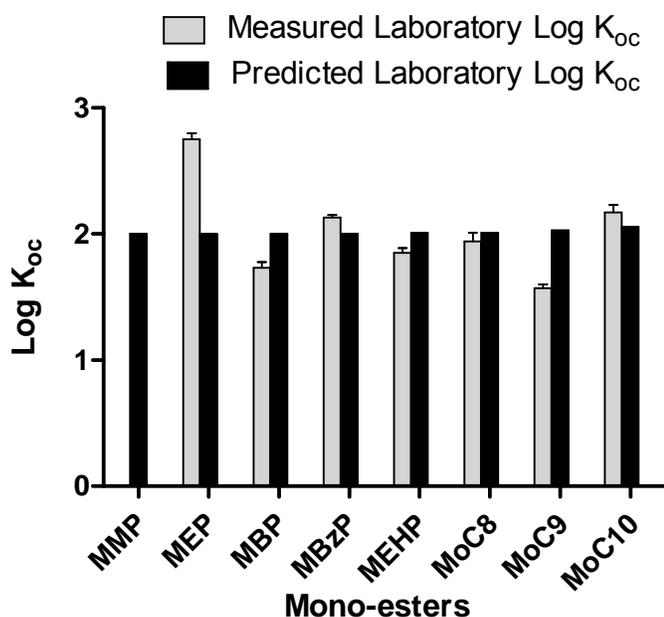
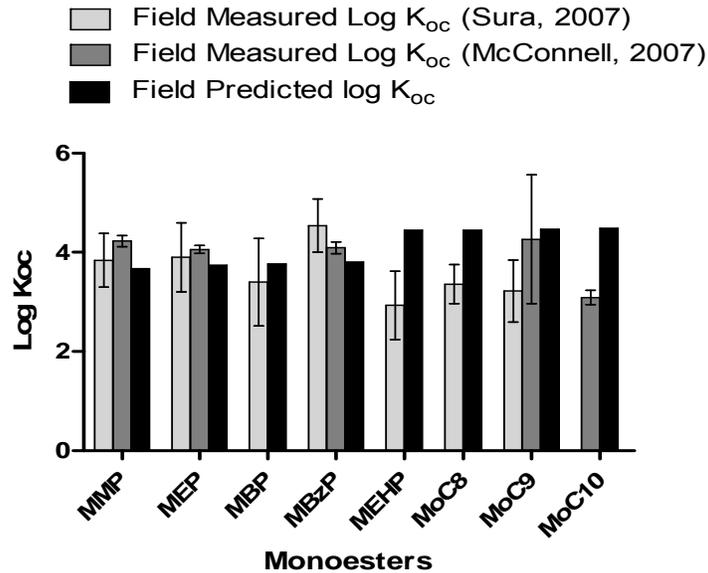


Figure 4.1-2 Comparison of the laboratory measured and predicted log K<sub>oc</sub> values of MPEs. Error bars represent 1 standard deviation of the mean. Measured values are adapted from Sura, 2007.

#### 4.1.3.2 Predicted log $K_{oc}$ values vs. log $K_{oc}$ values measured in the field

The results of the comparison of the field predicted log  $K_{oc}$  values for MPEs to the empirical field values are shown in Figure 4.1-3. **Error! Reference source not found.**



**Figure 4.1-3** Field measured and model predicted log  $K_{oc}$  values for MPEs. Log  $K_{oc}$  (Sura, 2007) are the mean log  $K_{oc}$  obtained from a study conducted by S. Sura (2007) and log  $K_{oc}$  (McConnell, 2007) are the mean log  $K_{oc}$  values obtained from a separate study conducted by M. McConnell (2007). The error bars represent standard deviation of the mean.

As it is demonstrated in Figure 4.1-3, there are two field measured Log  $K_{oc}$  values for each of the MPEs that were obtained from the two separate studies, with very similar results.

Table 4.1-7 illustrates that the model over-predicts the log  $K_{oc}$  values for MPEs by a logarithmic factor of 0.45 and a standard deviation of 0.85. Overall, the model's predictions are in reasonable agreement with the empirical data, but it slightly under-predicts log  $K_{oc}$  for the lower  $K_{ow}$  MPEs and slightly over-predicts log  $K_{oc}$  for the higher  $K_{ow}$  MPEs.

**Table 4.1-7 Measured (McConnell, 2007) and predicted log K<sub>oc</sub> values of MPEs (unitless) and calculated Mean Model Bias ±1 standard deviation of the mean.**

	<i>MMP</i>	<i>MEP</i>	<i>MnBP</i>	<i>MBzP</i>	<i>MEHP</i>	<i>MoC8</i>	<i>MoC9</i>	<i>MoC10</i>	
Measured Log K <sub>oc</sub>	3.84	3.90	3.40	4.54	2.93	3.36	3.22	-	
Predicted Log K <sub>oc</sub>	3.69	3.77	3.79	3.84	4.60	4.60	4.62	4.64	
Mean MB K <sub>oc</sub> ± STDEV									10 <sup>0.45±0.85</sup>

The log K<sub>oc</sub> values for MPEs measured in the field and in the laboratory are not in agreement with one another, as demonstrated previously (Sura, 2007; McConnell, 2007). This could be due to the absence of microbial activities after autoclaving the collected sediment in the laboratory. In addition, processes such as hydrolysis and photo-degradation often play a minor role in the natural environment (Staples, *et al.*, 1997). Overall, at the natural environment, MPE degradation is expected and the lack of biodegradation of MPEs in the lab can be explained.

#### **4.1.4 Environmental Fate Profiles for Each of the DPEs and Their MPE Metabolites**

To understand the environmental fate of each of DPEs, the overall fluxes of each DPE were examined separately. Processes such as the biodegradation of DPEs into their specific MPE metabolite, MPE ionization, and further degradation of MPE to phthalic acid could play key roles in the overall fate of these chemicals and need to be considered in understanding the overall fate of these chemicals.

To obtain a more complete understanding of the fate of phthalates and to simplify the discussion of the fate of phthalates in the environment, DPEs were divided into two groups: low log K<sub>ow</sub> phthalates and high log K<sub>ow</sub> phthalates. The low log K<sub>ow</sub> phthalates are DMP, DEP, DnBP, BBP and their respective metabolites. These substances share similarities in their environmental behaviour. The higher log K<sub>ow</sub> phthalates are DEHP,

C8, C9, C10, and their metabolites which also show similar environment behaviours among each other.

Figure 4.1-4 to Figure 4.1-19 illustrate the fate of each of the DPEs. These figures show model-predicted fluxes into different compartments of the conceptual model (Figure 2.1-1). The arrows indicate the relative magnitude of the flux in comparison to the rest of the fate processes of the specific chemical. The curved arrows indicate biodegradation pathways. The chemical enters the system through both the water and sediment compartments. In the water compartment, DPE biodegrade, volatilize, enter the sediment compartment, or flow out of the system. Similarly, once the DPE enters the sediment compartment, it can enter the water compartment, be buried, or be broken down via biodegradation pathways.

As described previously, DPEs can be broken down to form MPEs, thereby introducing MPEs into the system. The environmental fate profiles of the MPEs outlined below represent MPE formed from the parent DPE; there is assumed to be no significant external source of MPEs. At the pH of 8 in False Creek water, all MPEs overwhelmingly (99.99%) exist in their ionized form.

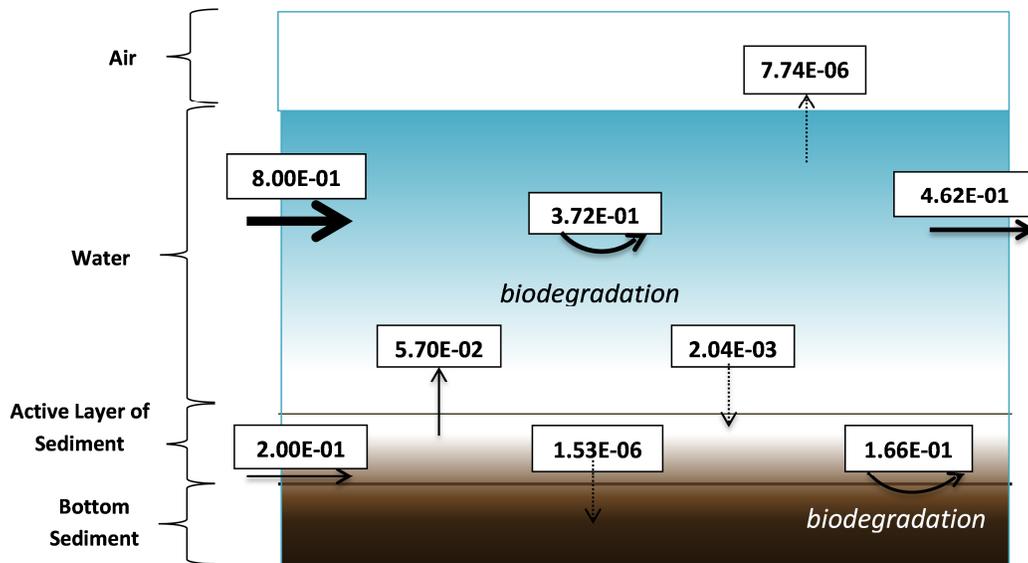
#### **4.1.4.1 Lower log $K_{ow}$ DPE and MPE environmental fate profiles**

DMP has the lowest molecular weight and  $K_{ow}$ . Due to unknown loadings of DPEs into False Creek, an arbitrary loading of 1 mol/day was used. As is shown in Figure 4.1-4, the model predicts that 0.8 mol/day and 0.2 mol/day DMP enter the water and sediment compartments, respectively. From the 0.8 mol/day entering the water compartment, a little less than half (0.37 mol/day) is biodegraded, but the majority leaves the system unchanged. There is little volatilization that takes place ( $7.74E-06$  mol/day). In addition, a small amount of  $2.04E-03$  mol/day enters the sediment compartment via

diffusion or settling processes. DMP has a much higher tendency to enter the water compartment in comparison to the sediment compartment. In fact, the overall sediment to water transport is 20 times higher than the water to sediment flux ( $5.70\text{E-}02$  mol/day vs.  $2.04\text{E-}03$  mol/day).

In the sediment compartment, of the  $0.2$  mol/day DMP that has entered sediment,  $1.66\text{E-}01$  mol/day is biodegraded and a very small amount is buried ( $1.53\text{E-}06$  mol/day). As shown here, volatilization and burial play insignificant roles in the overall fate of the DMP whereas biodegradation and outflow fluxes are the major contributors to the overall fate of the DMP.

A very similar pattern is observed for DEP in Figure 4.1-5, DnBP in Figure 4.1-6, and BBP in Figure 4.1-7. In addition, the water-to-sediment and sediment-to-water fluxes are very similar for DnBP and BBP.



**Figure 4.1-4 DMP Environmental fate profile showing the fluxes of DMP (mol/day) between different compartments of the model.**

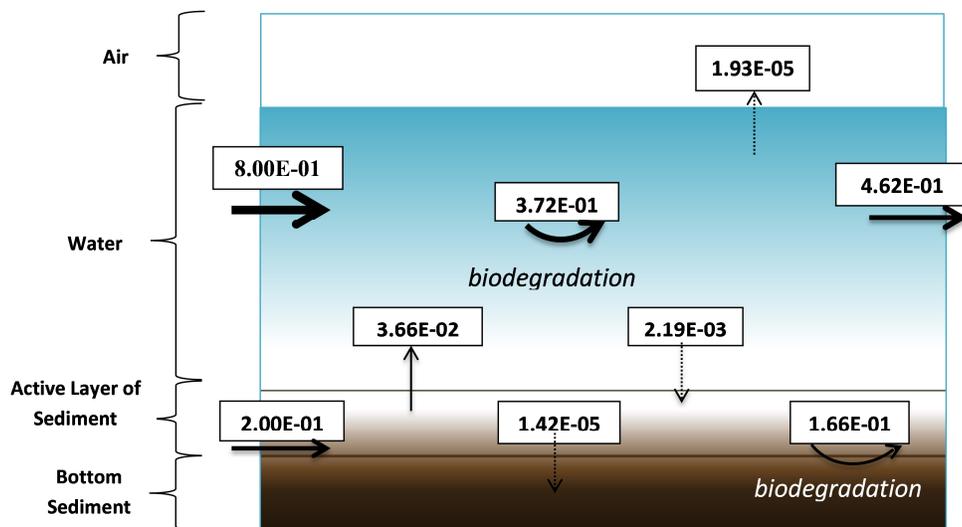


Figure 4.1-5 DEP Environmental fate profile showing the fluxes of DEP (mol/day) between different compartments of the model.

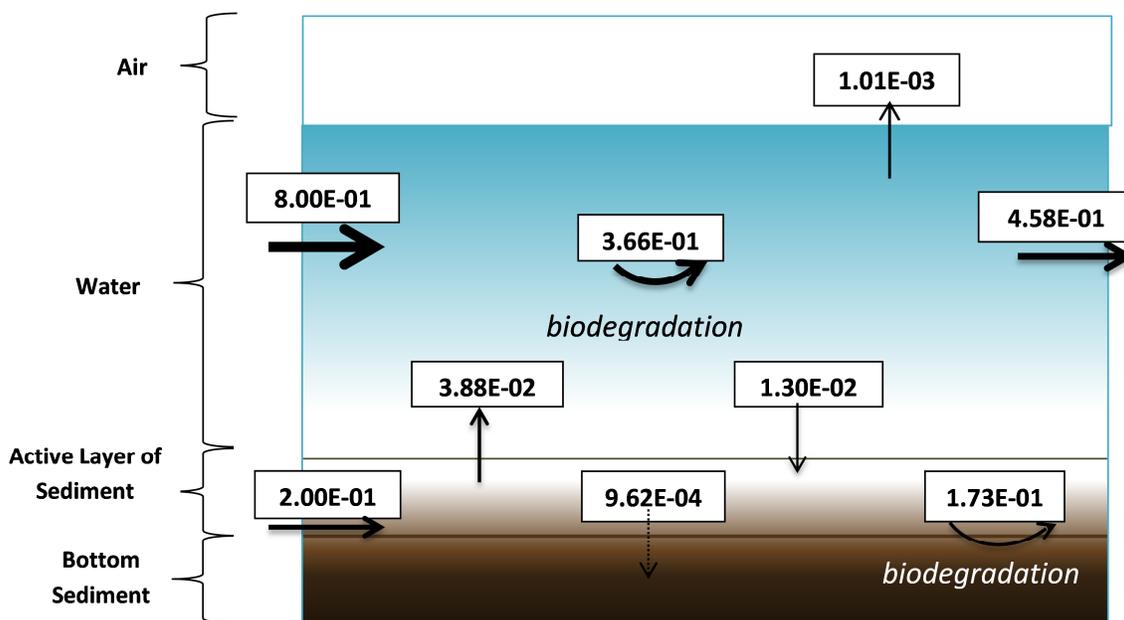
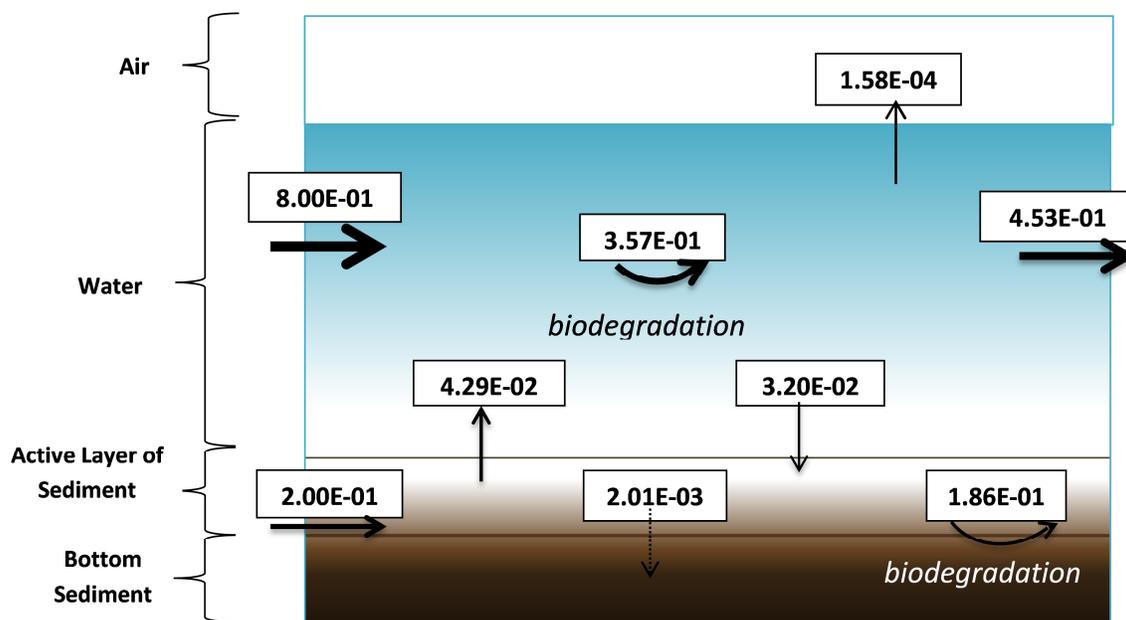


Figure 4.1-6 DnBP environmental fate profile showing the fluxes of DnBP (mol/day) between different compartments of the model.



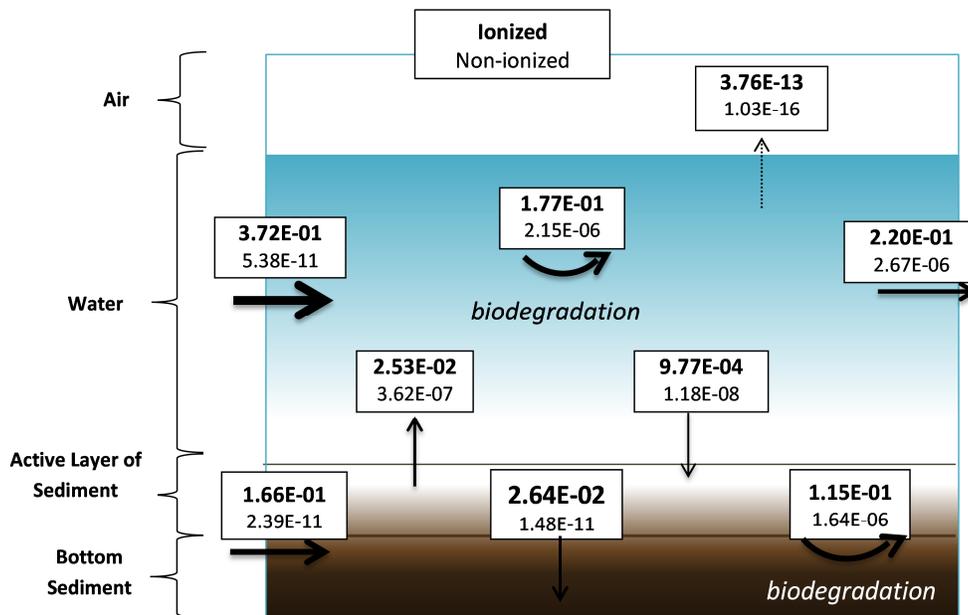
**Figure 4.1-7 BBP environmental fate profile showing the fluxes of BBP (mol/day) between different compartments of the model.**

A multimedia mass balance model for DBP has similar results to what has been found in this study (Cousins and Mackay, 2003). The authors used physical-chemical properties and a regional population based model to describe the concentrations of DnBP. However, the model does not include the fate of the metabolites and processes such as ionization.

