Science of the Total Environment 551–552 (2016) 438–451

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evaluating the roles of biotransformation, spatial concentration differences, organism home range, and field sampling design on trophic magnification factors

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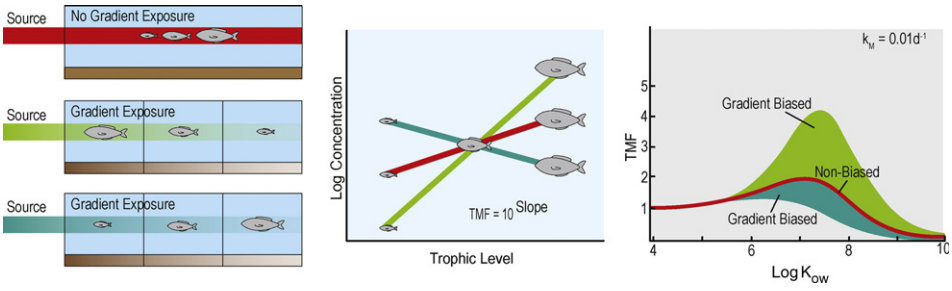
HIGHLIGHTS

- A new model was developed to evaluate bioaccumulation in aquatic food webs.
- Model parameters having the greatest influence on bioaccumulation were evaluated.
- Model results in excellent agreement with field results for a well-studied ecosystem.
- Spatial concentration differences may bias interpretation of bioaccumulation.
- Model is useful for a priori design and a posteriori evaluation of field studies.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 September 2015
Received in revised form 29 January 2016
Accepted 2 February 2016
Available online 15 February 2016

Editor: J. P. Bennett

Keywords:
Bioaccumulation
Trophic magnification factor (TMF)
Concentration gradient
Home range
Biotransformation
Sediment-water fugacity ratio

ABSTRACT

Trophic magnification factors (TMFs) are field-based measurements of the bioaccumulation behavior of chemicals in food-webs. TMFs can provide valuable insights into the bioaccumulation behavior of chemicals. However, bioaccumulation metrics such as TMF may be subject to considerable uncertainty as a consequence of systematic bias and the influence of confounding variables. This study seeks to investigate the role of systematic bias resulting from spatially-variable concentrations in water and sediments and biotransformation rates on the determination of TMF. For this purpose, a multibox food-web bioaccumulation model was developed to account for spatial concentration differences and movement of organisms on chemical concentrations in aquatic biota and TMFs. Model calculated and reported field TMFs showed good agreement for persistent polychlorinated biphenyl (PCB) congeners and biotransformable phthalate esters (PEs) in a marine aquatic food-web. Model testing showed no systematic bias and good precision in the estimation of the TMF for PCB congeners but an apparent underestimation of model calculated TMFs, relative to reported field TMFs, for PEs. A model sensitivity analysis showed that sampling designs that ignore the presence of concentration gradients may cause systematically biased and misleading TMF values. The model demonstrates that field TMFs are most sensitive to concentration gradients and species migration patterns for substances that are subject to a low degree of biomagnification or trophic dilution. The model is useful in anticipating the effect of spatial concentration gradients on the determination of the TMF; guiding species collection strategies in TMF studies; and interpretation of the results of field bioaccumulation studies in study locations where spatial differences in chemical concentration exist.

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http://dx.doi.org/10.1016/j.scitotenv.2016.02.013

1. Introduction

Globally, chemicals are routinely evaluated for their bioaccumulation potential (European Chemicals Agency, 2008; European Parliament and the Council of the European Union, 2006; Government of Canada, 1999; Government of Canada, 2000; UNEP, 2001). Several metrics for assessment of chemical bioaccumulation in aquatic organisms and food webs can be considered, including the octanol-water partition coefficient (K_{OW}), bioconcentration factor (BCF), bioaccumulation factor (BAF), biomagnification factor (BMF), and trophic magnification factor (TMF) (Burkhard et al., 2012; Gobas et al., 2009; Weisbrod et al., 2009). The BCF is often preferred over K_{OW} (considered a surrogate for lipid-water partitioning in aquatic biota) because the BCF considers absorption and biotransformation processes in addition to simple organism-water partitioning. However, the BCF is determined under laboratory conditions and does not include dietary exposures and hence excludes the potential for biomagnification (Connolly and Pedersen, 1988; Gobas et al., 1999). In the environment, the diet is often the dominant exposure pathway for very hydrophobic chemicals (Connolly and Pedersen, 1988; Qiao et al., 2000), and the need to consider bioaccumulation metrics that include dietary exposures is generally well recognized (Abelkop et al., 2013; Gottardo et al., 2014; Moermond et al., 2012). Field-derived BAFs, BMFs and TMFs are environmentally relevant because they include all routes of chemical exposure and ecosystem processes. It is notable that TMF and BMF, which were proposed as the most relevant metrics for the identification and categorization of bioaccumulative chemicals, based on a threshold TMF or BMF > 1.0 (Gobas et al., 2009), are explicitly included in weight-of-evidence assessments of bioaccumulation under REACH (ECHA, 2011; ECHA, 2014). Similarly, it has been proposed that the greatest weight-of-evidence ought to be given to high quality field studies when assessing the potential for bioaccumulation and biomagnification (Bridges and Solomon, unpublished manuscript). However, interpretation of field data is susceptible to systematic bias because of uncertainty due to spatial heterogeneity and temporal variability in environmental concentrations (Burkhard, 2003), uncertainty in trophic interactions, species migration and organism home range (Borgå et al., 2012), limited statistical power (Conder et al., 2012), and other ecosystem-specific factors such as sediment-water disequilibrium conditions (Gobas and MacLean, 2003). In some cases, the between-study and within-study variability in exposure conditions is so great that the field data may be questionable and its usefulness severely limited unless experimental designs are implemented that control or account for such variation (Cressie, 1993; Gilbert, 1987). Starrfelt et al. (2013) used Bayesian inference to reduce uncertainty and increase precision of field TMFs. However, this approach does not decrease variability or systematic bias of the TMF that may occur, for example, as a result of spatial differences in sediment-water concentration distributions.

Field TMFs of well-studied hydrophobic chemicals that are known to biomagnify in aquatic food webs, such as several polychlorinated biphenyl (PCB) congeners and other legacy contaminants, are regularly determined with relatively high precision for individual study areas and hence are often used as reference chemicals (e.g., PCB-153 and PCB-180) for trophic magnification studies. However, several studies have reported that TMFs are highly variable when compared across study areas, which has been attributed to uncertainty in the determination of TMF, especially for legacy contaminants and emerging chemicals that have been identified as being very bioaccumulative. For example, Franklin (2015) highlighted the variability and uncertainty in field BMFs and TMFs for per- and poly-fluoroalkyl substances (PFASs) from various ecosystems. Published field TMFs for the most intensively studied PFASs ranged from 0.58 to 13 (n = 10 studies) for perfluorooctanoic acid (PFOA) and from 1.0 (TMF not statistically significant; $p > 0.05$) to 20 (n = 12 studies) for perfluorooctane sulfonic acid (PFOS). The variability and uncertainty were hypothetically attributed to such factors as non-achievement of steady state, differences in feeding ecology, biotransformation, seasonal and annual growth rates, gender, reproductive off-loading, and failure to co-locate prey and predators, among others. Franklin (2015) thus concluded that given the possible confounding factors in field studies, it was preferable to base regulatory decisions on tests conducted under strictly monitored laboratory conditions with selected species and use field observations as only one component of a broader weight of evidence evaluation.

Similar to that observed for PFAS, review of published field TMFs for the most intensely studied polychlorinated biphenyls in aquatic poikilothermic food webs ranged from 0.48 to 15 (n = 49 studies) for PCB-153 and from 0.56 to 17 (n = 43 studies) for PCB-180 (D. E. Powell, unpublished results). Review of published and reported field TMFs for the most intensely studied cyclic volatile methylsiloxanes (cVMS) ranged from 0.54 to 1.5 (n = 20 studies) for octamethylcyclotetrasiloxane (D4), from 0.25 to 3.2 (n = 21 studies) for decamethylcyclopentasiloxane (D5) (Gobas et al., 2015), and from 0.32 to 2.7 (n = 20 studies) for dodecamethylcyclohexasiloxane (D6); Table S1 of the of the Supplemental information, SI. For a subset of the cVMS (n = 11 study areas) and the PCB congeners (n = 6 study areas), differences between field TMFs do not appear to be explained by systematic differences between the study areas—i.e., between environment (marine vs. freshwater), type of food web (pelagic vs. demersal), length of the sampled food webs, or species composition of the sampled food webs (Table S1 of the SI). Rather, the TMF contradictions between study areas may be related to differences in food web dynamics and variable conditions of exposure. Similarly, Guildford et al. (2008) concluded that the variability associated with field TMFs for PCBs in salmonid food webs was influenced by habitat use and lake characteristics.

The contradictions in reported field TMFs between study areas emphasizes the importance of identifying the apparent causes of variability, including whether the different findings are due to different ecosystems investigated, sampled food web species, insufficient understanding of food web dynamics (i.e., predator prey relationships and trophic level structure), or other differences in food web characteristics, study methodology, and experimental design. For example, it is typically assumed when calculating a field TMF that all individuals and species in the sampled food web are exposed to the same conditions across the study area such that the confounding factors of non-uniform patterns of organism movement and variable conditions of exposure may therefore be ignored (Borgå et al., 2012). Consequently, the location from where samples are taken may not be considered important even for environments where spatial concentration differences are inevitably present. Spatial concentration differences of a chemical in the water and sediment are expected to exist due to the presence of point source(s) of the chemical, as may occur, for example, from a wastewater treatment facility or a production facility. However, spatial concentration differences may also occur across thermoclines, pycnoclines, and other physical interfaces in areas that are remote from point sources, which is where most TMF studies have thus far been conducted. Sediment focusing and advective transport of sediment bound contaminants from high energy erosional areas to low energy depositional areas may also cause spatial concentration differences to exist in areas that do not receive point source emissions. Also, sediment-water fugacity ratios can vary among locations as a result of temporal changes of contamination levels and differences in the degree of carbon utilization among locations (Gobas and MacLean, 2003).

It is recognized that, while the use of environmentally-relevant bioaccumulation metrics is highly desirable, the current variability in data generated from field studies may hinder widespread use of field derived bioaccumulation data for regulatory assessment. Improved quality and scientific understanding of field bioaccumulation metrics, such as the TMF, and the factors that affect these metrics are thus needed to reduce variability and foster confidence in using this type of data for decision-making (Burkhard et al., 2013). A better recognition of the factors controlling field derived bioaccumulation metrics may also provide

guidance and/or protocols for conducting field bioaccumulation studies that reduce uncertainty associated with these confounding factors.

Differences in the biotransformation rates of a chemical among organisms have the potential to dominate the bioaccumulation process. However, BMFs and TMFs for some compounds can also be low due to a low dietary assimilation efficiency, caused by intestinal biotransformation (Lo et al., 2015b) and/or a reduced gastro-intestinal absorption rate (Gobas et al., 1988). For hydrophobic compounds, toxicokinetics (i.e., the culmination of the combined effects of absorption, distribution, metabolism, and excretion or ADME) are often important contributors to the primary determinant of observed differences in the concentration of chemicals (i.e., bioaccumulation) among various wildlife species (Nichols et al., 2007). The toxicokinetic parameters required for effective bioaccumulation modeling include uptake rate constants from water and food, biotransformation/metabolism rate coefficients, and elimination rate constants from the animal. For aquatic organisms exposed to hydrophobic compounds, the role of dietary uptake to total chemical exposure becomes increasingly pronounced with increasing chemical hydrophobicity and often becomes dominant when K_{OW} exceeds a value of approximately 10^6 due to more efficient mass transfer (Barber, 2008; Connolly and Pedersen, 1988; Gobas et al., 1989; Qiao et al., 2000; Thomann, 1989). A critical parameter in understanding chemical transfer and food web accumulation via the diet is the assimilation efficiency (E_D) from ingested food/prey (Landrum et al., 1992; Liu et al., 2010; Thomann, 1981; Wang and Fisher, 1999). In addition, the rate of metabolism or biotransformation (k_M) can vary greatly among chemicals and this parameter has the potential to dominate the bioaccumulation process and markedly influence cumulative ecological toxicity (Arnot et al., 2008b; Brown et al., 2012; Lech and Bend, 1980; Nichols et al., 2006). The rate of chemical elimination from aquatic species is sufficiently important that Goss et al. (2013) have proposed use of the overall elimination rate as an alternative bioaccumulation metric for chemical assessment. Thus further evaluation of these factors (i.e., E_D and k_M) via in vivo testing is important for quantifying biomagnification in fish and higher trophic level organisms (Mackay et al., 2013; Nichols et al., 2015).