The MPEs in the system are assumed to be formed resulting from the breakdown of the parent DPEs. The curved arrows in the fate and transport profiles indicate the input of monoesters into water and sediment and represent the breakdown of the DPE into its MPE metabolite. For example, in the case of DMP (Figure 4.1-4), 0.372 mol/day and 0.166 mol/day DMP undergo the biodegradation in the water and sediment compartments, respectively. As it is shown in Figure 4.1-8, 0.372 mol/day of MMP thus enters the water column and 0.166 mol/day MMP enters the sediment. The flux of non-ionized MPEs entering the system at the pH of False Creek is negligible.

Due to the high fraction that is ionized at pH 8, their high water solubility and a log D of -1.97, MMP has a much greater tendency (25 times) to reside in the water column rather than in the sediment compartment. As a result, some of the ionized MMEs ( $2.53\text{E-}02$  mol/day) leave the sediment compartment and enter the water column through both diffusion as well as the re-suspension of sediments. Overall, about half of the ionized MMP that has entered the water column is further biodegraded, while the remaining 50% leaves the system through outflow processes.

Biodegradation in the sediment also plays a significant role in the overall fate of MMP as the majority of MMP that has entered the sediment compartment will be biodegraded. Volatilization and burial play insignificant roles in the overall fate of the MMP.



**Figure 4.1-8 MMP Environmental fate profile showing the fluxes of MMP (mol/day) between the compartments. The ionized (the top bold values) and non-ionized MMP fluxes (the lower values) are shown in each box.**

A similar pattern is observed for other low log  $K_{ow}$  MPEs: MEP (Figure 4.1-9), MnBP (Figure 4.1-10), and MBzP (Figure 4.1-11). Overall, as MPEs are overwhelmingly ionized in the aquatic environment, they have relatively high water solubility and thus have a greater tendency to remain in the aquatic environment compared to the sediment compartment. In addition, the model shows that all of the low log  $K_{ow}$  MPEs readily undergo biodegradation processes.

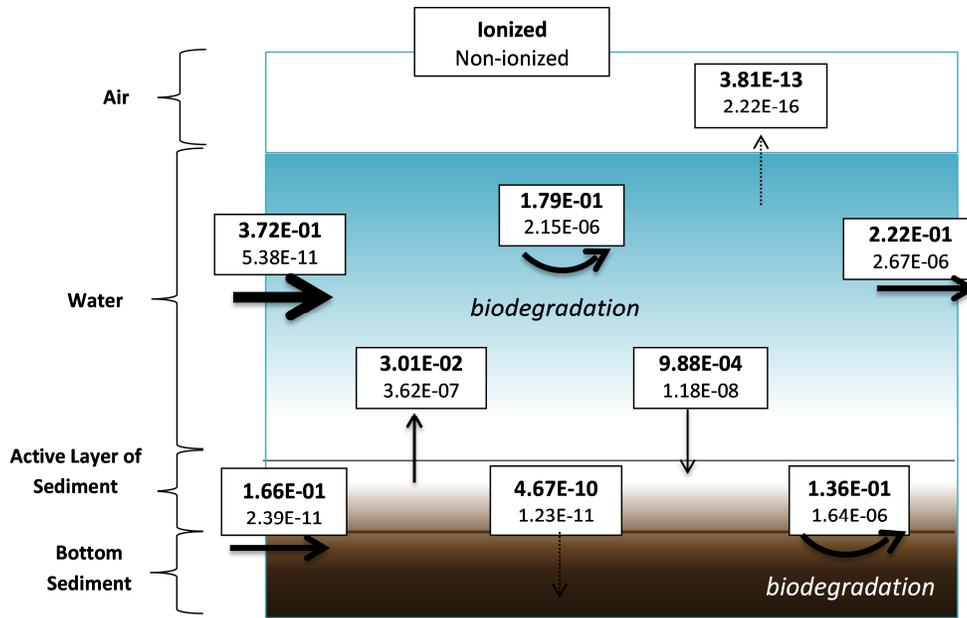


Figure 4.1-9 MEP Environmental fate profile showing the fluxes of MEP (mol/day) between the compartments. The ionized (the top bold values) and non-ionized MEP fluxes (the lower values) are shown in each box.

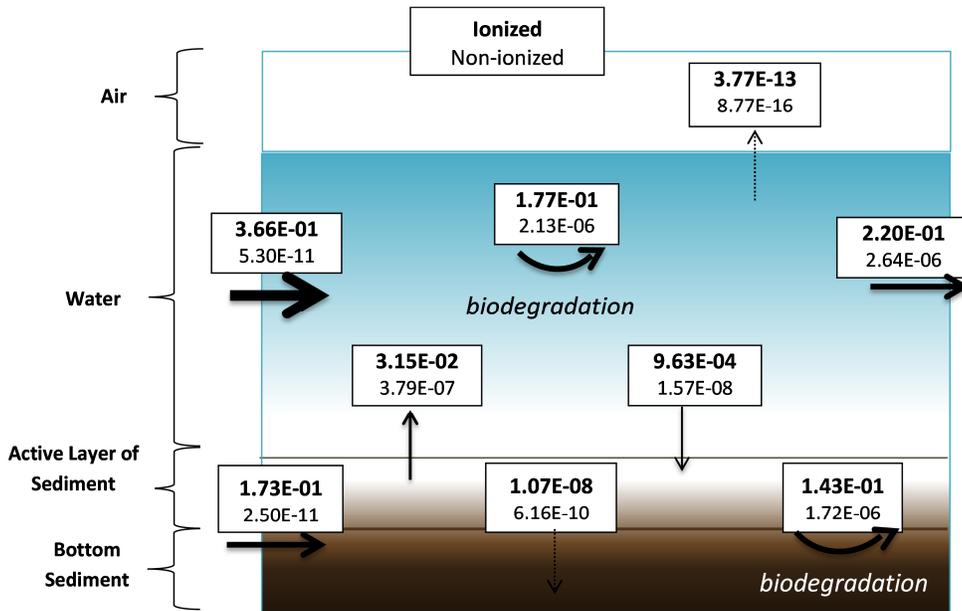
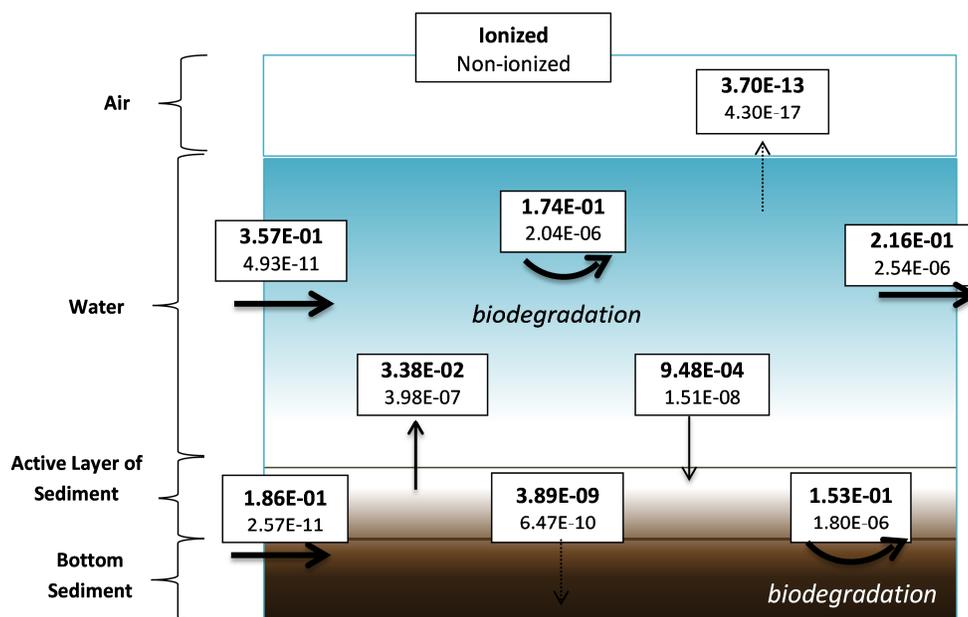


Figure 4.1-10 MnBP Environmental fate profile showing the fluxes of MnBP (mol/day) between the compartments. The ionized (the top bold values) and non-ionized MnBP fluxes (the lower values) are shown in each box.



**Figure 4.1-11 MBzP Environmental fate profile showing the fluxes of MBzP (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MBzP fluxes (the lower values) are shown in each box.**

#### 4.1.4.2 Higher log $K_{ow}$ DPE and MPE environmental fate profiles

High log  $K_{ow}$  phthalate esters have a different fate than the lower log  $K_{ow}$  ones. The following section analyses the behaviour of the higher molecular phthalates.

From examination of Figure 4.1-12, Figure 4.1-13, Figure 4.1-14, and Figure 4.1-15, it is evident that biodegradation of the higher log  $K_{ow}$  DPEs plays an insignificant role in their environmental fate, both in sediment and water. Sediment burial is the most important process. These chemicals have extremely high log  $K_{ow}$  values (log  $K_{ow}$  ranges from 8.2 to 10.6) and therefore have a much higher tendency to occur in the sediment compartment in comparison to water. Therefore, the overall water to sediment transport is higher than the overall sediment to water transport fluxes.

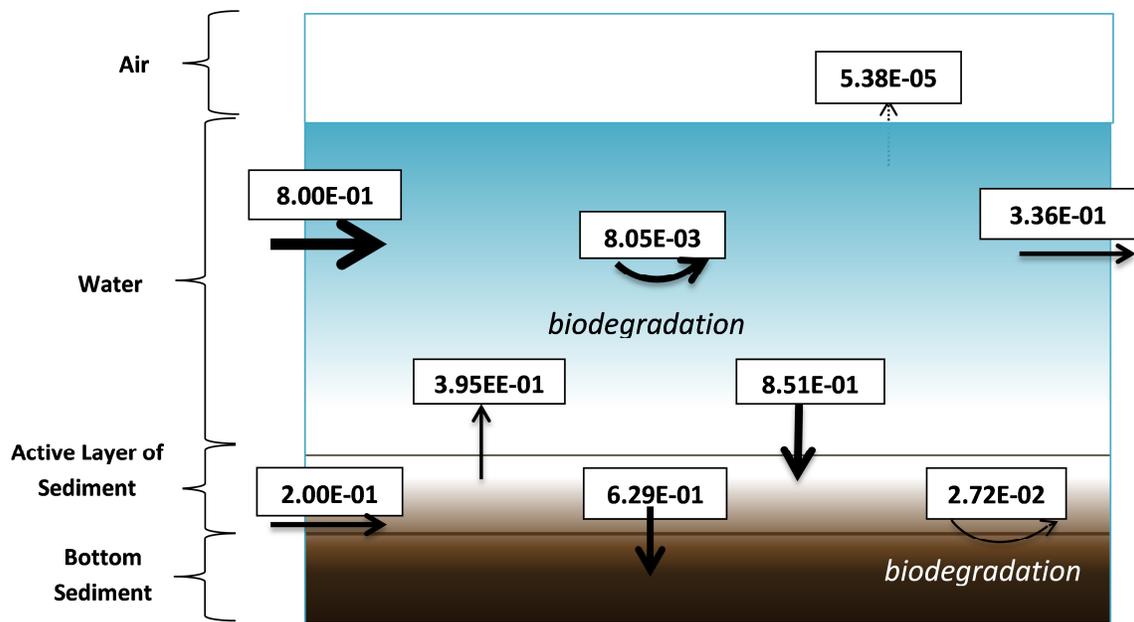


Figure 4.1-12 DEHP environmental fate profile showing the fluxes of DEHP (mol/day) between different compartments of the model.

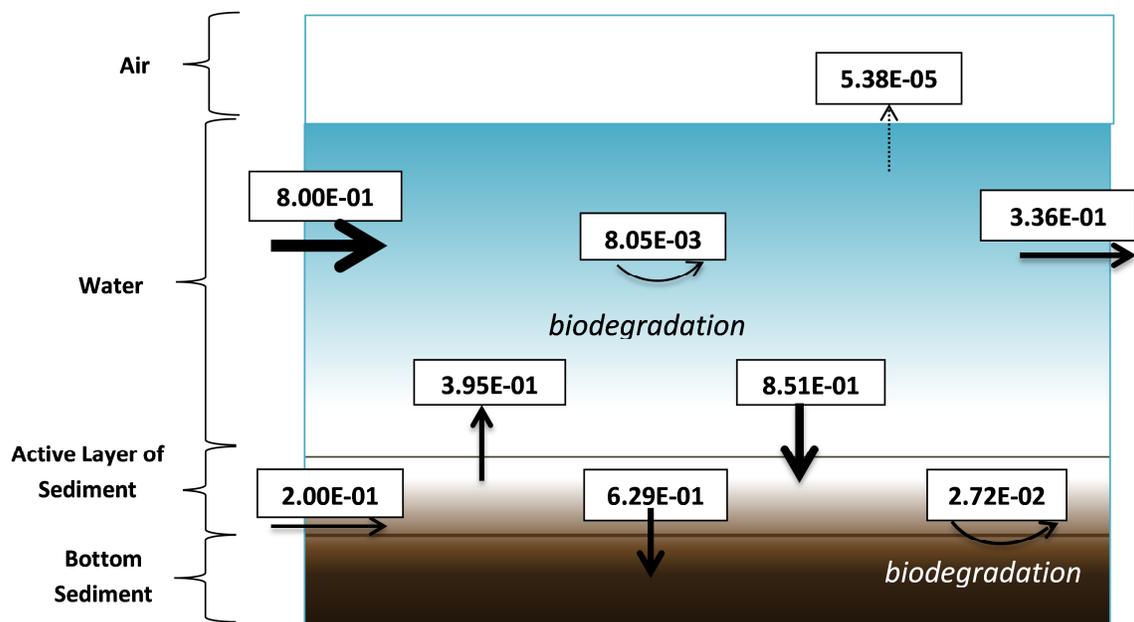


Figure 4.1-13 C8 environmental fate profile showing the fluxes of C8 (mol/day) between different compartment of the model.

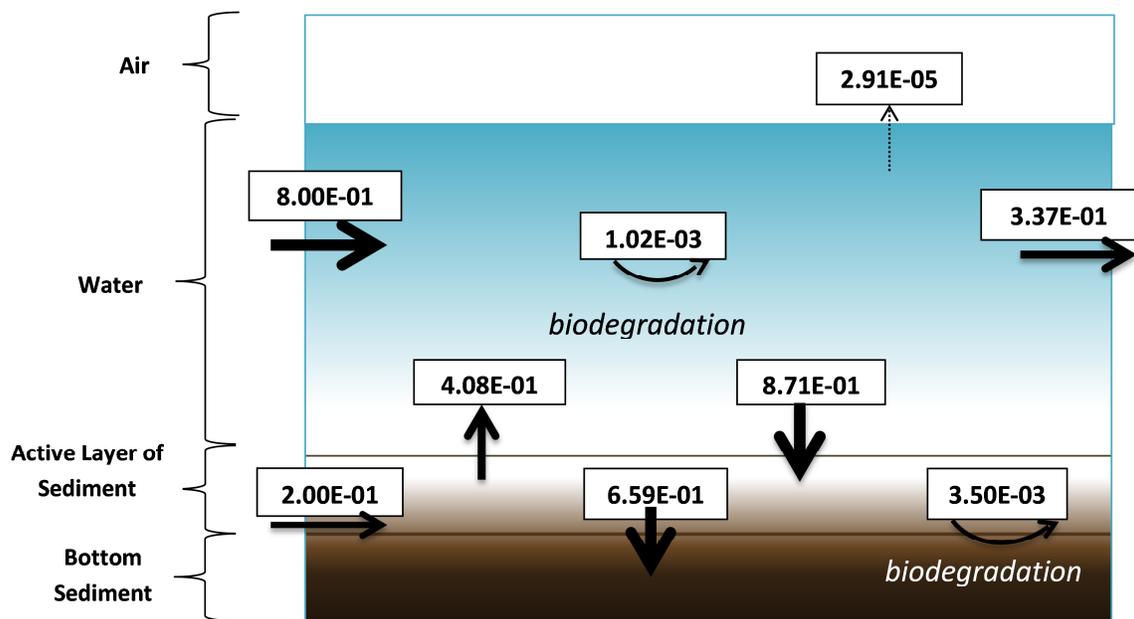


Figure 4.1-14 C9 environmental fate profile showing the fluxes of C9 (mol/day) between different compartment of the model.

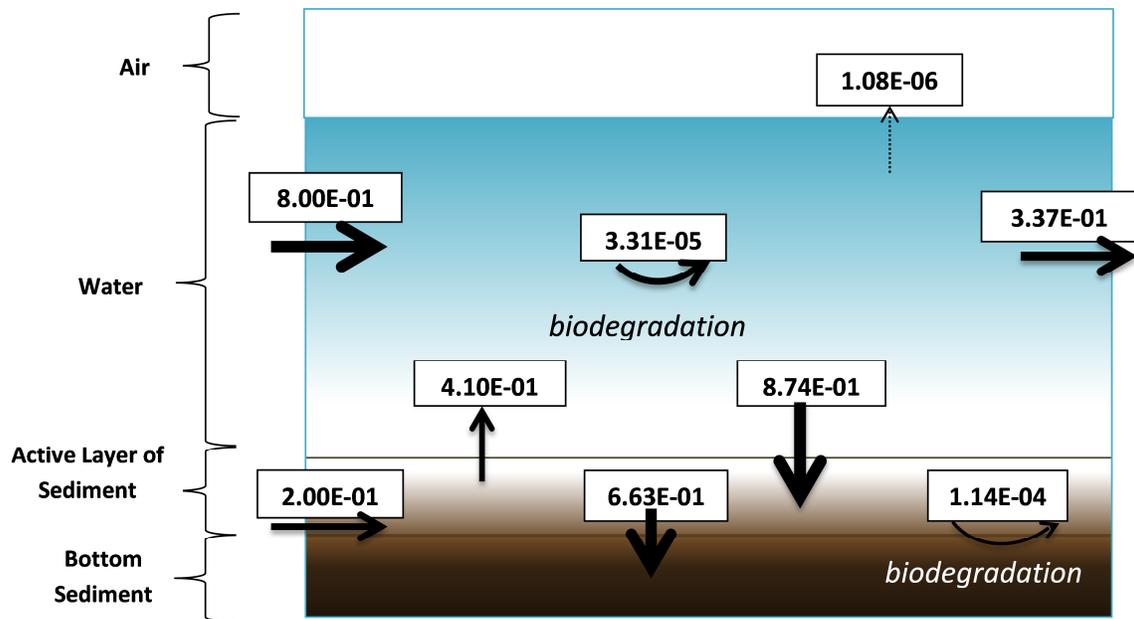
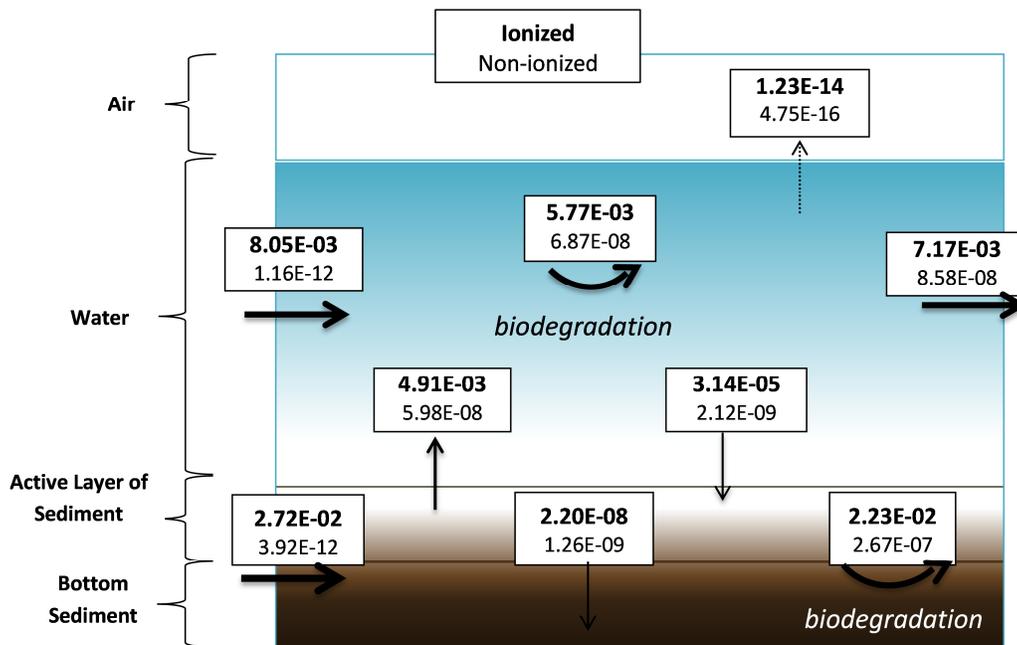


Figure 4.1-15 C10 environmental fate profile showing the fluxes of C10 (mol/day) between different compartments of the model.