Mass balance food web bioaccumulation models have been developed and applied to calculate chemical concentrations and BAFs in various species (Barber et al., 1991; Campfens and Mackay, 1997; Morrison et al., 1997; Morrison et al., 1999; Thomann and Connolly, 1984; Thomann et al., 1992). Models are often required to interpret environmental data and they provide mechanistic insights by integrating knowledge on chemical, biological, and ecosystem properties. Model sensitivity and uncertainty analyses can identify key processes underlying the model calculations and measured information (Gobas and Arnot, 2010; MacLeod et al., 2002; McLeod et al., 2015; Morgan and Small, 1992; Morrison et al., 1996) and can also be used to illustrate the roles of various chemical properties and processes (Moermond et al., 2007; Thomann, 1989) that influence bioaccumulation metrics, such as K_{OW} and the biotransformation rate constant, k_M (Arnot et al., 2008a; Burkhard, 2003; McLeod et al., 2015). The AQUAWEB model and variations of this model have been applied and evaluated in several diverse ecosystems (Arnot and Gobas, 2004; Gewurtz et al., 2009; Gewurtz et al., 2006; Gobas and Arnot, 2010), and the model has been used to calculate TMFs (McLeod et al., 2015; Walters et al., 2011). Recently, McLeod et al. (2015) used the AQUAWEB model to demonstrate uncertainty in the TMFs of PCBs in the Detroit River due to fish migration and spatial concentration gradients.

The objective of the present study was to investigate the role of selected factors on derivation of field based bioaccumulation metrics. A new Multibox-AQUAWEB (MBAW) model was developed in which organisms could migrate through two-dimensional chemical concentration gradients (vertically and horizontally). The model was applied and tested against a marine ecosystem for which measurements of spatially varying chemical concentrations in water, sediments and biota were available (Mackintosh et al., 2004). Reported field TMFs and model calculated TMFs for two classes of hydrophobic organic chemicals, i.e., persistent PCBs and the more labile phthalate esters (PEs), were compared. The model was also used to explore the implications of non-uniform exposure as a consequence of chemical concentration gradients, ratios of fugacities in sediment and water, species migration patterns, organism home range, and spatial sampling design. The model provides guidance on both the conduct and interpretation of field bioaccumulation studies and highlights the need for development of detailed protocols for field bioaccumulation studies in aquatic food webs. Recommendations for further model revisions and evaluations are also discussed.

2. Theory

2.1. Spatial model description

For most "one-box" environmental multimedia models such as the Equilibrium Criterion (EQC) model (Hughes et al., 2012) and the Quantitative Water Air Sediment Interaction (QWASI) model (Mackay et al., 2014), each environmental compartment (water, sediment and individual organisms) is defined by a single (mean or median) concentration. In reality, however, concentrations of chemicals in environmental compartments can vary significantly in space and time necessitating the use of multiple boxes or "plume" models. The MBAW model, therefore, divides the water column of an evaluative aquatic environment into multiple sub-compartments. For reasons of simplicity we have limited the current model to a total of nine water column sub-compartments with three horizontal ($i = 1,2,3$) sections and three vertical ($j = 1,2,3$) sections, with three sediment compartments at the bottom of each vertical section (Fig. 1).

The model requires users to define species composition, structure, and trophic dynamics of the aquatic food web to be evaluated. The model was developed to allow habitat ecology and utilization, migration patterns, home range, trophic level position, feeding ecology, dietary preferences, and guild structures of each species to be specified and considered by the model. The structure of the evaluative food web may include a variety of different feeding guilds; e.g., primary producers, detritivores, planktivores, invertivores, and piscivores. Biological properties required for each species include wet body weight mass and lipid content. Habitat utilization by each species across the model environment may be defined by the user or estimated using an allometric home range based on body size to represent the areal distribution over which an organism lived and regularly traveled.

The model assumes that each species resides in a defined zone in water or sediment (i.e., a home range). The users can define the fraction of the time that a species s is found in a particular compartment (i,j) by entering a home range factor $H_{s,i,j}$ (fraction between 0 and 1). This

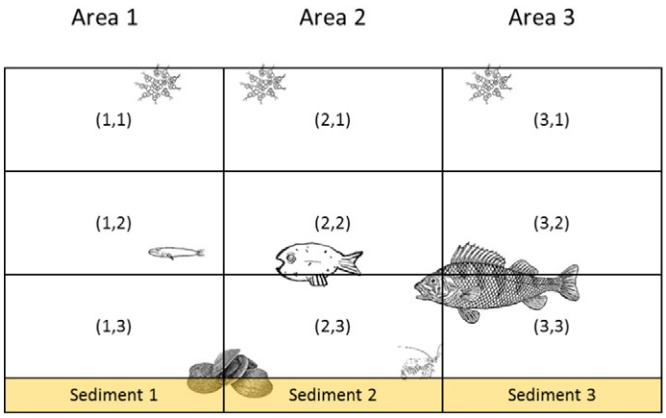

Fig. 1. Configuration of the new 2D Multibox-AQUAWEB model showing 9 water compartments and 3 sediment compartments used to define the False Creek ecosystem. The number pairs (i,j) in each compartment are the unique identifiers used in the model.

provides a method to limit the distribution of a species to a certain area and to specify the degree to which a species may be present across multiple compartments. For example, the diurnal vertical migration of mysids from bottom sediments to the surface may be represented by selecting the home range factors to define the fraction of time that mysids are present in each vertical compartment. Similarly, the foraging of higher trophic level species over multiple compartments may be represented by selecting appropriate home range factors that represent the fraction of the time that the predator is present in each compartment, which can vary both horizontally and vertically.

The model also provides the user with the option to specify the "sampling" location of each species by identifying the compartment(s) from which the species will be collected. This model feature provides a method for investigating the effect of sample collection location on the TMF in situations where spatial differences in concentrations exist.

2.1.1. Chemical properties

As in the original AQUAWEB model (Arnot and Gobas, 2004), the lipid-water partition coefficient (K_{LW}) was equal to the octanol-water partition coefficient (K_{OW}), based on the assumption that the fugacity capacity of octanol (Z_O) was equal to that of lipid (Z_L). The model also provides the option of allowing the user to enter an empirical organic carbon–water partition coefficient (K_{OC} in L/kg organic carbon) directly without the need to estimate this property from K_{OW}. Because, K_{OW} and K_{OC} are a function of temperature, and the model allows temperature to vary across compartments, K_{OW} and K_{OC} are referred to as $K_{OW,i,j}$ and $K_{OC,i,j}$ in the model derivation.

2.1.2. Site specific concentrations and environmental parameters

Total chemical concentrations in water ($C_{WT,i,j}$ in g/L) and the corresponding bottom-sediment/bottom-water compartment fugacity ratios ($f_{S/W,i,j}$ unitless) are typically specified by the user. Chemical concentrations and fugacity ratios may be obtained from empirical data or from environmental multimedia models such as EQC (Hughes et al., 2012) or QWASI (Mackay et al., 2014). Subscripts *i* and *j* denote the horizontal and vertical locations, respectively, of each box or compartment in the defined ecosystem. Total concentrations in bottom sediment ($C_{S,i}$ in g/kg dry weight sediment) were calculated for each compound in each compartment as:

$$C_{S,i} = f_{S/W,i,j} \cdot K_{OC,i,j} \cdot \phi_{S,i} \cdot C_{WD,i,j} \quad (1)$$

where $K_{OC,i,j}$ (L/kg OC) is the chemical's temperature-corrected partition coefficient between organic carbon and water at the temperature of compartment (i,j); $\phi_{S,i}$ is the fraction of organic carbon in sediment compartment i (kg organic carbon/kg dry sediment); and $C_{WD,i,j}$ (g/L) is the freely dissolved chemical concentration in water compartment (i,j), which is calculated from $C_{WT,i,j}$ as:

$$C_{WD,i,j} = \frac{C_{WT,i,j}}{1 + X_{POC,i,j} \cdot K_{OC,i,j} + OC_{W,i,j} \cdot (0.08 \cdot K_{OW,i,j})} \quad (2)$$

where $X_{POC,i,j}$ (kg OC/L) is the concentration of particulate organic carbon in water compartment (i,j); $OC_{Wi,j}$ (kg OC/L) is dissolved organic carbon content in water compartment (i,j); 0.08 is a proportionality constant (units of L/kg OC) that expresses the sorptive capacity of dissolved organic carbon for a chemical relative to that of octanol (Burkhard et al., 2008); and $K_{OW,i,j}$ (unitless) is the chemical's temperature-corrected partition coefficient between octanol and water at the temperature of compartment (i,j).

Other compartment-specific environmental parameters that users are to provide are water temperature, dissolved organic carbon content in water, organic carbon fraction of solids in water and sediment, particulate concentration in water, water column dissolved oxygen concentration, density of sediments and suspended solids and density of sediment organic carbon.

2.1.3. Concentrations in biota and TMF

The MBAW model uses the steady-state uptake equations of the AQUAWEB model (Arnot and Gobas, 2004) to calculate the chemical concentration in species s ($C_{B,s,i,j}$ in g/kg wet weight) in compartment (i,j) assuming that both the species and its diet occupy compartment (i,j) according to:

$$C_{B,s,i,j} = \frac{k_{1,s,i,j}(m_{0,s,i,j} \cdot C_{WD,i,j} + m_{P,s,i} \cdot C_{WP,i}) + k_{D,s,i,j} \sum_i \sum_j (P_r \cdot R_{r,i,j} \cdot C_{B,r,i,j})}{k_{2,s,i,j} + k_{E,s,i,j} + k_{G,s,i,j} + k_{M,s,i,j}} \quad (3)$$

where $C_{B,r,i,j}$ (g/kg wet weight) is the chemical concentration in prey species r in compartment (i,j); $k_{1,s,i,j}$ (L kg^{-1} d^{-1}) is the chemical uptake rate constant via respiration of species s in compartment (i,j); $k_{2,s,i,j}$ (d^{-1}) is the rate constant for chemical elimination via respiration of species s in compartment (i,j); $k_{D,s,i,j}$ (d^{-1}) is the rate constant for uptake via ingestion of food by species s in compartment (i,j); $k_{E,s,i,j}$ (d^{-1}) is the rate constant for elimination via excretion of contaminated feces by species s in compartment (i,j); $k_{G,s,i,j}$ (d^{-1}) is the growth rate constant of species s in compartment (i,j); $k_{M,s,i,j}$ (d^{-1}) is the rate constant for biotransformation by species s in compartment (i,j); $m_{0,s,i,j}$ (unitless) is the fraction of respiratory ventilation of overlying water in compartment (i,j) for species s; $m_{P,s,i,j}$ (unitless) is the fraction of respiratory ventilation of sediment pore-water for sediment dwelling organism species s in (horizontal) spatial compartment i; $C_{WD,i,j}$ (in g/L) is the freely dissolved concentrations of the chemical in compartment (i,j) for species s; $C_{WP,i}$ (in g/L) is the freely dissolved concentrations of the chemical in pore water of sediment compartment i for species s organisms; P_r (unitless) the fraction of diet containing prey r; $R_{r,i,j}$ (unitless) is the presence factor for prey species r in compartment (i,j).

Rate constants for chemical biotransformation by species s ($k_{M,s,i,j}$) may be individually entered by the user or estimated for phytoplankton, zooplankton, invertebrates and fish. A reference value ($k_{M,N}$ for a 10 g fish at 15 °C) is used to determine model values as a function of the weight of species s and water temperature in compartments i,j in Eq. (4) (Arnot et al., 2008a; Arnot et al., 2008b).

$$k_{M,s,i,j} = k_{M,N} \cdot \left(\frac{W_{B,s,i,j}}{W_{B,N}}\right)^{-0.25} \cdot e^{0.01(T_{i,j} - T_{ref})} \quad (4)$$

where $W_{B,S,i,j}$ is the wet weight of the organism in compartment (i,j); $W_{B,N}$ is the wet weight of reference fish N (i.e., 10 g); T is the water temperature in compartment (i,j); and T_{ref} is the reference temperature (15 °C).

2.1.4. Spatially averaged concentrations for sampling scenarios

To investigate the effect of sampling design on the calculation of TMF, concentrations in species that occupy multiple compartments were derived as a weighted average of the concentrations ($C_{B,s}$) in each of the compartments that are accessed by the species. The weighting is based on the relative amount of time of the species in each of the compartments, as identified by the home range of the species

$$\overline{C_{B,s}} = \sum_i \sum_j (C_{B,s,i,j} \cdot H_{s,i,j}) \quad (5)$$

where $H_{s,i,j}$ is the home range factor for species s in compartment (i,j).

The model requires the user to define wet body weight, lipid content, trophic interactions, and diet of each species s in the form of a feeding matrix for the defined food web. The relative Trophic Position (TP_s) of each consumer species s is estimated from the diet composition of the

species using a trophic position model (Vander Zanden and Rasmussen, 1996):

$$TP_s = \left(\sum_{r=1}^{R} TP_r \times P_r\right) + 1 \quad (6)$$

where TP_s is the mean trophic position of the predator species s, TP_r is the trophic position of prey species r in the diet of species s, P_r is the fraction of prey species r in the diet of species s, and the R is the number of prey species in the diet of species s.

The model calculates whole body wet weight chemical concentrations ($C_{B,S}$ in g/kg ww) and lipid-equivalent concentrations ($C_{BL,s}$ in g/kg equivalent lipid) for each species. TMFs are calculated as the antilog of the linear regression slope of log-transformed lipid equivalent concentrations regressed on trophic position:

$$\log\left(\overline{C_{\mathrm{BL},s}}\right) = a + b \cdot TP_s \text{ and } \mathrm{TM}F = 10^b \quad (7)$$

where b is the slope of the regression line. The lipid equivalent concentrations recognize the sorptive capacities of lipid (i.e., equal to that of octanol), protein (i.e., equal to 5% of octanol (deBruyn and Gobas, 2007)), and water (i.e., equal to that of octanol divided by K_{OW}) in each organism. The TMF can be calculated for various sampling scenarios. This provides the option to investigate the effect of sampling design on the determination of the TMF in areas where significant spatial concentration differences exist.