Due to very low biodegradation rates of high log  $K_{ow}$  DPEs both in the sediment and water compartments, very little formation of MPE occurs. Of the very low amounts of MEHP and MoC8 that enter the system, the majority is biodegraded. The outflow flux of ionized MoC8 is less than 1% of the overall fate (Figure 4.1-20). This flux is even more insignificant in the case of MoC9 (less than 0.1%) and almost non-existent in the case of MoC10. The chemical specific fate for each of these high log  $K_{ow}$  MPEs is given in Figure 4.1-16 through Figure 4.1-19.

A model constructed by Cousins and Mackay (2003) also modelled the fate of DEHP in an aquatic environment. The behaviour of the DEHP and the portioning behaviour predicted in this model are very similar to their predicted fate. Their model did not include the fate of the corresponding MEHP and its ionization.



**Figure 4.1-16 MEHP Environmental fate profile showing the fluxes of MEHP (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MEHP fluxes (the lower values) are shown in each box.**

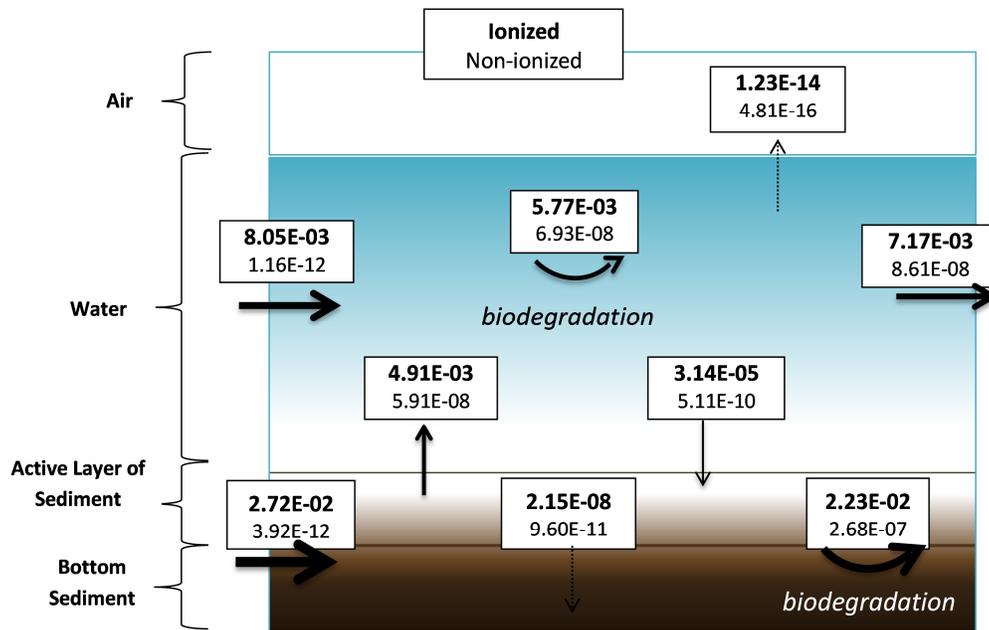


Figure 4.1-17 MoC8 Environmental fate profile showing the fluxes of MoC8 (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MoC8 fluxes (the lower values) are shown in each box.

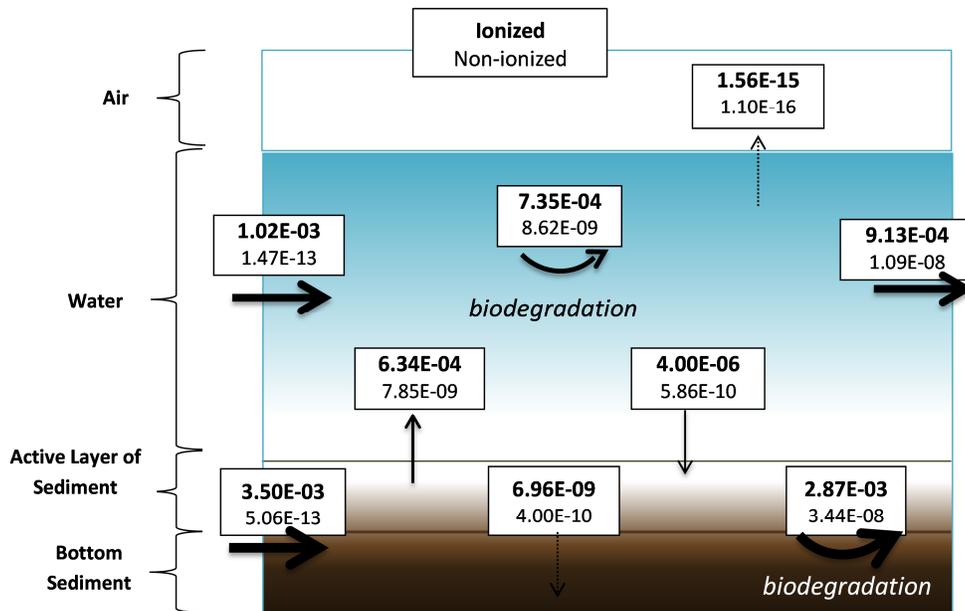


Figure 4.1-18 MoC9 environmental fate profile showing the fluxes of MoC9 (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MoC9 fluxes (the lower values) are shown in each box.

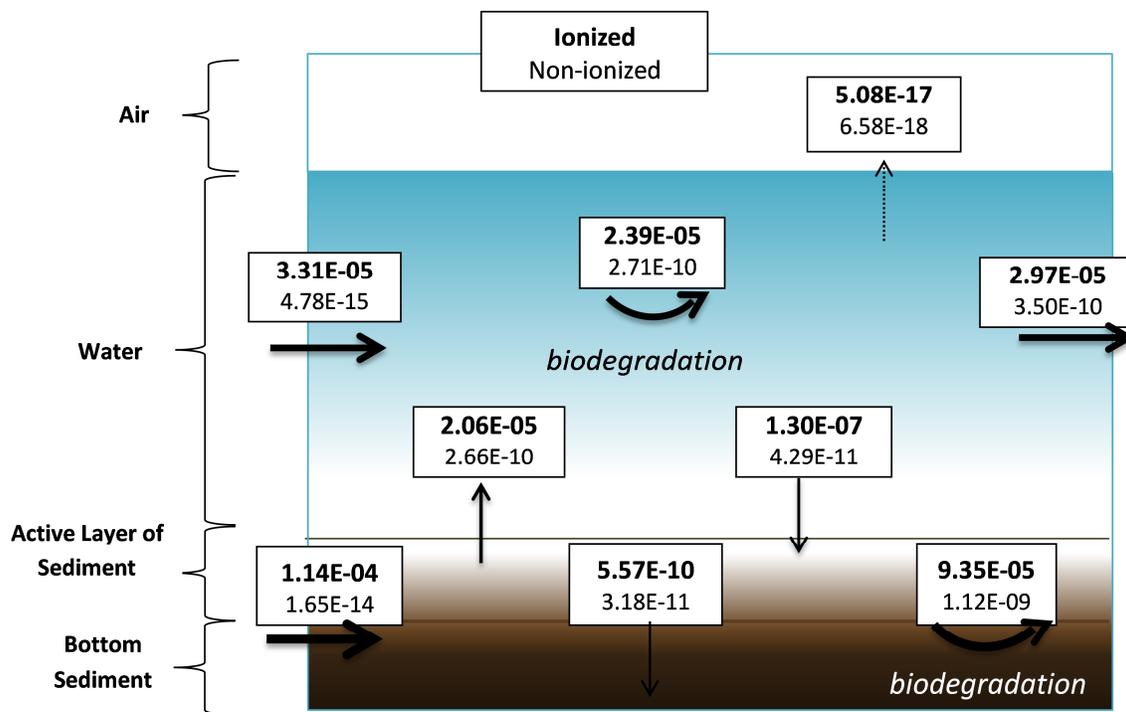


Figure 4.1-19 MoC10 environmental fate profile showing the fluxes of MoC10 (mol/day) between different compartments. The ionized (the top bold values) and non-ionized MoC10 fluxes (the lower values) are shown in each box.

#### 4.1.5 Overall environmental fate of phthalates

The fate of each of the phthalates varies with the physicochemical properties of each chemical. Figure 4.1-20 demonstrates the overall fate of each chemical. As is shown in Figure 4.1-20, the low log  $K_{ow}$  DPEs behave similar to each other but very differently from what is predicted for the high log  $K_{ow}$  DPEs.

Approximately 50% of low log  $K_{ow}$  PE flow out in the form of DPEs, about 30% of it is broken down to MPEs and ultimately to phthalic acid and other metabolites, and the remaining 20% flows out the system in the form of ionized MPE. In the case of the high log  $K_{ow}$  DPEs, 65% are buried, and the majority of the remaining 35% flows out of the system in the form of the unmetabolized DPE. In general, very little biodegradation takes place among the high log  $K_{ow}$  phthalates. Previous studies have also

demonstrated that in conditions similar to the natural environment, high log  $K_{ow}$  PEs degrade more slowly than the lower log  $K_{ow}$  PEs (Kickham, 2010, Zhang, *et al.*, 1998, Painter, *et al.*, 1990).

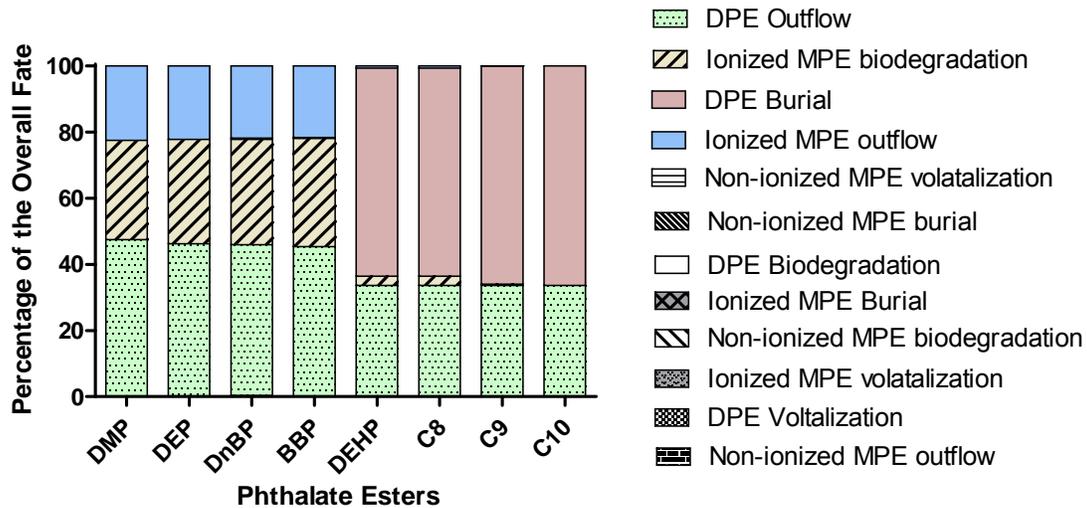
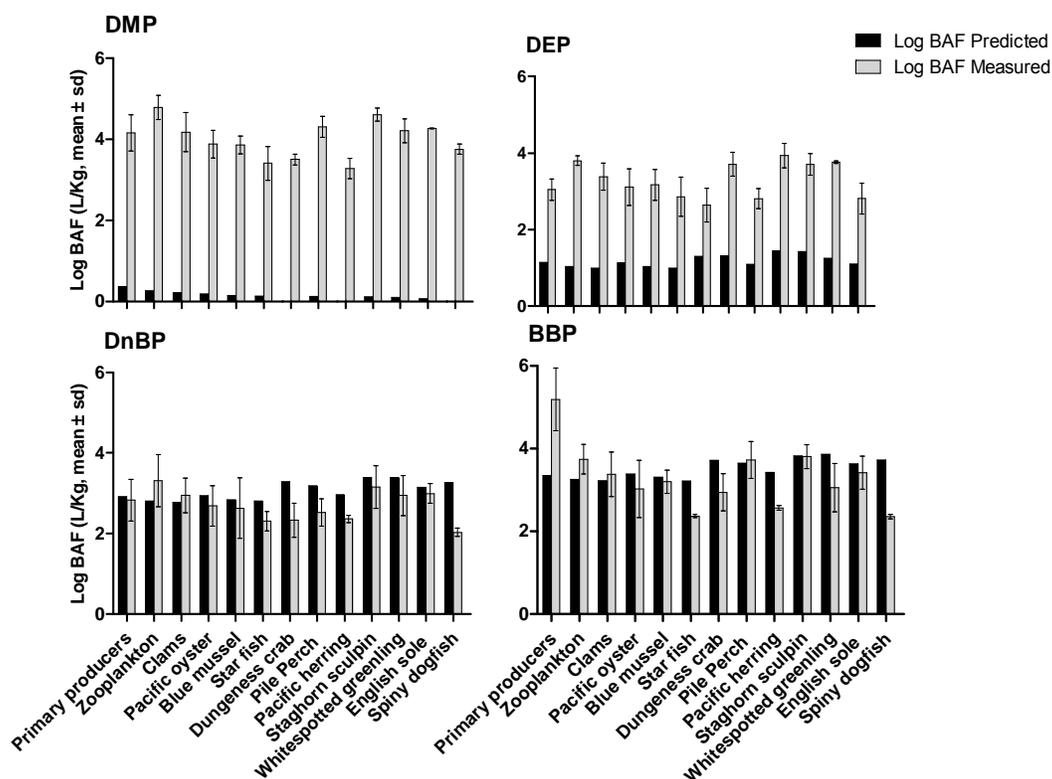


Figure 4.1-20 Environmental fate pathways of phthalate esters

## 4.2 Food Web Sub-model

### 4.2.1 Model calibration

Predicted BAF values as a result of model simulations in the absence of biotransformation processes are described in this Section. Figure 4.2-1 provides the log BAF values for the biota used in the model for the lower log  $K_{ow}$  DPE chemicals (DMP, DEP, DnBP, and BBP). Figure 4.2-2 provides the same results for the high log  $K_{ow}$  DPEs (DEHP, C8, C9, and C10).



**Figure 4.2-1 Model predicted and empirical log BAF values for low log  $K_{ow}$  DPEs prior to model calibration, when  $k_m = 0$ .**

As is demonstrated in Figure 4.2-1, the model grossly under-predicts the log BAF for DMP and DEP in all of the biota used in the model. Model predictions of the log BAF for DnBP and BBP are reasonable for most of the biota, except in a few cases. For DnBP, the log BAF value is over-predicted for starfish, pile perch, pacific herring, white-spotted greenling, and spiny dogfish. In the case of BBP, the model under-predicts log BAF values for primary producers and zooplankton, and it over-predicts the value for starfish, pacific herring, white-spotted greenling, as well as spiny dogfish.

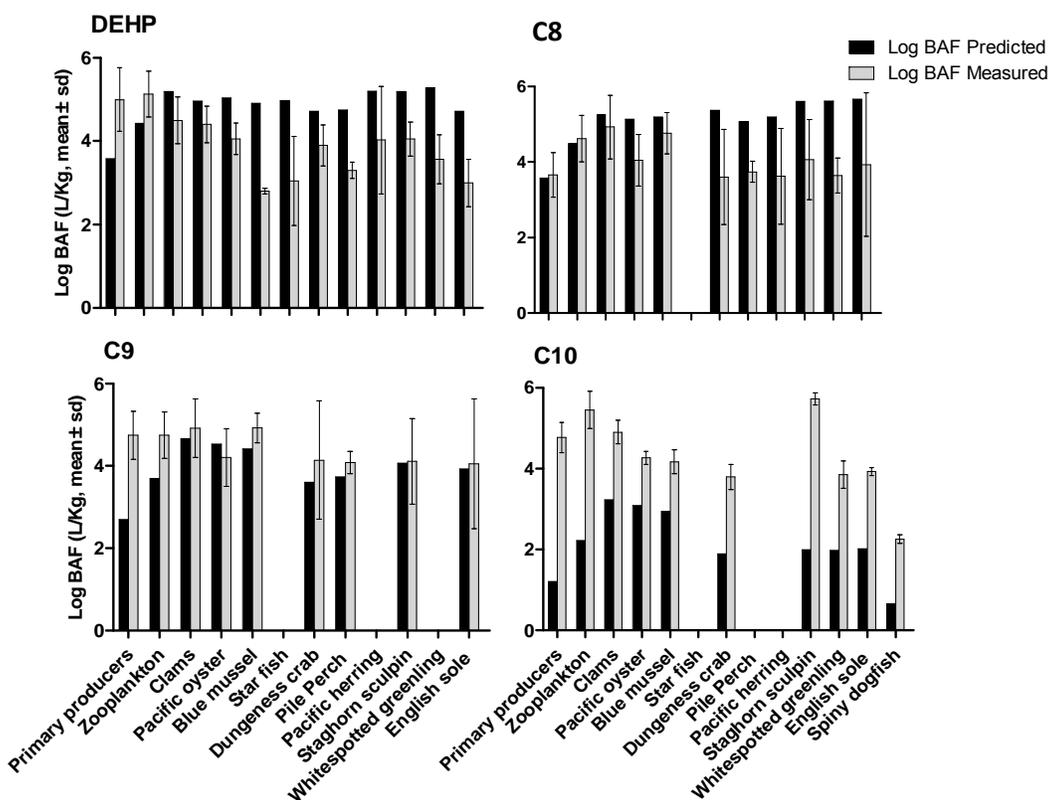


Figure 4.2-2 Model predicted and empirical log BAF values for high log  $K_{ow}$  DPEs prior to model calibration, when  $k_m = 0$ .

For DEHP, the model under-predicts the log BAF values for primary producers and zooplanktons while it over-predicts the value for blue mussels, starfish, Dungeness crab, pacific herring, and English sole (Figure 4.2-2). For C8, the model over-predicts the log BAF for pacific oysters, starfish, Dungeness crab, pile perch, and white-spotted greenling. For C9, the model under-predicts the log BAF for primary producers and zooplankton. Finally, for C10, the model under-predicts the log BAF for all the biota used in the model when compared with the available empirical log BAFs.