2.2. Model implementation

The MBAW model was coded as a Microsoft Excel 2013 workbook. Model outputs include chemical concentrations, species-specific bioaccumulation metrics, and TMFs for the defined food web used in the model; only TMF values are reported for the present study. TMF values were calculated based on lipid-equivalent concentrations using the built-in array function LOGEST, which generates statistical information such as slope, standard error, r^2, p-value (based on F-distribution) and 95% confidence interval. When calculated using LOGEST the slope is equal to the TMF value. TMF values may also be calculated based on log-transformed lipid-equivalent concentrations using the built-in array function LINEST, which generates identical statistical information as LOGEST, except for slope and standard error. When based on LINEST, TMF is equal to the antilog of the slope.

3. Methodology

3.1. Model performance analysis

To evaluate the MBAW model for assessing the TMF of both persistent and readily biotransformed substances, the model was parameterized for the aquatic marine food web of False Creek (Table S2 of the SI) in British Columbia, Canada (Mackintosh et al., 2004). The False Creek ecosystem was selected for model performance analysis because the Mackintosh et al. (2004) study (1) provided detailed information on chemical concentrations in water (total and operationally defined as dissolved) and in sediments at three different locations in the sampled study area, thus providing information used to characterize spatial concentration differences and sediment-water fugacity ratios; (2) included a well-defined food web that was characterized by feeding surveys and $^{14}N/^{15}N$ and $^{12}C/^{13}C$ stable isotope ratios; (3) provided contaminant concentrations in 24 selected species, representing trophic positions ranging from 1 to 4.5; (4) was conducted with attention to QA/QC during contaminant analyses; (5) included both persistent and readily biotransformed substances (Arnot et al., 2009; Brown et al., 2012; U.S. Environmental Protection Agency, 2014); and (6) reported substantial differences in aqueous and sedimentary concentrations among the three locations investigated.

The PCBs and PEs were selected for model performance analysis because most of the relevant information required for the analyses was available. The physical-chemical properties of the PCBs and PEs applicable to the marine environment (Table 1), the biological and environmental parameters used to parameterize the MBAW model (Table 2), and the feeding matrix used to parameterize the food web component of the MBAW model (Table S2 of the SI) were taken from Mackintosh et al. (2004, 2006). All sampled species were used in the MBAW model except for a marine bird (i.e., surf scoters). The species included three phytoplankton/algae, one zooplankton, 10 invertebrates, and 10 fish. For all test substances, measured concentrations (n = 3 or 4) in the sediments of three sub-areas of the False Creek system, i.e., North Basin (Area 1), South Basin (Area 2) and East Basin (Area 3) were available and used in the model performance analysis. Measured aqueous concentrations were available for all PEs and for PCB-18 in all three sub-areas. Aqueous concentrations of PCB-99, PCB-180 and PCB-194, were only available for one sub-area. Aqueous concentrations in the subareas for which PCB concentrations were below the method detection limit were estimated from the area specific sediment concentrations using sediment-water partition coefficients that were determined in the one sub area where both aqueous and sedimentary concentrations were detected. For PCBs −118 and −209, no detectable concentrations in water were reported for any area. Hence, PCB concentrations were estimated from the concentrations in the sediments using the sediment-water partition coefficient reported by Mackintosh et al. (2006).

Model performance was evaluated by comparing model TMFs, which were derived from the model calculated chemical concentrations in the biota (Table S4 of the SI), to the field TMFs (based on trophic position) reported by Mackintosh et al. (2004). The mean model bias (MB) was calculated to quantitatively express the model's performance across the combined results for n = 1 to N chemicals, as shown in Eq. (8)):

$$MB = 10^{\left(\sum_{n=1}^{N} \frac{\left[\log(TMF_{C,n}/TMF_{O,n})\right]}{N}\right)} \quad (8)$$

where $TMF_{C,n}$ is the model calculated TMF for chemical n, $TMF_{O,n}$ is the reported field TMF for chemical n, and N is the total number of chemicals included in the model performance evaluation. In essence, MB is the geometric mean of the ratio of modeled and reported TMFs for all chemicals in the evaluated food web for which empirical data were available. As it is used here, MB is a measure of the systematic bias (i.e., MB > 1 or MB < 1) of the model relative to the systematic bias of the field data. For example, MB = 2 indicates that the model in general overestimates the reported field TMF by a factor of 2. A MB = 0.5 indicates that the model underestimates the reported field TMF by a factor of 2. The 95% confidence intervals of the MB represent the accuracy of the model, relative to the field data, expressed as a factor (rather than a term) of the geometric mean. The inherent assumption is that the False Creek field data and results were not systematically biased and that the residuals of reported and modeled TMFs followed a log normal distribution rather than a normal distribution. This method has the advantage that it prevents the calculation of uncertainty bounds that may include implausible TMF values < 0. The MB and its 95% confidence intervals include all possible sources of error inherent to the performance analysis including model parameterization errors, errors in model structure, analytical errors in the empirical data (e.g., chemical concentrations in water, sediment and biota), and uncertainty in the empirical data used for the performance analysis. However, without having a benchmark TMF value it is not possible to identify if systematic model bias or systematic field bias was the greater source of error. Model

Table 1
Major physico-chemical properties of 13 phthalate esters (PEs) and 6 polychlorinated biphenyls (PCBs) for the False Creek ecosystem, as reported by Mackintosh et al. (2004).

CAS	Chemical name	Abbr.	Log K_{OW}[a]	Log K_{OC}	$f_{S/W}$[b]	$k_{M,N}$[c] (d^{-1})	TMF
84-66-2	Diethyl phthalate ester	DEP	2.77	2.31	0.037	0.31	1.0
84-69-5	Di-isobutyl phthalate ester	DiBP	4.58	4.12	0.048	0.31	0.81
84-74-2	Di-*n*-butyl phthalate ester	DBP	4.58	4.12	0.066	0.31	0.70
85-68-7	Butylbenzyl phthalate ester	BBP	5.03	4.57	0.174	0.31	0.77
117-81-7	Di(2-ethylhexyl) phthalate ester	DEHP	8.20	7.74	0.936	0.31	0.34
117-84-0	Di-*n*-octyl phthalate ester	DnOP	8.20	7.74	0.191	0.31	0.29
68515-51-5	Di-*n*-nonyl phthalate ester	DNP	8.50	8.04	0.045	0.31	0.28
37680-65-2	2,2′,5-Trichlorobiphenyl	PCB-18	5.46	5.00	0.058	0.0004	2.0
38380-01-7	2,2′,4,4′,5-Pentachlorobiphenyl	PCB-99	6.65	6.19	4.000	0.0004	4.9
31508-00-6	2,3′,4,4′,5-Pentachlorobiphenyl	PCB-118	7.00	6.54	4.000	0.0004	7.0
35065-29-3	2,2′,3,4,4′,5,5′-Heptachlorobiphenyl	PCB-180	7.66	7.20	3.950	0.0004	6.5
35694-08-7	2,2′,3,3′,4,4′,5,5′-Octachlorobiphenyl	PCB-194	8.12	7.66	2.129	0.0004	3.5
2051-24-3	Decachlorobiphenyl	PCB-209	8.53	8.07	2.000	0.0004	2.2

[a] Salinity-corrected log K_{OW} value.
[b] $f_{S/W}$ is the sediment-water fugacity ratio.
[c] $k_{M,N}$ is the biotransformation rate constant normalized for a 10-g fish; $k_{M,N}$ for phthalates was selected using a read across approach from 9 in vivo based estimates for DEHP (Arnot et al., 2008a,b); a slow, negligible $k_{M,N}$ of 0.0004 d^{-1} was assumed for the PCB congeners.

calibration (i.e., the adjustment of model parameters to improve model performance) was not applied.

3.2. Model sensitivity analysis

3.2.1. Spatial concentration gradients

Various model calculation scenarios were used to explore the sensitivity of the model calculated TMF to (i) spatial concentration gradients; (ii) differences in sediment-water concentration distributions (as expressed by the fugacity ratio); and (iii) spatial sampling design choices. Model TMFs were calculated for six PCB congeners and seven PE congeners (Table 1) in each of the three areas depicted in Fig. 1. Each defined area represented a water column with a bottom sediment layer and assumed that (i) all species remained within their designated area (i.e., no migration); (ii) the total concentration of test chemical in the water of each compartment within each area was calculated from the total concentration in sediment and the sediment-water fugacity ratio defined for each area (i.e., no vertical concentration gradients), and (iii) probability sampling (n = 10,000 independent Monte Carlo simulations) was used following systematic random designs where (a) all species were randomly collected from within a single area or (b) where each species was randomly collected from across the 3 areas.

Systematic random sampling designs are recommended when trends or patterns of exposure over space are not present or they are known to exist a priori or when strictly random methods are impractical (Gilbert, 1987). However, judgment sampling must often be implemented in the field because organisms may only be collected from within their home range (i.e., the area in which an organism normally lives and travels), which may overlap for some but not all organisms in the sampled food web. Field studies based on judgment sampling thus have a systematic sample selection bias because the target population is not clearly defined, is not homogeneous, and is not completely assessable for sample collection. Therefore, biased or judgment sampling was also explored in addition to systematic random sampling designs.

The model calculation scenarios for exploring the sensitivity of the TMF to differences in spatial concentrations, sediment-water fugacity ratios, and biased sampling designs are described below (additional details provided in Table 3 and Table S3 of the SI):

- Scenario 1: This is the "control" or "reference" scenario with concentrations in sediment defined as 1 μg/kg-dw and the sediment-water fugacity ratio defined as 1 for all three areas. Hence, the concentrations of chemical in water and sediment were constant and proportional across the defined ecosystem. Scenario 1 explored the effect of sampling design on determination of TMF when concentration gradients in water or sediment were not present. Results from other scenarios are compared to results from Scenario 1.
- Scenario 2: This simulation was the same as that used in Scenario 1 except that concentrations in sediment were defined as 1 μg/kg dw in Area-1, 10 μg/kg dw in Area-2, and 100 μg/kg dw in Area-3. Hence, concentrations of the chemical in sediments and in water were different but proportional across the defined study area. Scenario 2 explored the effect of sampling design on determination of TMF when spatial concentration gradients in water and sediment were both present.
- Scenario 3: This simulation was the same as Scenario 1 except that sediment-water fugacity ratios were defined as 0.1 in Area-1, 1 in Area-2, and 10 in Area-3. Hence, concentrations of the chemical in the sediments were the same in all areas, but concentrations of the chemical in the water differed. Scenario 3 explored the effect of sampling design on determination of TMF when spatial concentration gradients were present in water but not in sediment.
- Scenario 4: Concentrations in sediment were defined as 1 μg/kg dw in Area-1, 10 μg/kg dw in Area-2, and 100 μg/kg dw in Area-3 (the same as Scenario 2). Sediment-water fugacity ratios were defined as 0.1 in Area-1, 1 in Area-2, and 10 in Area-3 (the same as Scenario 3). Hence, concentrations of the chemical in water were the same in all areas, but concentrations of the chemical in sediment differed. Scenario 4 explored the effect of sampling design on the determination of the TMF when spatial concentration gradients were present in sediment but not water.
- Scenario 5: This simulation was the same as Scenario 2 (i.e., spatial concentration gradients present in both water and sediment) except that biased or judgment sampling (Gilbert, 1987) was used rather than systematic random sampling. Biased sampling was implemented here using a simple random sampling design to collect species that occupied trophic positions between 1 and 2 from Area-1 (where the lowest exposure concentrations existed), to collect species that

Table 2
Environmental properties used to parameterize the MBAW model for the aquatic marine ecosystem of False Creek (Table S2 of the SI) in British Columbia, Canada (Mackintosh et al., 2004).

Input	False creek
Dissolved organic carbon content in water (mg/L)	0.26
Organic carbon content in suspended solids	40%
Organic carbon content in sediment	2.8%
Particulate organic carbon (mg/L)	1.5
O_2 saturation (%)	80%
Density of solids (kg/L)	1.5
Density of organic carbon (kg/L)	0.9
Sediment:water fugacity ratio	2
Temperature	15

Table 3
Modeling scenarios used to explore the sensitivity of the calculated TMF to (i) spatial concentration gradients; (ii) differences in sediment-water concentration distributions (as expressed by the fugacity ratio); and (iii) spatial sampling design choices. Additional details provided in Table S2 of the Supporting information.