The over-prediction of the model could be due to biotransformation rates which can be addressed by model calibration. However, the under-prediction of the model is

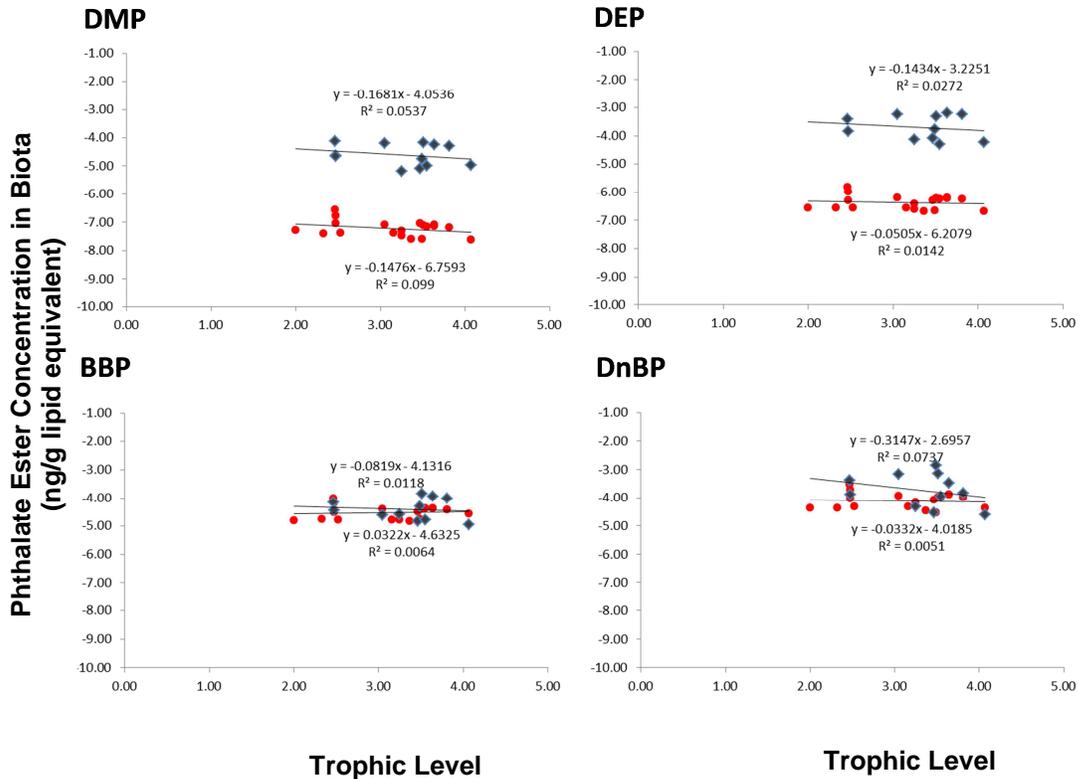
not easily addressed by calibration. For DEHP and DOP for which BAF in biota were over-predicted by the model, the model was calibrated by estimating a biotransformation rate constant that is applied to all the species in the food-web. Figure 4.2-3 provides an overview of the relationship between the predicted and measured log lipid normalized concentrations for the low log  $K_{ow}$  DPEs in various biota and the trophic position of each biota. The result of the regression analysis, comparing the predicted and observed TMF slopes, is presented in Appendix B-6.

As is shown in Figure 4.2-3, the slopes in the linear regressions of the measured and predicted log lipid normalized concentrations versus the trophic level of the low log  $K_{ow}$  DPEs are very similar. In fact, based on the result of the linear regression analysis conducted in S-Plus, the two slopes are not significantly different from one another for any of phthalate esters used in this study (please refer to Appendix B-7 for the relevant *p*-values).

Figure 4.2-3 and Figure 4.2-4 show the result of the regression for the predicted and observed slopes of lipid normalized biota concentrations compared with the trophic position of the biota for lower log  $K_{ow}$  and higher log  $K_{ow}$  phthalate esters, respectively. It is important to note that the log lipid normalized biota concentrations are dependent on the loadings of DPEs into False Creek. In other words, the observed and predicted concentrations can be tuned by adjusting the DPE loadings. The slope of the line however, is independent of the loading concentrations and therefore the comparison of the measured and predicted slopes gives valuable information about the model performance.

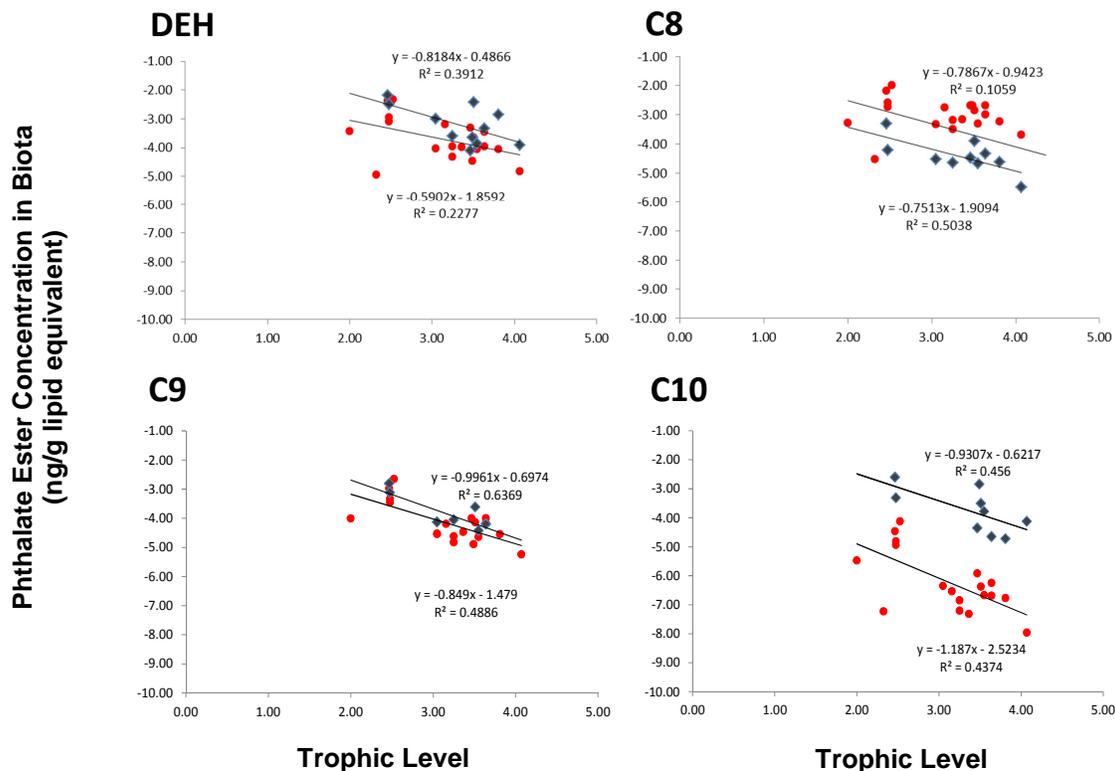
The flat regression lines observed in Figure 4.2-3 indicate the absence of biodilution of these chemicals which is consistent with previous studies (McConnell, 2007). The absence of biodilution in the lower log  $K_{ow}$  phthalate esters could be explain

by the lower biotransformation rate constant ( $k_m$ ) in comparison to the remaining elimination rate constants ( $k_2+k_e+k_g$ ).



**Figure 4.2-3** Log lipid normalized concentration versus trophic level for the lower log  $K_{ow}$  DPEs, DMP, DEP, DnBP, and BBP. The blue diamonds represent measured concentrations (Mackintosh, *et al.*, 2004) and the red circles represent the model predicted concentrations.

For the higher log  $K_{ow}$  DPEs (Figure 4.2-4), the negative slope of the regression analysis between the measured biota concentrations and trophic level of the biota for DEHP, C9, and C10 was significant (McConnell, 2007). Similarly, the predicted slopes of these phthalate esters were also significantly different from zero and were consistent with the observed slopes. The significant negative slope is indicative of biodilution in these higher log  $K_{ow}$  phthalate esters (Mackintosh, 2002; McConnell, 2007). For further information on the  $p$ -values and other relevant statistical measures, please refer to Appendix B-6.



**Figure 4.2-4** Log lipid normalized concentration versus trophic level for the higher log  $K_{ow}$  DPEs, DEHP, C8, C9, and C10. The blue diamonds represent measured concentrations (Mackintosh, et al, 2004) and the red circles represent the model predicted concentrations.

Solver was not able to provide a value for a universal (across species) biotransformation rate constant that minimized the difference between the two slopes (measured and predicted) for DMP, DEP, DnBP, BBP, C9 and C10 phthalate esters since the predicted concentrations were less than the measured values.

As mentioned earlier, because no measured DPE biotransformation rate constants are available for the biota used in the model, a universal biotransformation rate for each DPE was estimated by estimating the difference between measured and model predicted TMF values (Figure 4.2-3 and Figure 4.2-4).

Table 4.2-1 contains the measured and predicted TMFs and the 95% confidence levels, as well as the Excel Solver solution for minimizing the difference between these values. TMF values for most of the PEs (DMP, DEP, DnBP, BBP, C9, and C10) were under-predicted by the model. In such instances, no universal biotransformation rate could be derived. This is mainly because it is difficult to account for other input routes of DPEs into the biota in addition to the gill respiration and dietary uptake routes used in this study.

In case of DEP and C8, where the measured concentrations were smaller than the predicted ones, solver provides a solution to minimize the difference between the two slopes and the model was calibrated by the estimated biotransformation rates (Table 4.2-1). It is possible that in cases where the model could not estimate the biotransformation, the biotransformation rates are too small when compared with other routes of elimination.

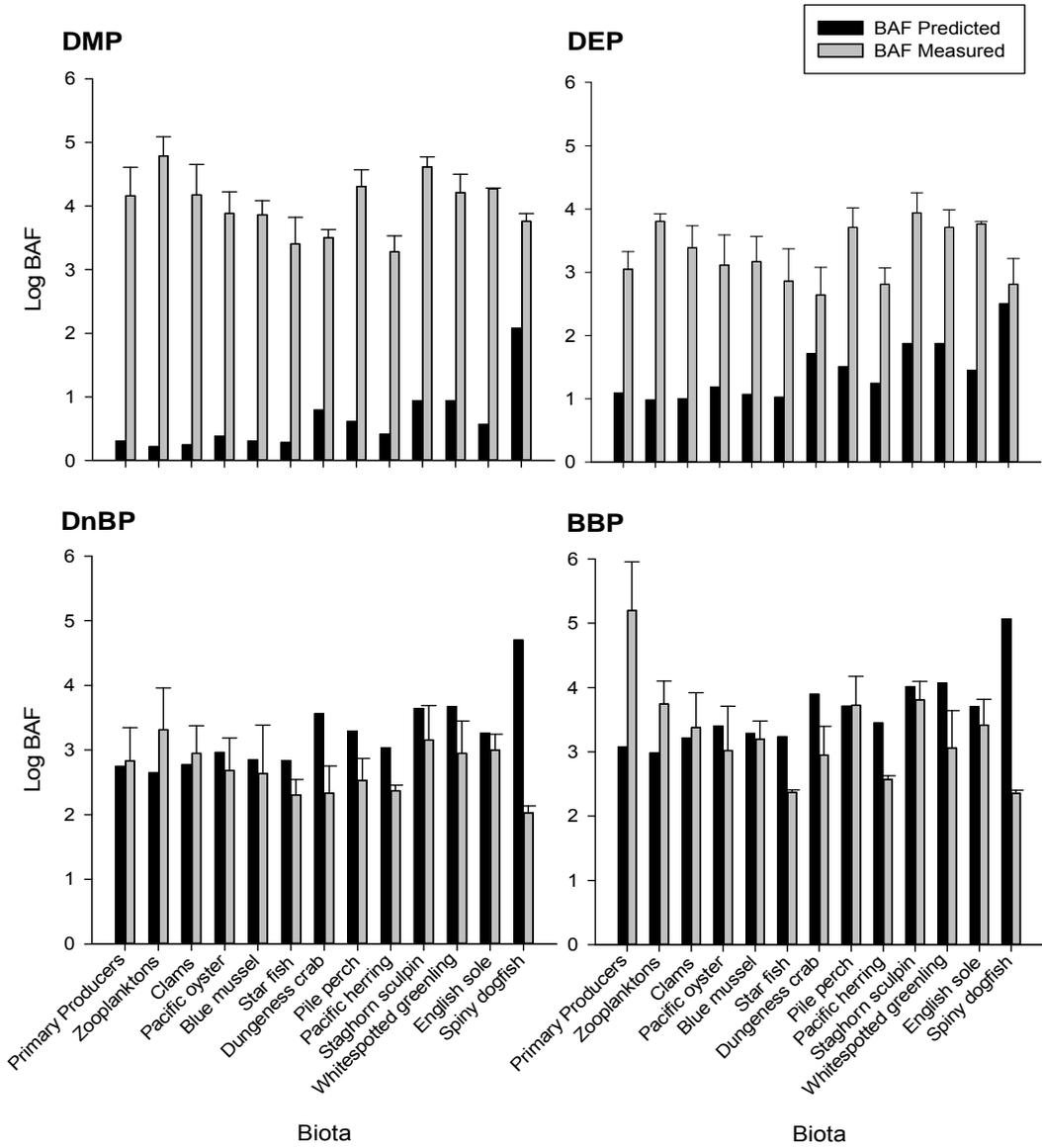
**Table 4.2-1 Measured and predicted Trophic Magnification Factors (TMF) for DPEs, the Solver Solution for Minimizing the Difference between the Two Slopes and the Estimated Universal Biotransformation Rate Constant. Values in the parenthesis are the 95% Confidence Limit range.**

Chemical	Measured TMF (TMF <sub>M</sub> )	Model Predicted TMF (TMF <sub>P</sub> )	Solver Solution	Universal Biotransformation Rate Constant (k <sub>m</sub> )
<b>DMP</b>	0.68 (0.21 – 2.13)	0.68 (0.42 – 1.11)	n/a	-
<b>DEP</b>	0.72 (0.16 – 3.19)	0.89 (0.54 – 1.46)	n/a	-
<b>DnBP</b>	0.82 (0.22 – 3.04)	1.08 (0.67 – 1.73)	n/a	-
<b>BBP</b>	0.48(0.07 – 3.36)	0.93 (0.53 – 1.59)	n/a	-
<b>DEHP</b>	0.15 (0.03 – 0.89)	0.26 (0.07 – 0.92)	4.64E-07	1.42E-02
<b>C8</b>	0.21 (0.03 – 1.50)	0.78 (0.25 – 2.45)	9.28E-07	2.09E-03
<b>C9</b>	0.09 (0.01 – 0.80)	0.14 (0.05 – 0.39)	n/a	-
<b>C10</b>	0.12 (0.01 – 0.95)	0.06 (0.01 – 0.29)	n/a	-

As mentioned earlier, because no measured DPE biotransformation rate constants are available for the biota used in the model, a universal biotransformation rate for each DPE was estimated by estimating the difference between measured and model predicted TMF values (Figure 4.2-3 and Figure 4.2-4). Table 4.2-1 contains the measured and predicted TMFs and the 95% confidence levels, as well as the Excel Solver solution for minimizing the difference between these values.

Once the k<sub>m</sub> was estimated and included in the model, the empirical log BAFs were once again compared with model-predicted values that include estimates of the

biotransformation process (if available). Figure 4.2-5 and Figure 4.2-6 show the result of this comparison. The graphs for DMP, DEP, DnBP, BBP, C9, and C10 are identical to those previously discussed (Figure 4.2-1 and Figure 4.2-2) due to the absence of biotransformation rates. However, the predicted log BAF values for DEHP and C8 are in good agreement with the empirical log BAF values (Figure 4.2-5 and Table 4.2-2)



**Figure 4.2-5 Model predicted and empirical Log BAF values for low log  $K_{ow}$  DPEs after the estimation and inclusion of a universal biotransformation rate constant.**

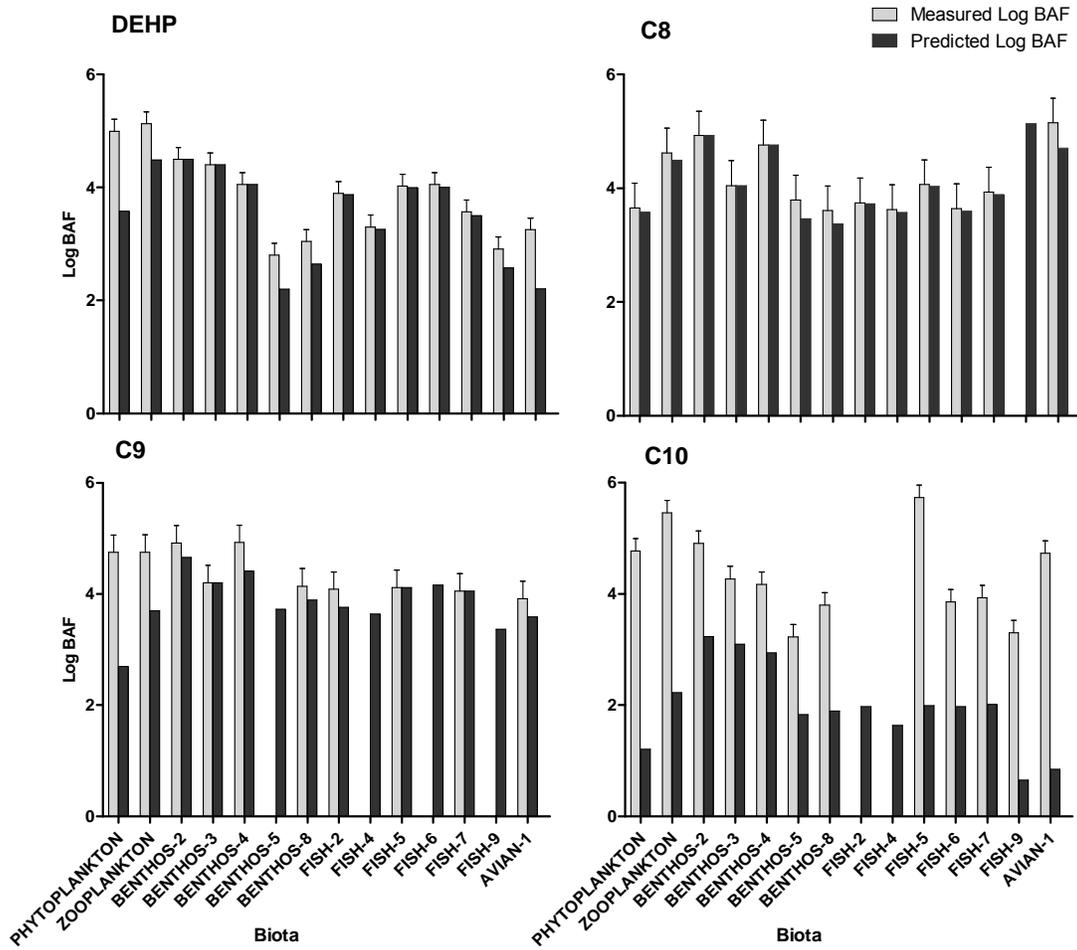


Figure 4.2-6 Model predicted and empirical log BAF values for higher log  $K_{ow}$  DPEs after the estimation and inclusion of a universal biotransformation rate constant.

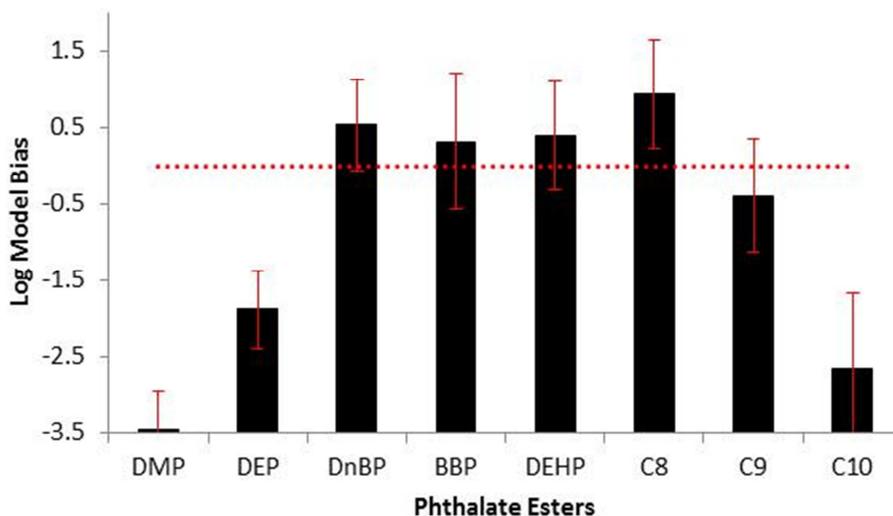
#### 4.2.2 Food Web Sub-model Model Performance

Overall, the model under-predicts the BAF values. Mean model bias based on individual DPEs across the food web for is shown in Table 4.2-2 and Figure 4.2-7.