Modeling scenario	Spatial gradient		Fugacity ratio ($f_{S/W}$)	Sampling design	Comments
	Water	Sediment			
1	No	No	Fixed	Systematic random sampling	Used to evaluate bias when spatial concentration gradients in water and sediment were not present. This scenario served as the reference scenario.
2	Yes	Yes	Fixed	Systematic random sampling	Used to evaluate bias when spatial concentration gradients were present in both water and sediment.
3	Yes	No	Varied	Systematic random sampling	Used to evaluate bias when spatial concentration gradients were present in water but not in sediment.
4	No	Yes	Varied	Systematic random sampling	Used to evaluate bias when spatial concentration gradients were present in sediment but not in water.
5	Yes	Yes	Fixed	Biased or judgment sampling	Used to evaluate bias when judgment sampling was used across spatial concentration gradients in water and sediment. Concentration gradient: (Area-1 < Area-2 < Area-3)
6	Yes	Yes	Fixed	Biased or judgment sampling	Used to evaluate bias when judgment sampling was used across spatial concentration gradients in water and sediment. Concentration gradient: (Area-1 > Area-2 > Area-3)

occupied trophic positions between 2 and 3 from Area-2, and to collect species that occupied trophic positions > 3 from Area-3 (where the highest exposure concentrations existed). Scenario 5 explored the effect of biased sampling on the determination of the TMF when spatial concentration gradients were present in both water and sediment.

- Scenario 6: This simulation was the same as Scenario 5 except that spatial concentration gradients across the three areas were reversed. A simple random sampling design was used to collect species that occupied trophic positions between 1 and 2 from Area-1 (where the highest exposure concentrations existed), to collect species that occupied trophic positions between 2 and 3 from Area-2, and to collect species that occupied trophic positions > 3 from Area-3 (where the lowest exposure concentrations existed).

Scenarios 5 and 6 illustrate the sensitivity of TMF to spatial concentration differences and demonstrated the potential effect of sampling design on determination of TMF in study locations where spatial concentration gradients were present in both water and sediment.

Each Monte Carlo simulation represented a single TMF study of the food web (24 species in total; Table S1 of the SI) that was sampled from within or across the three defined areas of the defined False Creek ecosystem (Fig. 1). The TMF was calculated for each simulation as the antilog of the slope obtained from ordinary least-squares (OLS) regression models. Log-transformed lipid equivalent chemical concentrations in the sampled species were regressed on trophic position of each species to obtain the slope, the correlation coefficient (r^2), and the p-value that the slope was statistically different from zero. The combined distribution of 10,000 individual TMF studies, was then investigated for the probability that spatial differences in conditions caused the TMF to be misidentified, i.e., a TMF ≥ 1.0 when the TMF in the absence of concentration gradients was <1.0 or conversely, a TMF < 1.0 when the TMF in the absence of concentration gradients was ≥1.0.

3.2.2. Biotransformation rate

To explore the sensitivity of TMF to the biotransformation rate constant, chemical space diagrams for the TMF were constructed as a function of K_{OW} (i.e., log K_{OW} range from 4 to 10) and the biotransformation rate constant normalized for a 10 g fish (*i.e.*, $k_{M,N}$, range from 0.0001 to 0.1 d^{-1}), and used to evaluate TMFs in the False Creek food web. Biotransformation rate constants $k_{M,s,i,j}$ for the various species in compartments *i,j* were calculated as a function of the body weight and $k_{M,N}$ according to Eq. (4). TMFs were calculated in the absence of concentration gradients (Scenario 1) and under various conditions where concentration gradients existed (Scenarios 2–4). The model calculations simulated a systematic random sampling design where each species was sampled from one of the 3 areas. In total, 10,000 independent Monte Carlo simulations were conducted, each mimicking a single TMF study involving random sampling of each species (24 in total) from the 3 subareas of the defined False Creek ecosystem. Each simulation involved the calculation of the TMF and the probability (p) that the TMF was statistically different from a value of 1. The distribution of the 10,000 individual TMF studies was used to estimate the probability that chemicals with a given K_{OW} and $k_{M,s,i,j}$ could be expected to exhibit a TMF ≥ 1.0 or conversely, a TMF < 1.0.

4. Results and discussion

4.1. Model performance analysis

Model calculated TMFs for the PCB congeners in the defined False Creek food web varied from 1.9 to 6.3, indicating the occurrence of trophic magnification commonly observed for these PCB congeners (Fig. 2). In general, the model calculated TMFs increased with increasing log K_{OW} for the lower chlorinated congeners, followed by a decrease in the TMF for the higher chlorinated PCB congeners. The model calculated TMFs were in good agreement with the reported field TMFs for the PCB congeners in False Creek (Fig. 2) where spatial concentration differences in water and sediments and varying sediment-water fugacity ratios were observed (Mackintosh et al., 2004; Mackintosh et al., 2006). The mean model bias (MB) for the six PCB congeners was 1.02, suggesting little or no systematic bias existed between the model calculated TMFs and the reported field TMFs. This finding was in good agreement with performance analyses of the AQUAWEB model for PCB congeners in food webs from several Great Lakes (Arnot and Gobas, 2004), San Francisco Bay (Gobas and Arnot, 2010) and the British Columbia Coast

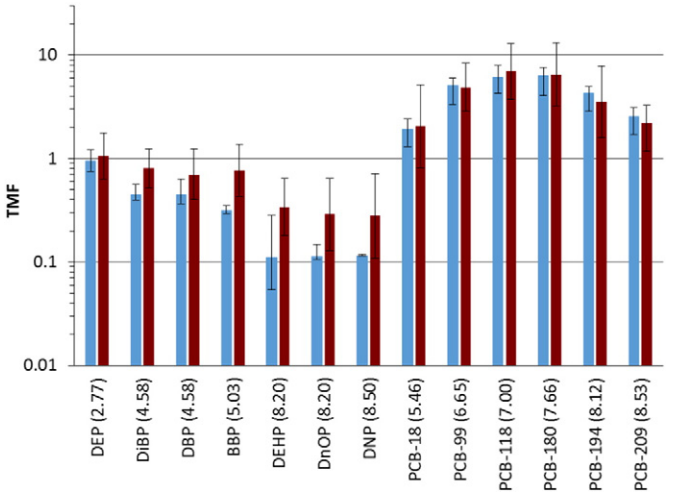

Fig. 2. Comparison of modeled calculated TMFs (blue bars) and reported field TMFS (red bars) of 7 phthalate esters (PEs) and 6 polychlorinated biphenyls (PCBs) in the False Creek food web. Error bars are the 95% confidence intervals of the mean TMF. Values of log K_{OW} are shown in parenthesis next to the compound names.

(Alava et al., 2012). The 95% confidence intervals of the MB for the 6 PCBs was a factor of 1.25, indicating that model TMFs were within 25% of the reported field TMFs. This high level of agreement between modeled and reported values is uncharacteristic for a bioaccumulation metric. Apparently, errors in the model's ability to assess bioaccumulation of PCBs in individual species across the food web appear to cancel out to a considerable degree in the calculation of the TMF, producing reasonable estimates of TMF that exhibit a low level of systematic bias. In general, model calculations for of the individual PCB congeners appeared to capture the over-all bioaccumulation behavior of PCBs in the False Creek ecosystem.