**Table 4.2-2 Chemical based log Mean Model Bias and the associated standard deviation of the mean.**

<i>Chemical</i>	<i>Mean MB ± STDVE</i>
<b>DMP</b>	$10^{(-3.44276 \pm 0.50)}$
<b>DEP</b>	$10^{(-1.87809 \pm 0.51)}$
<b>DnBP</b>	$10^{(0.538499 \pm 0.59)}$
<b>BBP</b>	$10^{(0.322206 \pm 0.88)}$
<b>DEHP</b>	$10^{(0.399914 \pm 0.70)}$
<b>C8</b>	$10^{(0.939105 \pm 0.71)}$
<b>C9</b>	$10^{(-0.38438 \pm 0.73)}$
<b>C10</b>	$10^{(-2.6538 \pm 0.99)}$

The model under-predicts BAF for the low log  $K_{ow}$  DPEs such as DMP and DEP, as well as for the PEs with higher log  $K_{ow}$ , i.e., C8 and C10. For the remaining DPEs, the model predictions are within one standard deviation of log MB = 0, and provide an acceptable MB for these chemicals.

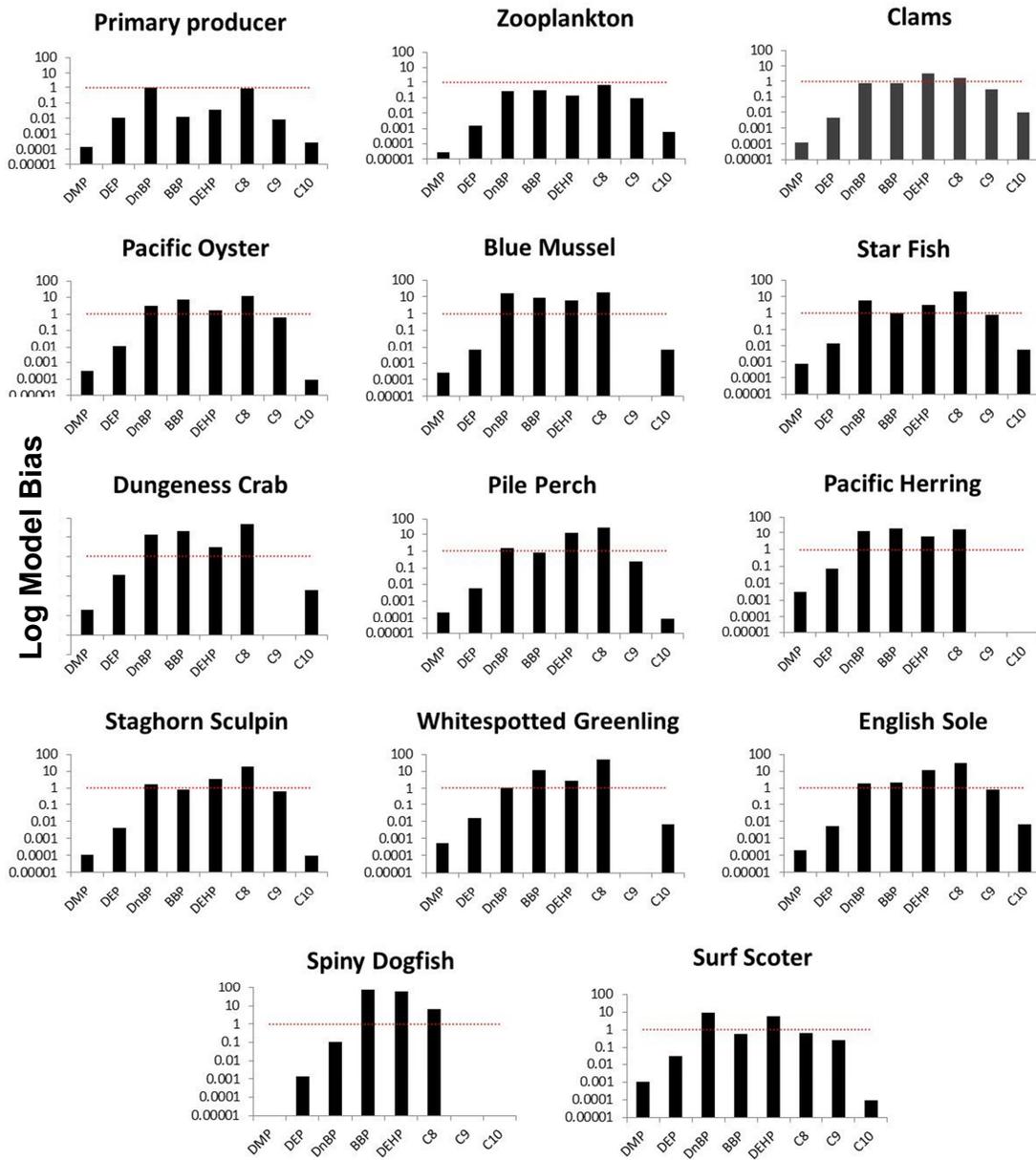


**Figure 4.2-7 Overall log model bias of the individual DPEs. Values above the dashed red line (log MB=0) are over predicted by the model and values below the dashed red line are under predicted. The error bars represent one standard deviation from the mean.**

Figure 4.2-8 provides a more detailed examination of MB for each DPE in each biota. Log BAF of DMP, DEP, and C10 are under-predicted in all the biota in this study.

This is probably due to incorrect measured concentrations of DPEs because of the very low concentrations of DPEs. The model under-predicts log BAF for almost all of the DPEs in primary producers and zooplankton. Log BAF of DnBP is over-predicted for most of the biota except in lams. Model bias based on log BAF for DnBP in white-spotted greenling, English sole, and spiny dogfish is very close to the value of 1.

Log BAFs of BBP are also over-predicted in most of the biota species, except in clams and surf scoter. However, model bias of log BAF for BBP in pile perch, staghorn sculpin, and English sole is close to the value of 1. DEHP log BAF model bias exceeds a value of 1 in all of the biota, but is closest to a value of 1 in organisms that are primarily benthic dwelling (pacific oyster, starfish, Dungeness crab, and white-spotted greenling). The model bias for C8 exceeded the value of 1 for all of the species in this study, except in spiny dogfish and surf scoter which are on top of the food chain. Model bias for C9 was close to the value of 1 for most species.



**Figure 4.2-8 Model bias calculated from the ratios of model predicted and empirical BAFs for individual DPEs in various biota.**

Under-prediction of BAF by the model in most of the species could be due to several reasons. High mobility of some organisms in the food web (e.g. fish) may cause the modelled BAF values to be unrepresentative. It is unclear whether the biota concentrations are truly the result of the exposure in False Creek and representative of the concentrations in this area.

Since the environmental fate model is based on the relationship between DPE concentrations in water and organic carbon normalized sediment, the model is highly sensitive to changes in this relationship. If water concentrations are over-estimated due to sampling artefacts or if the concentrations have not reached equilibrium in water, the model is likely to over-predict BAFs. Since the model is able to predict the log  $K_{oc}$  values for both monoester and di-esters with reasonable precision, the low model bias for most of the species is likely to be due to sampling artefacts. However, any deviations of the predicted log  $K_{oc}$  from the true environmental partitioning of phthalates are expressed through uncertainties associated with the food web sub-model, which could result in the under-predictions and over-predictions observed in the model.

#### **4.2.3 Fate of DPEs in biota**

Figure 4.2-9 to Figure 4.2-16 show the calculated fluxes of DPEs in four of the biota used in the model: blue mussels, Dungeness crabs, Pacific staghorn sculpin, and spiny dogfish.

Blue mussels and Dungeness crabs are at trophic levels of 2.53 and 3.55, respectively, and represent benthic organisms. Pacific staghorn sculpin and spiny dogfish are at trophic levels of 3.18 and 3.54, respectively, and represent pelagic species. Blue mussels and Dungeness crabs are less mobile and more representative of the

resident species exposed to DPEs in False Creek. Pacific staghorn sculpin and spiny dogfish spend a considerable time in the False Creek area but are mainly residents of the Georgia Basin area (Mackintosh, 2002).

For each figure,  $D_1$  represents the gill uptake flux (mol/day),  $D_2$  represents gill elimination flux (mol/day),  $D_d$  represents dietary uptake flux (mol/day),  $D_e$  represents fecal egestion flux (mol/day),  $D_g$  represents the growth dilution flux (mol/day), and  $D_m$  represents the biotransformation flux (mol/day) within each organism.

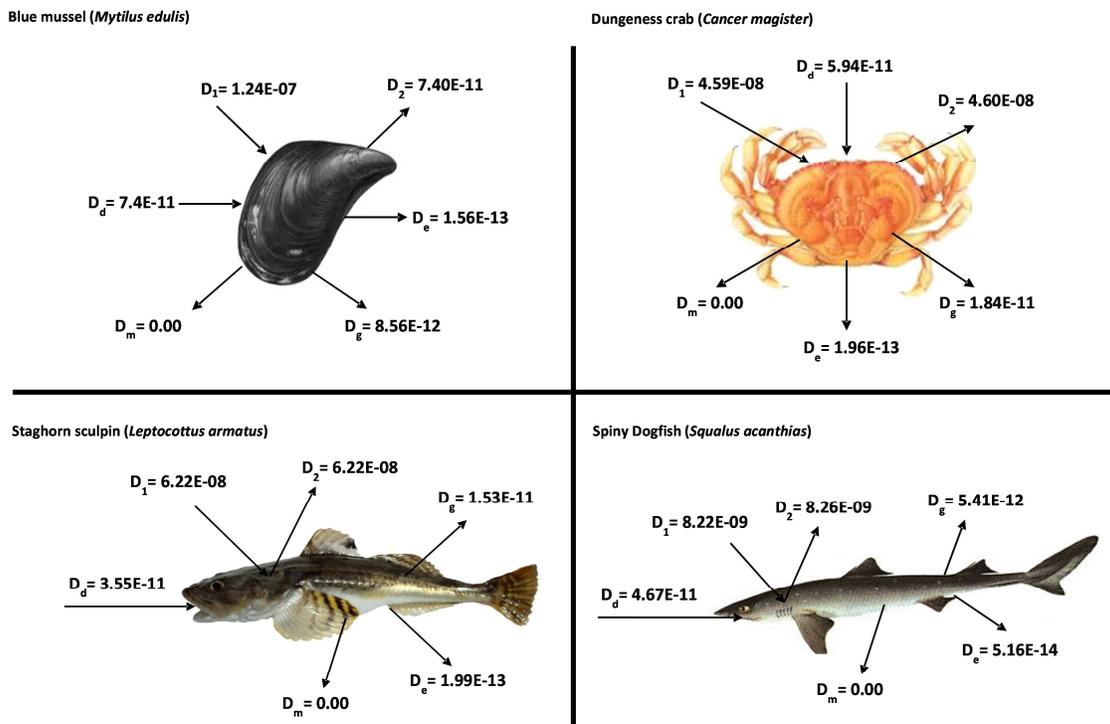


Figure 4.2-9 DMP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish.

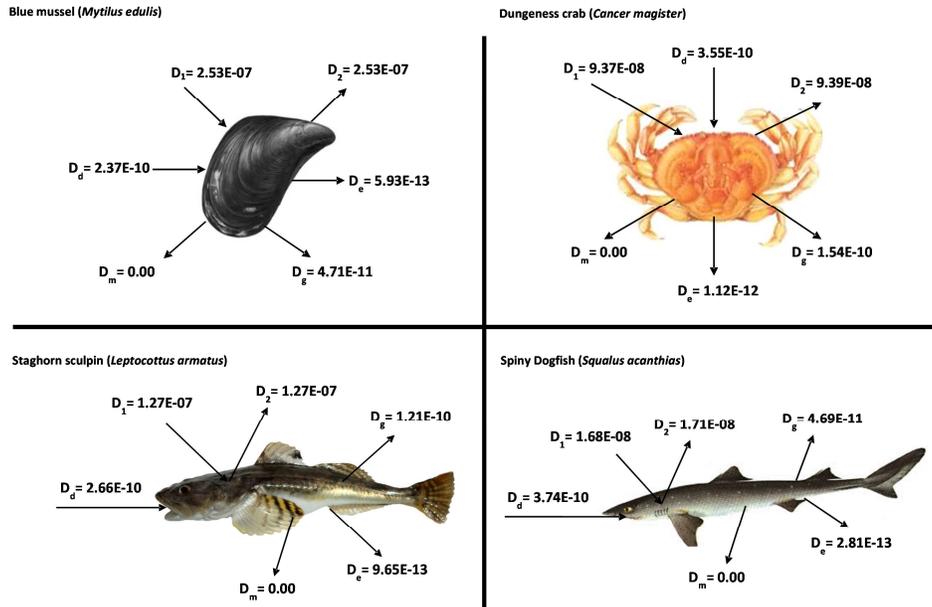


Figure 4.2-10 DEP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish.

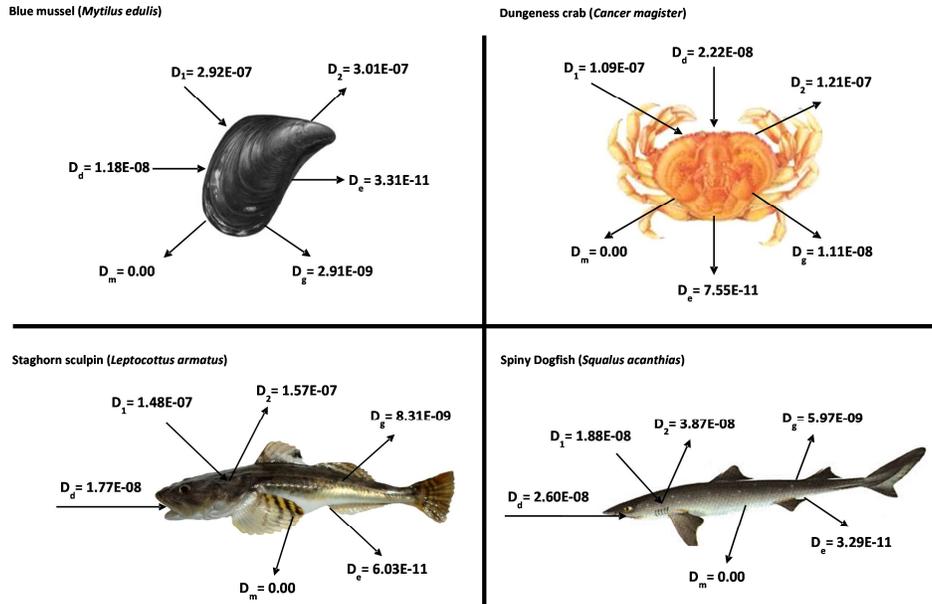


Figure 4.2-11 DnBP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish.

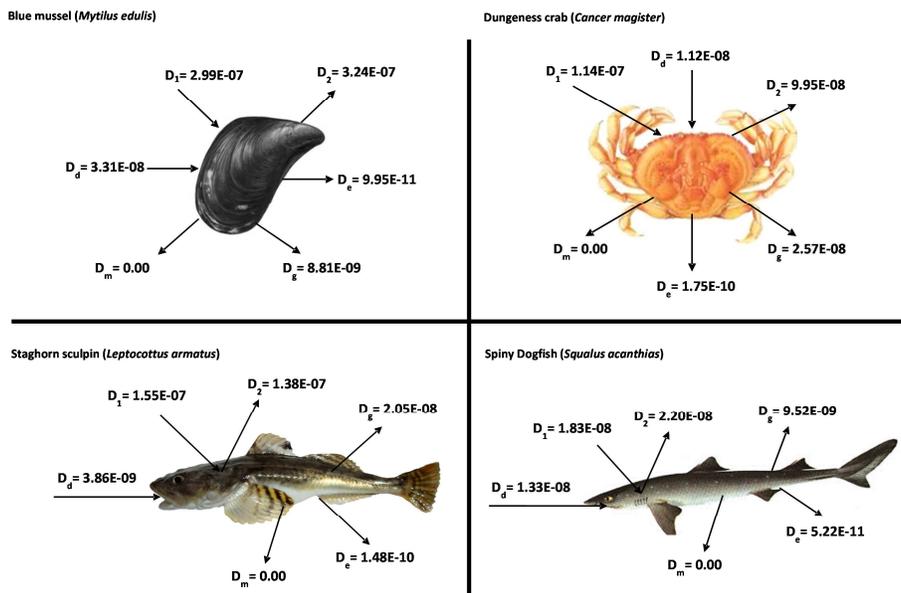


Figure 4.2-12 BBP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish.

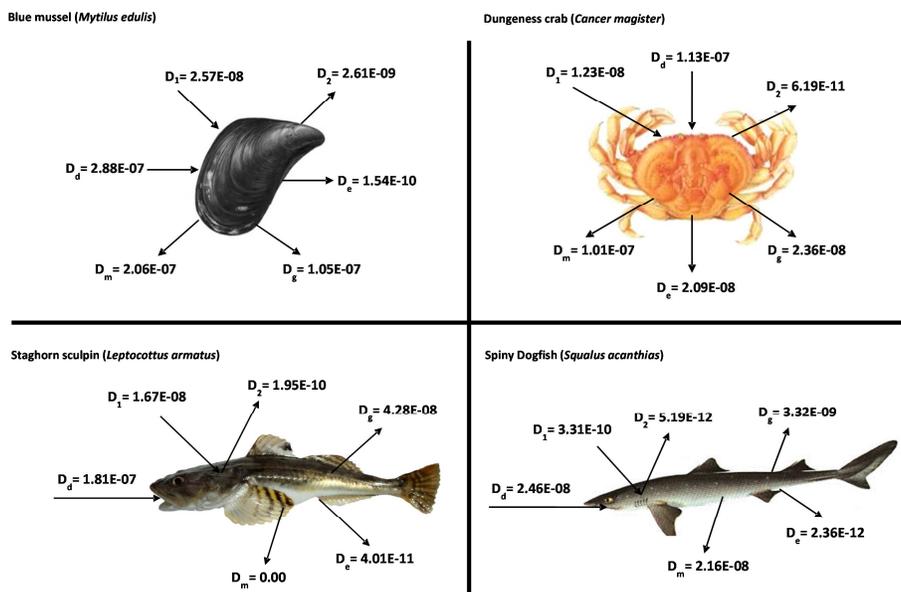


Figure 4.2-13 DEHP fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish.

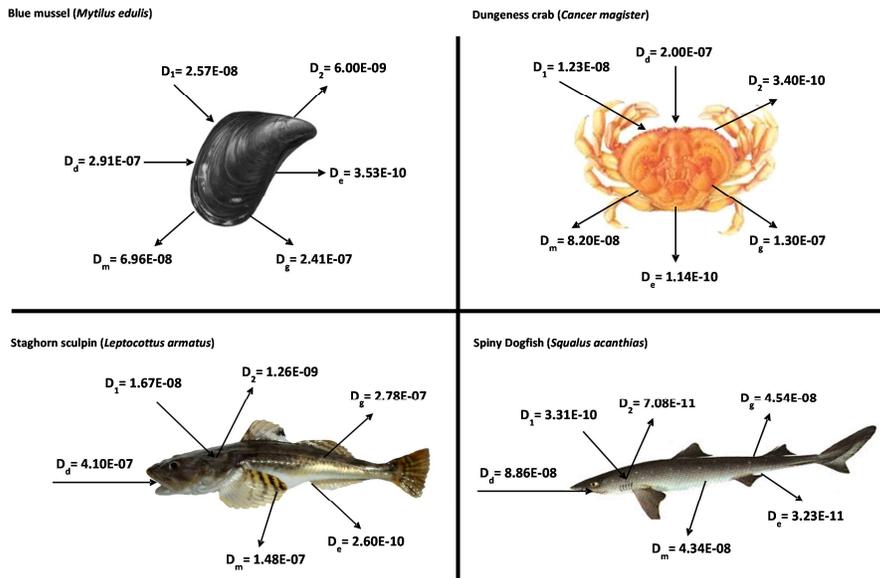


Figure 4.2-14 C8 fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish.

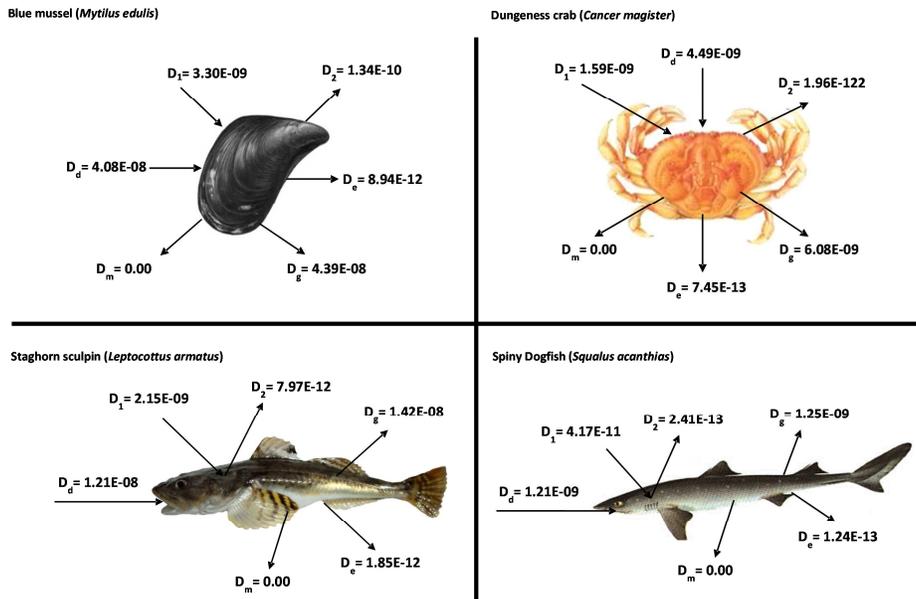


Figure 4.2-15 C9 fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish.

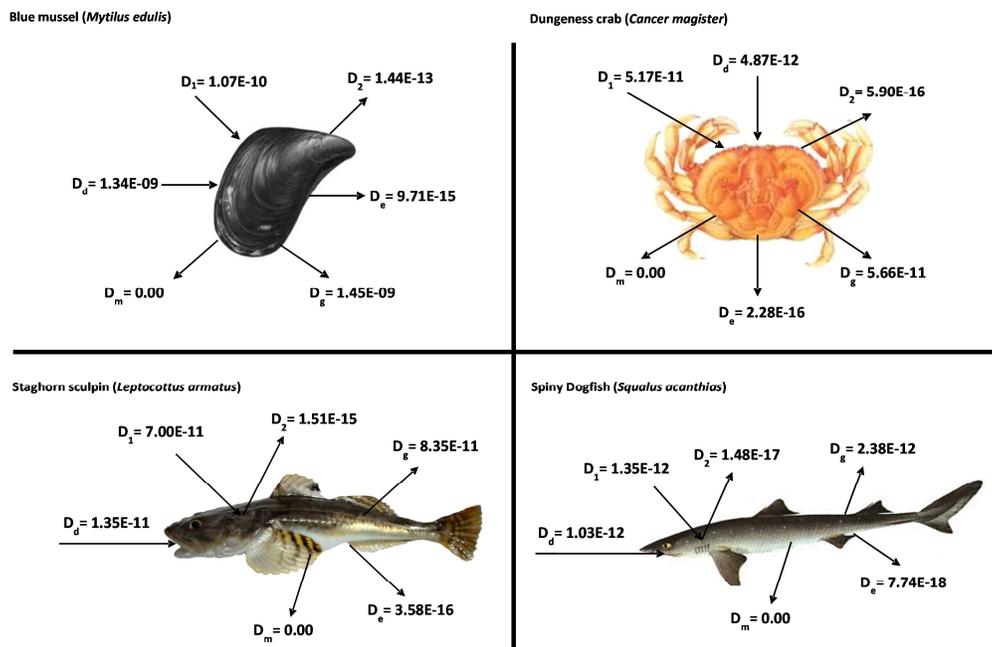
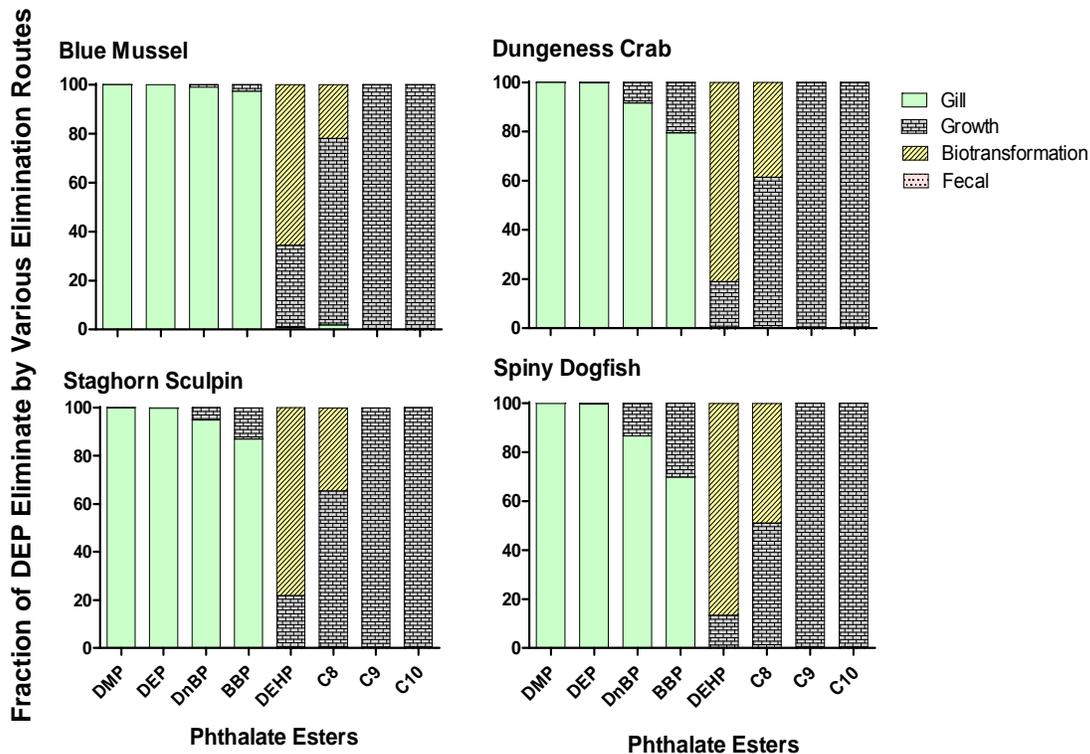


Figure 4.2-16 C10 fluxes (mol/day) in and out of blue mussel, Dungeness crab, staghorn sculpin, and spiny dogfish.

#### 4.2.4 Overall fate of DPEs in biota

Overall, gill elimination fluxes were the highest in the lower log  $K_{ow}$  DPEs (up to 99% of all fluxes leaving the body of the biota) and decreased dramatically with increasing log  $K_{ow}$  and molecular weight of the DPE (minimum of 6.22 E-4 %) (Figure 4.2-17). Growth dilution fluxes followed an opposite pattern; growth dilution fluxes decreased with increasing log  $K_{ow}$  and molecular weight of the PEs.



**Figure 4.2-17 Overall percentage of elimination fluxes of DPEs (%) in four organisms, blue mussels, Dungeness crabs, staghorn sculpin, and spiny dogfish;  $D_2$  is gill elimination flux (mol/day),  $D_e$  is fecal egestion rate constant (mol/day),  $D_g$  is growth dilution rate constant (mol/day), and  $D_m$  is metabolic transformation rate constant (mol/day).**

Biotransformation fluxes above zero value were only present in DEHP and C8 PEs (Figure 4.2-17). The model predicts no biotransformation rates in the lower log  $K_{ow}$  phthalate esters and biotransformation fluxes are at zero for C9 and C10. Biotransformation fluxes are higher for DEHP (65.63 to 86.63%) than for C8 (21.96 to 48.85%).

The unique behaviour of biotransformation fluxes could be due to a few principles. The nonexistence of biotransformation flux in the lower log  $K_{ow}$  phthalate esters could be due to the relatively high gill elimination rates of these DPEs. Due to their relatively low log  $K_{ow}$  and molecular weight, these DPEs readily undergo gill

elimination. In order for biotransformation to play a significant role in the depuration process, relatively high biotransformation fluxes are necessary. As a result, even if biotransformation occurs, biotransformation can be insignificant compared to gill elimination fluxes.

On the other hand, when gill elimination fluxes are low due to high  $\log K_{ow}$  and molecular weight of the DPE, the relative contribution of biotransformation fluxes is expected to be greater. This is observed in the case of DEHP and C8. In these cases, it is possible that although these DPEs have high  $\log K_{ow}$  and molecular weight, a significant portion of these chemicals is present in a freely dissolved form that could undergo biotransformation reactions in the biota. As the  $\log K_{ow}$  and molecular weight of the DPEs increase further, such as C9 and C10 chemicals, the freely dissolved fraction decreases and therefore C9 and C10 availability for reactions in the body may decrease. In other words, these chemicals may become unavailable to biotransformation processes, probably due to the very low free fractions (Peterson and Staples, 2002; Kickham, 2012).

As a result, high  $K_{ow}$  DPEs (C9 and C10) have very low gill elimination and fecal elimination fluxes and they are suspected to have an insignificant rate of biotransformation. For these DPEs, the growth dilution rates appear to control the depuration rates of DEPs in aquatic biota.

#### **4.2.5 Model applications**

Under the Canadian Environmental Protection Act, PEs are being evaluated for persistence, bioaccumulation, and toxicity (UNEP, 2001). If they are found to have these characteristics, a screening level risk assessment will be conducted and based on risk manager's decisions, these chemicals are being dealt with legally. However, if the

environmental concentrations of PEs are below the toxic reference values (TRVs), no further action is required under the Act. Therefore, further production and release of the chemical of concern will not be further scrutinized unless the chemical goes under another assessments and the second assessment indicates that concentrations have reached above the TRV values.

Increases and continuous input of PE into False Creek will result in an increase in the environmental concentrations, and possibly increases in the resultant body burden in biota. One of the applications of the current model would be to estimate the loading values of PEs that could result in TRVs associated with health effects on biota after a preliminary risk assessment is conducted even if no further action is required by the Act. Having this valuable information would provide an important tool for a proactive approach that can predict allowable safe loadings of PEs into the system before concentrations in the system reach critical levels.

Higher log  $K_{ow}$  MPEs are more toxic than the lower log  $k_{ow}$  MPEs (Staples, *et al.*, 2011). Also, the lower log  $K_{ow}$  DPEs are more toxic than the higher log  $K_{ow}$  DPEs due to their higher bioavailability. Since changes in environmental conditions result in the changes in the biodegradation capability of DPEs into MPEs as well as changes in the percent ionization of the MPEs, the overall fate of DPEs can greatly vary. The model is able to provide an insight into DPE and MPE variations based on these environmental changes.

As it was noted, PEs have a very wide range of solubility, partitioning properties, as well as bioavailability that can have a significant effect on their environmental fate and transport. Model predictions imply that neutral pH values result in very low non-ionized levels of the mono-esters present in False Creek. However, considering trends in increases in the greenhouse gases in our atmosphere and the resultant acidification of

our oceans, it is important to determine the effect of such fluctuations on the overall fate of PEs. In addition, since the model can be applied to other systems and phthalate esters are present in different media globally, it is important to run model simulations for systems with lower pH levels or future expected pH levels.

Some acidified lakes, for example, can reach pH levels below pH of 3 (Gordon and Gorham, 1963). Therefore, in these systems, the overall fate of PEs and their metabolites is expected to be very different from water bodies with neutral or slightly basic pH levels. Non-ionized portions of mono-esters in systems with lower pH levels are expected to play a major role in the overall fate of PEs. Running simulations with changes in other parameters expected to vary such as increases in the temperature as result of global climate changes could also provide important insight into the future PE fate. It also can provide a useful tool for the decision makers, and information for choosing appropriate strategies necessary to regulate these chemicals under these foreseeable environmental changes.

## 5: CONCLUSIONS AND RECOMMENDATIONS

In an effort to improve the understanding of the behaviour of DPEs and their monoester metabolites in the environment and improve the decision making capacity of the environmental managers, an environmental fate and bioaccumulation model for eight DPEs was developed, parameterized, and tested.

The model was comprised of two sub-models and therefore, performance analysis was conducted separately for each sub-model. The environmental fate sub-model performance analysis indicated that the model-predicted log  $K_{oc}$  values for DPEs and MPEs were in reasonable agreement with empirical values from False Creek. This suggests that the model has some capacity to represent the fate of DPEs and MPEs in False Creek ecosystem.

Due to their low sorptive capacity and low log  $K_{ow}$ , a large fraction of lower log  $K_{ow}$  DPEs that enter False Creek are biodegraded to MPEs which are further biodegraded as well. A large proportion of the lower log  $K_{ow}$  DPEs also flow out of the system in their unmetabolized form.

In the case of the higher log  $K_{ow}$  DPEs, burial of the parent compounds played a significant role in their overall fate while biodegradation to monoesters was insignificant. The model also suggests that a significant portion of this group of DPEs flow out of the system in their original chemical form. High amounts of the higher log  $K_{ow}$  PE in the environment are most likely to be buried in the sediment due to the very low fraction present as a freely dissolved form, and therefore have low bioavailability to microbial metabolizers.

Some toxicological studies indicate that higher log  $K_{ow}$  DPEs such as DEHP have low toxicity effects to biota since they have low bioavailability. However, their metabolites are toxic since they are highly soluble. Often very high production DPEs with high log  $K_{ow}$  values are of concern to risk assessors and risk managers because of their potential to bioaccumulate. The results of this study suggest that the fraction of DEHP (log  $K_{ow}$  = 8.2) biodegraded to MEHP in the environment is very low. The small amounts of MEHP are also quickly further broken down ( $t_{1/2} = 1 - 2 \text{ days}$ ). Therefore, exposure to MEHP can be expected to be low. *In situ* toxicological tests could help understand the possible effects of DPEs and their monoester metabolites present in False Creek.

Model generated concentrations in water and sediment were used as inputs to the food web sub-model and phthalate ester concentrations were estimated in the biota. Due to a lack of biotransformation studies, no biotransformation rate constants were available to be used in the model. To test the performance of the food web sub-model, observed and measured log BAF were compared.

The model was calibrated by estimating a universal (for all biota)  $k_m$  for each of the DPEs for which the predicted log BAF was greater than the measured value. The model predicts universal  $k_m$  values for DEHP and C8 PEs only. This could be due to the very high bioavailability and therefore availability for hydrolysis reaction in the case of the lower log  $K_{ow}$  phthalate esters. The high affinity to organic carbon and therefore lower degree of bioavailability of the higher log  $K_{ow}$  DPEs such as C9 and C10, results in negligible biotransformation fluxes for these chemicals. In the case of DEHP and C8, bioavailability of these chemicals is relatively higher than C9 and C10 since they have a slightly lower affinity to organic carbon. However, in comparison to the lower DPEs,

these chemicals are not readily available for biodegradation. Therefore, since no bioaccumulation or biomagnification has been observed for these chemicals, the biotransformation rates become significant in the overall fate of DEHP and C8.

Although the model provides some insight into biotransformation rate constants, in reality it is more likely that each species will have its own biotransformation rate constant for each of the PEs. Therefore, further investigations to measure biotransformation rates are needed to fully understand the overall fate of these chemicals in the environment.

The overall model bias indicates that the lower log  $K_{ow}$  DPEs such as DMP and DEP as well as the higher log  $K_{ow}$  DPEs such as C10 are often slightly under-estimated by the model. On the other hand, the model is able to predict log BAF values DnBP, BBP, DEHP, C8, and C9 that are comparable to empirical values.

Considering the observed toxicity of the higher log  $K_{ow}$  MPEs as well as the lower log  $K_{ow}$  DPEs, the fate of DPEs, the degree of biodegradation of DEPs and ionization of MPEs provide important information on the toxicity and possible exposure scenarios for these chemicals. The model is able to provide this valuable information.

The model can be used to evaluate the behaviour of DPEs and MPEs at other locations and be used as a tool for screening level risk assessment of DPEs. It can also be used to predict the outcome of different production volume scenarios; however, establishing the true loadings of DPEs into False Creek would be helpful in further testing and refining the model. In addition, toxicological testing of DPEs and their main metabolite MPEs would be vital in comparing the environmental concentrations and assessing toxicological risk of these chemicals to the biota as well as human population.

The model can be used as a proactive tool, in determining and regulating the loadings of PEs into the system and prevent reaching unsafe water concentrations and the resultant unsafe body burdens. Since the fate of PEs are dependent on many environmental factors, such as pH and temperature, model simulations using the forecasted information for these parameters could provide important insight into the behaviour of these chemicals in the future and again provide important information to the regulatory agencies and decision makers.

Despite the fact that phthalate esters and their metabolites do not biomagnify, they are readily measured in biota, water and sediment. Therefore, it is important to establish toxicity reference value for human health as well as for the species of concern. Once toxic benchmarks are established, sediment and water quality guidelines can be back-calculated in order to derive meaningful protective guidelines.

## 6: REFERENCES

- Arnot, J.A., Gobas, F.A.P.C., 2004a. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environmental Toxicology and Chemistry*. 23: 2343-2355.
- Arnot, J.A., Gobas, F.A.P.C., 2004b. A generic QSAR for assessing the bioaccumulation potential of organic chemicals in aquatic food webs. *QSAR & Combinatorial Science*, 22, 337-345 (2003).
- Adam, W.J., Biddinger, G.R., Robillard, K.A. 1995. Summary of the acute toxicity of 14 phthalate esters to representative aquatic organism. 14: 1569-1574.
- Brase A.B, Chakrabarti, T., Ghosh, T.K. Pal, A.K., Jadhao, S.B. 2007. Endocrine disruption and metabolic changes following exposure of *Cyprinus carpio* to diethyl phthalate. *Pesticide Biochemistry and Physiology*. 88:36-42.
- Brown, D., Thompson, R.S. 1982. Phthalates and the aquatic environmentL: Part I. The effect of di-2-ethylhexyl phthalate (DEHP) and di-isodecyl phthalate (DIDP) on the reproduction of *Daphnia magna* and observations on their bioconcentration. *Chemosphere*. 11:417-426.
- Burkhard, L.P., 2000. Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. *Environmental Science and Technology*. 34: 4663-4668.
- Chang, B.B., Liao, C.S., Yuan, S.Y., 2005. Anaerobic degradation of diethyl phthalate, di-n-butyl phthalate, and di-(2-ethylhexyl) phthalate from river sediment in Taiwan. *Chemosphere*. 58: 1601-1607.
- Chemical, biological, and functional aspects of food lipids, edited by Zdzislaw, Z.E., Kolakowska, A., 2011. CRC press 275-276.
- Colm, D.C. 1997. Development, evaluation, and application of a food web bioaccumulation model for PCB s in the Strait of Georgia, British Columbia. Master Project.
- Copper, J.A., and Chapleau, F. 1998. Monophyly and intrarelationships of the family Pleuronectidae (Pleuronectiformes), with a revised classification. *Fisheries Bulletin*. 96:686-726.
- Cousins, I., Mackay, D. 2000. Correlating the physical-chemical properties of phthalate esters using the “three solubility” approach. *Chemosphere*. 41:1389-1399.
- Cousins, I.T., Mackay, D. 2003. Multimedia mass balance modelling of two phthalate esters by regional population-based model (RPM). *Handbook of Environmental Chemistry. Part Q*. 179-200.

- Cousins, I.T., Mackay, D., Parkerton, T.F. 2002. Physical-chemical properties and evaluative fate modelling of phthalate esters. In: Staples, C. (Ed.). Handbook of Environmental Chemistry, Phthalate Esters. Springer, Berlin, pp. 57-84.
- Dalziel, J.A., Harding, G., Sunderland, E. 2006. The mercury flux of an east coast marine embayment. 8<sup>th</sup> International Conference on Mercury as a Global Pollutant, Madison, WI, USA.
- David, W.P. 1988. Reproduction and developmental responses in the self-fertilizing fish, *Rivulus marmoratus*, induced by plasticizer, di-n-butylphthalate. *Environmental Biology of Fishes*. 21:81-90.
- David, R.M., Gans, G. 2003. Summary of mammalian toxicity and health effects of phthalate esters. Handbook of Environmental Chemistry 3 (Part Q): 299-316.
- DeFoe, D.L., Holcombe, G.W., Hammermeister, D.E., Biesinger, K.E. 1990. Solubility and toxicity of eight phthalate esters to four aquatic organisms. *Environmental Toxicology and Chemistry*. 9:623-636.
- EFED, Comments on April 23<sup>rd</sup> BASF parameter "Shopping List" for water quality model: metaflumizone-specific sensitivity analysis. Draft May 8, 2007.
- Froese, R., Pauly, D. 2011. FishBase, version 01/2011. www.fishbase.org
- Gledhill, W.E., Kaley, R.G., Adam, W.J., Hicks, O., Michael, P.R., Saeger, V.W., Leblanc, G.A. 1980. An environmental safety assessment of butyl benzyl phthalate. *Environmental Science and Technology*. 14:301-305.
- Gobas, F.A.P.C. 1993. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food-webs: application to Lake Ontario. *Ecological Modelling*. 69:1-17.
- Gobas, F.A.P.C., and Arnot, J. 2005. San Francisco Bay PCB Food-web model. Vancouver, BC, Simon Fraser University: 152pp.
- Gobas, F.A.P.C., Pasternak, J.P., Lein, K., Duncan, R.L. 1998. Development and field validation of a multimedia exposure assessment model for waste load allocation in aquatic ecosystems: Application to 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin and 2, 3, 7, 8-Tetrachlorodibenzofuran in the Fraser River Watershed. *Environmental Science and Technology*. 32:2442-2449.
- Gobas, F.A.P.C., Sura, S., Otton, V., Ikanomou, M.G. 2010. Sorption of di- and mono-phthalate esters in natural sediments: Role of pH,  $K_{ow}$ , and transformation. Society of Environmental Toxicology and Chemistry, 2010 Portland. RP153.
- Gordon, A.G., Gorham, E. 1963. Ecological aspects of air pollution from an iron-sintering plant at Wawa, Ontario. *Canadian Journal of Botany*. 41: 1063-1078.
- Guckel, W., R. Kastel, J. Lewerenz, G. Synnatschke. 1982. A method for determining the volatility of active ingredients used in plant protection. Part III: the temperature

- relationship between vapor pressure and evaporation rate. *Pesticide Science*. 13: 161-168; DOI 10.1002/ps.2780130208
- Harris, C.A., Henttu, P., Parker M.G., Sumpter, J.P. 1997. The estrogenic activity of phthalate esters *in Vitro*. *Environmental Health Perspective*.105:802-811.
- Health Canada, Phthalates regulations fact sheet. 2011. [http://www.hc-sc.gc.ca/ahc-asc/media/nrcp/\\_2011/2011\\_07fs-eng.php](http://www.hc-sc.gc.ca/ahc-asc/media/nrcp/_2011/2011_07fs-eng.php). Retrieved on August 24, 2012.
- Hoppin, J.A., Brock, J.W., Davis, B.J., Baird, D.D. 2002. Reproducibility of urinary phthalate metabolites in first morning urine samples. *Environmental Health Perspective*. 110: 515-518.
- Howdeshell, K.L., Wilson, V.S., Furr, J., Lambright, C.R., Rider, C.V., Blystone, C.R., Hotchkiss, A.K., Gray, L.E., Jr. 2008. A Mixture of five phthalate esters inhibits fetal testicular testosterone production in the Sprague-Dawley rat in a cumulative, dose-additive manner. *Toxicological Sciences*. 105: 153:165.
- Huynh, M.D., Kitts, D.D. 2009. Evaluating nutritional quality of pacific fish species from fatty acid signatures. *Food Chemistry*. 114:912-918.
- Jobling S. Raynolds, T., White, R., Parker, M.G., Sumpter, J.P. 1995. A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. *Environmental Health Perspective*. 103: 582-587.
- Johannessen, S.C., Macdonald, R.W., Eek, K.M. 2005. Historical trends in mercury sedimentation and mixing in the Strait of Georgia, Canada. *Environmental Science and Technology*. 39:4361-4368.
- Kickham, P. 2010. Biodegradation of phthalate esters in False Creek sediments. Master Thesis
- Kickham, P., Otton, S.V., Moor, M.M., Ikanomou, M.G., Gobas, F.A.P.C. 2012. Relationship between biodegradation and sorption of phthalate esters and their metabolites in natural sediments. *Environmental Chemistry*. 30: 1-8; DOI 10.1002/etc.1903.
- Kuhn, R., Pattard, M, Pernak, K.D., Winter, A. 1989. Results of the harmful effects of water pollutants to *Daphnia magna* in the 21 day reproduction test. *Water Research*. 23:501-510.
- Lai, H.F. thesis. 2010. Development, validation and application of a time-dependent food web bioaccumulation model for organic pesticides in aquatic ecosystems . Master Thesis.
- Liang, D.; Zhang, T.; Fang, H.; He, J. 2008. Phthalates biodegradation in the environment. *Applied Microbiology & Biotechnology* 80:183-198; DOI 10.1007/s00253-008-1548-5.
- Liu, Y., Guan, Y., Zang, Y., Cai, Z., Mizuno, T., Tsuno, H., Zhu, W., Zhang, X. 2009. Toxicity of several phthalate esters to embryonic development of the abalone *Haliotis diversicolor supertextata*. *Ecotoxicology*. 18:293-303.
- Mackintosh, C. 2002. Distribution of phthalate esters in a marine food web. Master Thesis.

- Mackintosh, C., Maldonado, J., Hongwu, J., Hoover, N., Chong, A., Ikonomou, M.G., Gobas, F.A.P.C. 2004. Distribution of phthalate esters in a marine aquatic food web: comparison to polychlorinated biphenyls. *Environmental Science and Technology*. 38: 2011-2020.
- Mackintosh, C., Maldonado, J.A., Ikonomou, M.G., Gobas, F.A.P.C. 2006. Sorption of phthalate esters and PCBs in a marine ecosystem. *Environmental Science and Technology*. 40:3481-3488.
- McAllister, W.A. 1986. Early life stage toxicity of 14C-Butylbenzyl phthalate to rainbow trout (*Salmo gairdneri*). Final Report #33996. ABC Laboratories, Inc, Columbia, MO, USA
- McCarthy, J.F. 1983. Role of particulate organic matter in decreasing accumulation of polynuclear aromatic hydrocarbon by *Daphnia magna*. *Archives of Environmental Contamination and Toxicology*. 12: 559-568.
- McConnell, M. L. 2007. Distribution of phthalate monoesters in an aquatic food web. Master Thesis.
- Metcalf, C.D., Metcalfe, T.L., Kiparissis, Y., Koenig, B.G., Khan, C., Hughes, R.J., Croley, T.R. March R.E., Potter, T. 2001. Estrogenic potency of chemical detected in sewage treatment plant effluents as determined by in vivo assay with Japanese medaka (*Oryzias latipes*). *Environmental Toxicology and Chemistry*. 20:297-308.
- Nexant, 2007. PERP Program – Trends in plasticizers.  
<http://www.chemsystems.com/about/cs/news/items/PERP%200506S8%20Plasticizers.cfm>. Retrieved on August 24, 2012.
- Ortiz-Zarragoitia M., Trant, J.M., Cajaraville, M.P. 2006. Effects of dibutylphthalate and ethinylestrodol on liver peroxisomes, reproduction, and development of zebrafish (*Danio rerio*) *Environmental Toxicology and Chemistry*. 25:2394-2404.
- Ott, S.V., Sura, S., Blair, J., Ikonomou, M.G., Gobas, F.A.P.C. 2008. Biodegradation of monoalkyl phthalate esters in natural sediments. *Chemosphere*. 71: 2011-2016.
- Painter, S.E. and Jones, W.J. 1990. Anaerobic bioconversion of phthalic acid esters by natural inocula. *Environ. Technol.* 11:1015-1026; DOI 10.1080/09593339009384956.
- Paganetto, G. Campi, F., Varani, K., Piffanelli, A., Giovannini, G., Borea, P.A. 2000. Endocrine-disrupting agents on healthy human tissues. *Pharmacology and Toxicology*:86:24-29.
- Palomares, M.L/D/. Pauly, D. 2010. SeaLifeBase, version 01/2011. [www.sealifebase.org](http://www.sealifebase.org).
- Park, K., Kwak, I.S., 2008a. Characterization of heat shock protein 40 and 90 in *Chironomus riparius* larvae effects of di(2-ethylhexyl) phthalate exposure on gene expression and mouthpart deformities. *Chemosphere*. 74:89-95.
- Park, K., Kwak, I.S., 2008b. Expression of *Chironomus riparius* serine-type endopeptidase gene under di-(2-ethylhexyl) phthalate (DEHP) exposure. *Comparative Biochemistry and Physiology*. Part B. 151: 349-354.

- Park, S.S., Erstfeld, K.M. 1998. The effect of sediment organic carbon content on bioavailability of hydrophobic compounds in aquatic ecosystems. *Environmental pollution*. 105:9-15.
- Parkerton, T., Konkel, W. 2000. Evaluation of the production, consumption, end use and potential emissions of phthalate esters. Report for the American Chemistry Council.
- Patyna, P.J., Brown, R.P, Davi, R.A., Letinski, D.J., Thomas, P.E., Cooper, K.R., Parkerton, T.F. 2006. Hazard evaluation of diisononyl phthalate and diisodecyl phthalate in a Japanese medaka multigenerational assay. *Ecotoxicology and Environmental Safety*. 65:35-47.
- Peterson, D.R., Parkerton, T.F., 1999. The environmental fate and effects of phthalate monoesters. Report prepared for the CEFIC, Brussels, Belgium.
- Peterson, D., Staples, C. 2002. Degradation of phthalate esters in the environment. In: Staples. C. (Ed.). *Handbook of Environmental Chemistry, Phthalate Esters*, Springer, Berlin. 85-124.
- Rhodes, J.E., Adams, W.J., Biddinger, G.R., Robillard, K.A., Gorsuch, J.W., 1995. Chronic toxicity of 14 phthalate-esters to *Daphnia magna* and rainbow trout (*Oncorhynchus mykiss*). *Environmental Toxicology and Chemistry*. 14:1967-1976.
- Saillenfait, A.M., Sabate, J.P., Gallissot, F. 2009. Effects of in utero exposure to di-n-hexyl phthalate on the reproductive development of the male rat. *Reproductive Toxicology*. 28: 468-476.
- The Scientific Committee on Cosmetic Products and Non-Food Products Intended for consumers opinion concerning diethyl phthalate SCCNFP.2003. Adopted by the SCCNFP during the 26th Plenary Meeting of 9 December 2003, SCCNFP/0767/03: 7.
- Seth, R., Mackay, D., Muncke, J. 1999. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environ. Sci. Technol.* 33, 2390–2394.
- Sohoni, P. and Sumpter, J.P. 1998. Several environmental oestrogens are also anti-androgens. *Journal of Endocrinology*. 158:327-339.
- Soto, A.M., Sonnenschein, C., Chung, K.L. Fernandez, M.F., Olea, N., S., Serrano, F.O. 1995. The E-screen assay as a tool to identify estrogens: an update on estrogenic environmental pollutants. *Environmental Health Perspective*. 103(suppl 7): 113-122.
- Sura, S. 2007. Environmental partitioning of mono phthalate esters. Master Thesis.
- Staples, C.A., Guinn, R., Kramarz, K., and Lampi, M. 2011. Assessing the chronic aquatic toxicity of phthalate ester plasticizers. *Human and Ecological Risk Assessment*. 17: 1057-1076.
- Staples, C.A., Peterson, D.R., Parkerton, T.F., Adams, W.J. 1997. The environmental fate of phthalate esters: A literature review. *Chemosphere*. 35: 667-749; DOI 10.1016/S0045-6535(97)00195-1.

- Sultan, C., Balaguer, P., Terouanne, B., Georget, V., Paris, F., Jeandel, C., Lumbroso, S., Nicholas, J. 2001. Environmental xenoestrogens, antiandrogens, and disorders of male sexual differentiation. *Molecular and Cellular Endocrinology*. 178:99-105.
- United Nations Environment Program (UNEP). 2001. Final act of the conference of plenipotentiaries on the Stockholm convention on persistent organic pollutants, Stockholm, Sweden, 22 to 23 May 2001 (UNEP, Geneva, Switzerland, 2001).
- Vander Zanden, M.J., Rasmussen, J.B. 1996. A trophic position model of pelagic food webs: impact on contaminant bioaccumulation in lake trout. *Ecological monographs*. 66:451-477.
- Ware, D.M. 1985. Life history characteristics, reproductive value, and resilience of Pacific herring (*Clupea harengus pallasii*). *Canadian Journal of Fisheries and Aquatic Sciences*. 42(Suppl. 1):127-137.
- Webster, G. thesis, 2003. Dietary uptake and biotransformation of phthalate esters in Staghorn sculpin. Master Thesis.
- Wibe, A.E., Fjeld, E., Rosenqvist, G., Jenssen, B.M. 2004. Postexposure effects of DDE and butylbenzylphthalate on feeding behaviour in threespine stickleback. *Ecotoxicology and Environmental Safety*. 57: 213-219.
- Xu, X.R., Li, X.Y. 2009. Sorption behavior of benzyl butyl phthalate on marine sediments: Equilibrium assessments, effects of organic carbon content, temperature and salinity. *Marine chemistry*. 115:66-71.
- Zhang, W.X.; Bower, E.J. 1998. Bioavailability of hydrophobic organic contaminants: effects and implications of sorption-related mass transfer on bioremediation. *Ground Water Monit. Remediat.* 18: 126-138; DOI 10.1111/j.1745-6592.1998.tb00609.x.

## 7: APPENDICES

Appendix A-1 Chemical specific parameters for DPEs (Excel File)

Appendix A-2 Chemical specific parameters for MPEs (Excel File)

Appendix A-3 Environmental fate sub-model parameters and rate constant

Appendix A-4 Calculated rate constants for DPEs and their corresponding  
MPE metabolites (Excel File)

Appendix B-1 Food-web dietary matrix (Mackintosh, *et al.*, 2004) (Excel  
File)

Appendix B-2 Organism specific parameters (Excel File)

Appendix B-3 Food web sub-model parameters and rate constants

Appendix B-4 Calculated organism specific parameters for DPEs (Excel  
File)

Appendix B-5 Calculated organism specific parameters for MPEs (Excel  
File)

Appendix B-6 Predicted and measured TMF regression analysis results  
(Excel File)

Appendix B-7 S-plus statistics for predicted and observed TMFs (Excel  
File)

Appendix C-1 CD-Rom Data Appendix

## **Appendix A-1 Chemical specific parameters for DPEs**

Please refer to Excel file: G. Zandpour – Appendix Tables on Attached CD

## **Appendix A-2 Chemical specific parameters for MPEs**

Please refer to Excel file: G. Zandpour – Appendix Tables on Attached CD

## Appendix A-3 Environmental fate sub-model parameters and rate constants

The following equations are adapted from How-Feng Lai thesis (2010) with some modifications. The following equations describe how each rate constants is calculated:

### Outflow rate constant or $k_o$ (day-1)

$$k_o = \frac{F}{1000 \cdot V_w}$$

Where

$k_o$  = outflow rate constant (day<sup>-1</sup>)

F = water in- and out-flow (L/day)

$V_w$  = volume of water (m<sup>3</sup>)

### Volatilization rate constant or $k_v$ (day-1)

$$k_v = \frac{S_{aw} \cdot f_{DW} \cdot v_e}{V_w}$$

Where

$k_v$  = volatilization rate (day<sup>-1</sup>)

$S_{aw}$  = lake surface area (m<sup>2</sup>)

$f_{D,W}$  = fraction of freely dissolved chemical in water (unitless)

$v_e$  = volatilization mass transfer coefficient (m/day)

$V_w$  = volume of water (m<sup>3</sup>)

### Overall water to sediment transport rate constant ( $K_{ws}$ )

$$k_{ws} = k_{ws1} + k_{ws2}$$

Where

$k_{WS}$  = overall water to sediment transport ( $\text{day}^{-1}$ )

$k_{WS1}$  = solids settling rate ( $\text{day}^{-1}$ )

$k_{WS2}$  = water-to-sediment diffusion rate ( $\text{day}^{-1}$ )

### **Overall sediment to water transport rate constant (ksw)**

$$k_{SW} = k_{SW1} + k_{SW2}$$

Where

$k_{SW}$  = overall sediment to water transport ( $\text{day}^{-1}$ )

$k_{SW1}$  = solids re-suspension rate ( $\text{day}^{-1}$ )

$k_{SW2}$  = sediment-to-water diffusion rate ( $\text{day}^{-1}$ )

### **Solid settling rate constant (kws1)**

$$k_{WS1} = S_{aw} \cdot v_s \cdot \frac{1 - f_{DW}}{V_w}$$

Where

$k_{WS1}$  = solids settling ( $\text{day}^{-1}$ )

$S_{aw}$  = lake surface area ( $\text{m}^2$ )

$v_s$  = solids settling rate (m/day)

$f_{DW}$  = fraction of freely dissolved chemical in water (unitless)

$V_w$  = volume of water ( $\text{m}^3$ )

### **Water to sediment diffusion rate constant (kws2)**

$$k_{WS2} = S_{as} \cdot v_D \cdot \frac{f_{DW}}{V_w}$$

Where

$k_{WS2}$  = water to sediment diffusion ( $\text{day}^{-1}$ )

$S_{as}$  = sediment surface area ( $\text{m}^2$ )

$v_D$  = water to sediment diffusion mass transfer coefficient (m/day)

$f_{DW}$  = fraction of freely dissolved chemical in water (unitless)

$V_w$  = volume of water (m<sup>3</sup>)

### **Solids re-suspension rate constant (Ksw1)**

$$k_{sw1} = \left( \frac{ResFlux}{C_{SS}} \right) \cdot \frac{1 - f_{DS}}{1000 \cdot V_S}$$

Where

$k_{sw1}$  = solids re-suspension (day<sup>-1</sup>)

ResFlux = sediment solids mass balance and re-suspension flux (kg/d)

$C_{SS}$  = concentration of solids in sediment (kg/L)

$f_{DS}$  = fraction of freely dissolved chemical in sediment (unitless)

$V_S$  = volume of sediment (m<sup>3</sup>)

### **Sediment to water diffusion rate constant (ksw2)**

$$k_{sw2} = Sas \cdot v_D \cdot \frac{f_{DS}}{V_S}$$

Where

$k_{sw2}$  = sediment to water diffusion (day<sup>-1</sup>)

Sas = sediment surface area (m<sup>2</sup>)

$v_D$  = water to sediment diffusion mass transfer coefficient (m/day)

$f_{DS}$  = fraction of freely dissolved chemical in sediment (unitless)

$V_S$  = volume of sediment (m<sup>3</sup>)

### **Sediment burial rate constant (kB)**

$$k_B = v_B \cdot Sas \cdot \frac{1 - f_{DS}}{d_{SS}} \cdot \frac{10^{-6}}{V_S}$$

Where

$k_B$  = sediment burial rate constant (day<sup>-1</sup>)

$v_B$  = sediment burial mass transfer coefficient (m/day)

Sas = sediment surface area (m<sup>2</sup>)

$f_{DS}$  = fraction of freely dissolved chemical in sediment (unitless)

$d_{SS}$  = density of sediment solids (kg/L)

$V_S$  = volume of sediment ( $m^3$ )

### **Precursor for Chemical degradation rate constant in water (Prekwr)**

$$PreK_{wr} = \frac{hls}{1 + \alpha_{soc} \cdot d_{pw} \cdot OC_{pw} \cdot \left(\frac{C_{pw}}{d_{pw}}\right) \cdot (K_{ow})}$$

Where

PreKwr = precursor for chemical degradation rate constant in water ( $day^{-1}$ )

hls = inherent chemical half-life in sediment ( $day^{-1}$ )

$\alpha_{soc}$  = sediment OC octanol proportionality constant (unitless)

$d_{pw}$  = Density of suspended solids (Kg/L)

$OC_{pw}$  = Organic carbon constant of suspended solids (unitless)

$C_{pw}$  = Concentration of particles in water (Kg/L)

$d_{pw}$  = density of suspended solids (Kg/L)

$K_{ow}$  = octanol water partition coefficient (unitless)

### **Chemical degradation rate in water (Kwr)**

$$K_{wr} = IF(PreK_{wr} < hls, PreK_{wr}, hls)$$

Where

$K_{wr}$  = chemical degradation rate constant in water ( $day^{-1}$ )

IF = conditional statement

PreKwr = precursor for chemical degradation rate constant in water ( $day^{-1}$ )

hls = inherent chemical half-life in sediment ( $day^{-1}$ )

### **Precursor for Chemical degradation rate constant in sediment (Prekws)**

$$Prek_{ws} = hls / (\alpha_{soc} \cdot d_{ss} \cdot OC_{ss} \cdot (C_{ss}/d_{ss}) \cdot (K_{ow}))$$

Where

$PreK_{ws}$  = precursor for chemical degradation rate constant in sediment ( $day^{-1}$ )

$hls$  = inherent chemical half-life in sediment ( $day^{-1}$ )

$\alpha_{soc}$  = sediment OC octanol proportionality constant (unitless)

$d_{ss}$  = density of sediment solids (kg/L)

$OC_{ss}$  = Organic carbon content of bottom sediment (unitless)

$C_{ss}$  = concentration of solids in sediment (Kg/L)

$d_{ss}$  = density of sediment solids (Kg/L)

$K_{ow}$  = octanol water partition coefficient (unitless)

### **Chemical degradation rate in sediment (Kws)**

$$k_{ws} = IF(Prek_{ws} < hls, Prek_{ws}, hls)$$

Where

$kws$  = chemical degradation rate constant in sediment ( $day^{-1}$ )

IF = conditional statement

$Prekws$  = precursor for chemical degradation rate constant in sediment ( $day^{-1}$ )

$hls$  = inherent chemical half-life in sediment ( $day^{-1}$ )

### **Total water loss rate constant (KWW)**

$$k_{WW} = k_o + k_w + k_v + k_{wr}$$

Where

$k_{WW}$  = total water loss constant rate ( $day^{-1}$ )

$k_o$  = outflow rate constant ( $day^{-1}$ )

$k_{ws}$  = overall water to sediment transport rate constant ( $day^{-1}$ )

$k_v$  = volatilization rate constant ( $day^{-1}$ )

$k_{wr}$  = degradation in water rate constant ( $day^{-1}$ )

### **Total sediment loss rate constant (k<sub>SS</sub>)**

$$k_{SS} = k_{sw} + k_B + k_{sr}$$

Where

$k_{SS}$  = total sediment loss rate constant ( $\text{day}^{-1}$ )

$k_{sw}$  = overall sediment to water transport rate constant ( $\text{day}^{-1}$ )

$k_B$  = burial rate constant ( $\text{day}^{-1}$ )

$k_{sr}$  = degradation in sediment rate constant ( $\text{day}^{-1}$ )

**Appendix A-4 Calculated rate constant for DPEs and their corresponding MPE metabolites**

Please refer to Excel file: G. Zandpour – Appendix Tables on Attached CD

## **Appendix B-1 Food-web dietary matrix (Mackintosh, et al., 2004)**

Please find attached a CD containing an electronic copy of the environmental fate and food web bioaccumulation model for Phthalate esters in this document.

Microsoft Excel software is required to run the model.

The CD-ROM attached forms a part of this work. Data file can be opened with Microsoft Excel or other spread sheet program.

## **Appendix B-2 Organism specific parameters**

## **Appendix B-3 Food web sub-model parameters and rate constants**

### **Volume of lipid in organism (V<sub>l</sub>) excluding primary producers**

$$V_l = W_b \cdot vlb$$

Where

V<sub>l</sub> = volume of lipid in organism (Kg)

W<sub>b</sub> = weight of biota (kg)

vlb = lipid fraction in biota (including phytoplankton)

### **Volume of NLOM in organism (V<sub>nlom</sub>) excluding primary producers**

$$V_{nlom} = W_b \cdot V_{nb}$$

Where

V<sub>nlom</sub> = volume of NLOM (kg)

W<sub>b</sub> = weight of biota (Kg)

V<sub>nb</sub> = non lipid organic matter fraction in biota

### **Volume of water in organism (V<sub>w</sub>) excluding primary producers**

$$V_w = V_{wb} \cdot W_b$$

Where

V<sub>w</sub> = volume of water in organism (kg)

V<sub>wb</sub> = water fraction in biota (kg/kg)

W<sub>b</sub> = weight of biota (kg)

### **Dietary uptake rate constant (K<sub>D</sub>) excluding primary producers**

$$K_D = E_d \cdot G_d / W_b$$

Where

$K_D$  = dietary uptake rate constant (kg/kg.day)

$E_d$  = Efficiency of chemical transfer via intestinal tract (%)

$G_d$  = feeding rate (kg/day)

$W_b$  = weight of biota (kg)

### **Gill uptake rate constant ( $k_1$ )**

$$K_1 = E_w \cdot G_v / W_b$$

Where

$k_1$  = gill uptake rate constant (L/kg.day) excluding primary producers

$E_w$  = efficiency of chemical transfer via gill (%)

$G_v$  = gill ventilation rate (L/day)

$W_b$  = weight of biota (kg)

Gill uptake rate constant ( $K_1$ )

$$k_1 = \left( A + \left( \frac{\beta}{k_{ow}} \right) \right)^{-1}$$

Where

$k_1$  = Gill uptake rate constant (L/Kg.day) used only for primary producers

$A$  = resistance to chemical uptake through the aqueous phase (unitless)

$\beta$  = resistance to chemical uptake through the organic phase (unitless)

$K_{ow}$  = octanol-water partition coefficient (unitless)

Gill elimination rate constant ( $k_2$ ) excluding primary producers

$$k_2 = \frac{k_1}{k_{bw}}$$

Where

$k_2$  = Gill elimination rate constant ( $\text{day}^{-1}$ )

$k_1$  = Gill uptake rate constant ( $\text{L/kg}\cdot\text{day}$ )

$k_{bw}$  = biota water partition coefficient (unitless)

**Gill elimination rate constant ( $K_2$ ) used only for primary producers**

$$k_2 = \frac{k_1}{K_{pw}}$$

Where

$k_2$  = Gill elimination rate constant ( $\text{day}^{-1}$ )

$k_1$  = Gill uptake rate constant ( $\text{L/kg}\cdot\text{day}$ )

$k_{pw}$  = phytoplankton–water partition coefficient (unitless)

**Fecal egestion rate constant ( $k_e$ ) excluding primary producers**

$$k_E = G_f \cdot E_d \cdot \frac{K_{gb}}{W_b}$$

Where

$K_E$  = Faecal egestion rate constant ( $\text{day}^{-1}$ )

$G_f$  = faecal egestion rate ( $\text{kg/day}$ )

$E_d$  = Efficiency of chemical transfer via intestinal tract (%)

$K_{gb}$  = gut biota partition coefficient (unitless)

$W_b$  = weight of biota ( $\text{Kg}$ )

**Growth dilution rate constant ( $k_g$ ) excluding primary producers.**

For primary producers it is assumed to be  $0.1 \text{ day}^{-1}$ .

$$k_G = lgr \cdot W_b^{-2}$$

Where

$k_g$  = Growth dilution rate constant ( $\text{day}^{-1}$ )

$lgr$  = invertebrate growth rate coefficient (unitless)

W<sub>b</sub> = weight of biota (Kg)

**Total elimination rate constant ( $k_{total}$ )**

$$k_{total} = k_2 + k_E + k_G + k_M$$

Where

$k_2$  = gill elimination rate constant ( $\text{day}^{-1}$ )

$k_E$  = fecal egestion rate constant ( $\text{day}^{-1}$ )

$k_G$  = Growth dilution rate constant ( $\text{day}^{-1}$ )

$k_M$  = metabolic transformation rate constant ( $\text{day}^{-1}$ )

**Biota-water partition coefficient ( $K_{bw}$ )**

$$k_{bw} = v_{lb} \cdot K_{ow} + v_{nb} \cdot \beta \cdot K_{ow} + v_{wb}$$

Where

$k_{bw}$  = biota-water partition coefficient (unitless)

$v_{lb}$  = lipid fraction in biota/phytoplankton (kg/kg)

$K_{ow}$  = octanol water partition coefficient (unitless)

$v_{nb}$  = nonlipid organic matter fraction in biota/phytoplankton (kg/kg)

$\beta$  = nonlipid organic matter octanol proportionality constant (unitless)

$v_{wb}$  = water fraction in biota (kg/kg)

**Phytoplankton-water partition coefficient ( $K_{pw}$ )**

$$K_{pw} = v_{lb} \cdot K_{ow} + v_{nb} \cdot \alpha_{poc} \cdot K_{ow} + v_{wb}$$

Where

$k_{pw}$  = phytoplankton-water partition coefficient (unitless)

$v_{lb}$  = lipid fraction in biota/phytoplankton (kg/kg)

$K_{ow}$  = octanol water partition coefficient (unitless)

$v_{nb}$  = nonlipid organic matter fraction in biota/phytoplankton (kg/kg)

$\alpha_{poc}$  = POC-octanol proportionality constant (unitless)

$v_{wb}$  = water fraction in biota (kg/kg)

### **Gut-biota partition coefficient ( $k_{gb}$ ) excluding phytoplankton**

$$k_{gb} = \frac{vlg.K_{ow} + vng.beta.K_{ow} + vwg}{vlb.K_{ow} + vnb.beta.K_{ow} + vwb}$$

Where

vlg = lipid fraction in gut (kg/kg)

$K_{ow}$  = octanol-water partition coefficient (unitless)

vng = nonlipid organic matter fraction in gut (kg/kg)

vwg = water fraction in gut (kg/kg)

vlb = lipid fraction in biota / phytoplankton (kg/kg)

vnb = nonlipid organic matter fraction in biota/phytoplankton (kg/kg)

Beta = nonlipid organic matter-octanol proportionality constant (unitless)

vwb = water fraction in biota (kg/kg)

### **Gill ventilation rate ( $G_v$ ) excluding phytoplankton**

$$G_v = 1400. (W_b^{0.65}) / C_{ox}$$

Where

$G_v$  = Gill ventilation rate (L/day)

$W_b$  = weight of biota (kg)

$C_{ox}$  = dissolved oxygen concentration (mg  $O_2$ /L)

### **Feeding rate (mold) excluding phytoplankton**

$$G_d = 0.022 * (W_b^{0.85}) * 10^{0.06.T_w}$$

Where

$G_d$  = Feeding rate (kg/day)

$W_b$  = weight of biota (kg)

$T_w$  = waste temperature ( $^{\circ}C$ )

### **Faecal egestion rate ( $G_f$ ) excluding phytoplankton**

$$G_f = ((1 - el) \cdot vld + (1 - en) \cdot vnd + (1 - eww) \cdot vwd) \cdot G_d$$

Where

$G_f$  = faecal egestion rate (kg/day)

$el$  = dietary absorption efficient of lipid (%)

$vld$  = lipid fraction in diet (kg/kg)

$en$  = dietary absorption efficiency of nonlipid organic matter

$vnd$  = nonlipid organic matter fraction in diet

$eww$  = dietary absorption efficiency of water (%)

$vwd$  = water fraction in diet (kg/kg)

$G_d$  = feeding rate (kg/day)

### **Efficacy of chemical transfer via gill including phytoplankton**

$$e_w = \left( A_{ew} + \left( \frac{B_{ew}}{K_{ow}} \right) \right)^{-1}$$

Where

$e_w$  = efficiency of chemical transfer via gill (%)

$A_{ew}$  = Constant  $A_{ew}$  (unitless)

$B_{ew}$  = Constant  $B_{ew}$  (unitless)

$K_{ow}$  = octanol-water partition coefficient (unitless)

### **Efficiency of chemical transfer via intestinal tract ( $E_d$ )**

$$E_d = (A_{ed} \cdot K_{ow} \cdot B_{ed})^{-1}$$

Where

$E_d$  = Efficiency of chemical transfer via intestinal tract excluding phytoplankton

$A_{ed}$  = constant  $A_{ed}$  (unitless)

$B_{ed}$  = Constant  $B_{ed}$  (unitless)

$K_{ow}$  = octanol-water partition coefficient (unitless)

### **Lipid fraction in diet (v<sub>ld</sub>) excluding phytoplankton**

$$v_{ld} = \sum(\text{fraction in diet } (\%) \cdot v_{lb})$$

where

$v_{ld}$  = lipid fraction in diet (kg/kg)

$v_{lb}$  = lipid fraction in biota / phytoplankton (kg/kg)

### **lipid fraction in gut (v<sub>lg</sub>) excluding phytoplankton**

$$v_{lg} = (1 - el) \cdot \frac{v_{ld}}{(1 - el) \cdot v_{ld} + (1 - e_n) \cdot v_{nd} + (1 - e_{ww}) \cdot v_{wd}}$$

where

$v_{lg}$  = lipid fraction in gut (kg/kg)

$el$  = dietary absorption efficiency of lipid (%)

$v_{ld}$  = lipid fraction in diet (kg/kg)

$e_n$  = dietary absorption efficiency of nonlipid organic matter (%)

$v_{nd}$  = nonlipid organic matter fraction in diet (kg/kg)

$e_{ww}$  = dietary absorption efficiency of water (%)

$v_{wd}$  = water fraction in diet (kg/kg)

### **nonlipid organic matter fraction in diet (v<sub>nd</sub>) excluding phytoplankton**

$$v_{nd} = \sum(\text{fraction in diet } (\%) \cdot v_{nb})$$

where

$v_{nd}$  = nonlipid organic matter fraction in diet

$v_{nb}$  = nonlipid organic matter fraction in biota/phytoplankton

### **nonlipid organic matter fraction in gut (v<sub>ng</sub>) excluding phytoplankton**

$$v_{ng} = (1 - en) \cdot \frac{v_{ld}}{(1 - el) \cdot v_{ld} + (1 - e_n) \cdot v_{nd} + (1 - e_{ww}) \cdot v_{wd}}$$

where

$v_{ng}$  = nonlipid organic matter fraction in gut ( kg/kg)

$e_n$  = dietary absorption efficiency of nonlipid organic matter (%)

$v_{ld}$  = lipid fraction in diet

$e_l$  = dietary absorption efficiency of lipid (%)

$v_{nd}$  = nonlipid organic matter fraction in diet (kg/kg)

$e_{ww}$  = dietary absorption efficiency of water (%)

$v_{wd}$  = water fraction in gut (kg/kg)

### **water fraction in diet (v<sub>wd</sub>) excluding phytoplankton**

$$v_{wd} = \sum(\text{fraction in diet } (\%) \cdot v_{wb})$$

$v_{wd}$  = water fraction in diet (kg/kg)

$v_{wb}$  = water fraction in biota (kg/kg)

### **water fraction in gut (v<sub>wg</sub>) excluding phytoplankton**

$$v_{wg} = (1 - e_w) \cdot \frac{v_{wd}}{(1 - e_l) \cdot v_{ld} + (1 - e_n) \cdot v_{nd} + (1 - e_{ww}) \cdot v_{wd}}$$

where

$v_{wg}$  = water fraction in gut (kg/kg)

$e_{ww}$  = dietary absorption efficiency of water (%)

$v_{wd}$  = water fraction in gut (kg/kg)

$e_l$  = dietary absorption efficiency of lipid (%)

$v_{ld}$  = lipid fraction in diet (kg/kg)

$e_n$  = dietary absorption efficiency of nonlipid organic matter (%)

$v_{nd}$  = nonlipid organic matter fraction in diet

### **Dissolved oxygen concentration (C<sub>ox</sub>) including phytoplankton**

$$C_{ox} = ((-0.24 \cdot T_w) + 14.04) \cdot S$$

Where

C<sub>ox</sub> = Dissolved oxygen concentration (mg O<sub>2</sub>/L)

T<sub>w</sub> = water temperature (°C)

S = dissolved oxygen saturation (%)

**Oxygen consumption ( $V_{ox}$ ) excluding phytoplankton**

$$V_{ox} = 980 \cdot W_b^{0.65}$$

Where

$V_{ox}$  = oxygen consumption (mg  $O_2$ /day)

$W_b$  = weight of biota (kg)

## **Appendix B-4 Calculated organism specific parameters for DPEs**

## **Appendix B-5 Calculated organism specific parameters for MPEs**

## **Appendix B-6 Predicted and measured TMF regression analysis results**

## **Appendix B-7 S-plus statistics for Predicted and Observed TMFs**

## Appendix C: CD-ROM Data Appendix

Please refer to Excel file: G. Zandpour – Appendix Tables on Attached CD

The CD-ROM, attached, forms a part of this work.

Data file can be opened with MSEXcel or other spread sheet program.

The PDF file was created with Adobe Acrobat, but may be opened in any PDF program.

### Data Files:

• Mastersheet of Entering Parameters	340--KB
• DMP Model (1DMP NE)	196-- KB
• DEP Model (2 DEP NE)	196-- KB
• DnBP Model (3 DnBP NE)	198-- KB
• BBP Model (4 BBP NE)	197--KB
• DEHP Model (5 DEHP NE)	196--KB
• C8 Model (6 DOP NE)	195--KB
• C9 Model (7DINP NE)	222--KB
• C10 Model (DiDP Model)	224--KB
• Analysis	1,525-KB
• Metabolism	950-KB
• Appendices	390-KB