Model calculated TMFs of the PE congeners ranged from 0.11 for DnOP and DEHP to 0.95 for DEP and showed a general decline in the TMF with increasing K_{OW} (Fig. 2). Field TMFs, reported by Mackintosh et al. (2004), ranged from 0.28 for DNP to 1.0 for DEP and also showed a general decline in the TMF with increasing K_{OW} (Fig. 2). Both the model calculations and the field observations indicated a lack of trophic magnification for all of the evaluated PEs. This behavior is consistent with a high degree of biotransformation commonly observed for PEs in aquatic biota (Stalling et al., 1973). The model calculated TMFs and reported field TMFs were in reasonable agreement when considering the possible uncertainty that may be associated with the field results. However, the mean MB for the 7 PE congeners was 0.49, suggesting an approximately 2-fold systematic underestimation of the reported field TMFs by the model. Moreover, the 95% confidence intervals of the mean MB was a factor of 2.0, which was considerably greater than the factor of 1.25 obtained for the PCB congeners. The MB was the lowest for DEP, for which the median model calculated TMF was 0.95 and the reported field TMF was 1.0. The MB was the highest for DEHP, for which the model calculated TMF was 0.11 and the reported field TMF was 0.34.

The reason for the apparent underestimation of the reported field TMFs for the PE congeners is not clear and will be the subject of further investigations. Nonetheless, comparison of the reported field TMFs to the model calculated TMFs (Fig. 3) suggested that ecosystem parameters (e.g., spatial concentration differences) may have been confounding factors for PEs in False Creek, where uncertainty in the water and sediment data was observed. Other possibilities include an overestimation of the biotransformation rate constant $k_{M,S}$; as characterizing a single biotransformation rate constant $k_{M,N}$ value across a wide variety of species present in aquatic food webs may be difficult. Another possibility is that trophic dilution of phthalate esters may be, to a large extent, due to biotransformation in the gastrointestinal tract, which may not be adequately represented by the estimates of somatic biotransformation rates used in this study (Lo et al., 2015b).

McLachlan et al. (2011) concluded that the biotransformation rate k_M was the chemical property having the strongest influence on bioaccumulation. Nichols et al. (2015) proposed that the k_M represented the principal source of uncertainty in the bioaccumulation assessment of most chemicals with high bioaccumulation potential. In vivo k_M databases (Arnot et al., 2008b) and in silico models for predicting k_M from chemical structure have been proposed (Arnot et al., 2009; Long and Walker, 2003; Papa et al., 2014). Nichols et al. (2013) and Fay et al. (2014) have examined the in vitro-in vivo extrapolation methods for estimating k_M values for fish and the impact on chemical bioaccumulation assessment. A database of whole body fish biotransformation rates has been compiled by Arnot et al. (2008b) and the authors noted that, chemical structure aside, variability in k_M values was likely due to differences in body size, water temperature, exposure route, interspecies differences, gender, life stage, and enzyme competition, inhibition, and induction. Lastly, as discussed below, errors in sediment-water distribution (fugacity ratios) may result in errors in the TMF for benthic-coupled food webs.

Experimental uncertainty regarding determination of the assimilation efficiency led Xiao et al. (2013) to employ a chemical benchmarking approach to measure dietary assimilation efficiency of chemicals by fish, with 2,2′,5,6′-tetrachlorobiphenyl (PCB-53) and decabromodiphenyl ethane (DBDPE) selected as absorbable and non-absorbable benchmarks, respectively. Benchmarking did not improve overall precision of the measurements, however, after benchmarking, the median recovery for 15 chemicals was ~100%, and variability of recoveries was reduced, suggesting that benchmarking could account for incomplete extraction of chemical in fish and incomplete collection of feces.

4.2. Model sensitivity analysis

4.2.1. Spatial concentration gradients

Scenario 1 ("the control") showed that model calculated TMFs of the test PCBs and PEs ranged between 0.11 and 4.9 (Fig. S1 of the SI). The correlation coefficients (r^2) of the regression models used to derive the TMFs ranged from 0.23 for PCB-209 to 0.79 for DEP. Because of the large sample size (i.e., $n = 10{,}000$), all regression models exhibited a slope that was statistically different ($p < 0.05$) from 0 and hence a TMF that was statistically different from 1. The TMFs in all areas were identical (thus no uncertainty) because the chemical concentration in water and sediments, as well as other chemical, biological and environmental parameters were the same. Systematic random sampling of species from the three areas had no effect on the TMF, the goodness of fit of the regression model (r^2), or the significance of the slope (p-value) because chemical concentrations in any given species were not different across the three areas of the defined False Creek ecosystem.

In Scenario 2, where spatial concentration gradients were present in water and sediment, model calculated TMFs within each area (i.e., sampling within each area only), as well as the corresponding r^2 and p-value for the regression models, were the same across the three areas and were identical to those for Scenario 1, despite the fact that concentrations in Area-2 and Area-3 were, respectively, 10 and 100 times greater than in Area-1 (Fig. S1 of the SI). This illustrated that the model was linear in concentration, reflecting the model's assumption of first order kinetics where chemical uptake and elimination rates follow a linear function with chemical concentration in water, sediment, and prey. In other words, the model demonstrated that TMF was independent of exposure concentrations when the conditions of exposure were the same. Powell et al. (2010) reported that field TMFs for cyclic volatile methylsiloxanes (D4, D5, and D6) were not related to exposure and were essentially the same for sampled food webs in the inner and outer Oslofjord, Norway (summarized in Table S3 of the SI). Levels of exposure in the more polluted inner Oslofjord, relative to the less polluted outer Oslofjord, were estimated to be about 4× higher for D4, 38× higher for D5, and 7× higher for D6.

First order kinetics of PCB and PE transport processes is a reasonable assumption for animals exposed to relatively low concentrations in most field situations. Biotransformation processes, however, may be subject to Michaelis–Menten kinetics, which recognize the possibility of enzyme saturation. Little is known about the concentration dependence of in-vivo biotransformation rates in fish but some information is available indicating a high degree of concentration dependence of biotransformation rates in in-vitro systems (Lo et al., 2015a).

Systematic random sampling across the three areas of the defined False Creek ecosystem generated median model calculated TMF values that were essentially identical to median values that were obtained when sampling within an individual area (Fig. 3 and Fig. S1 of the SI). This means that for a study area where spatial differences in chemical concentrations exist, repeated TMF studies (i.e., 10,000 in the simulation) based on systematic random sampling across the study area can produce a median TMF that approaches the TMF that would have been obtained from a single TMF study if spatial concentration differences were not present. However, the 95% confidence limits for the mean TMFs were large (i.e., approximately a factor of 4 of the mean value) when spatial concentration gradients existed (Fig. 2, Scenario 2). Consequently, large differences may exist between results of individual TMF studies if spatial concentration differences are present across

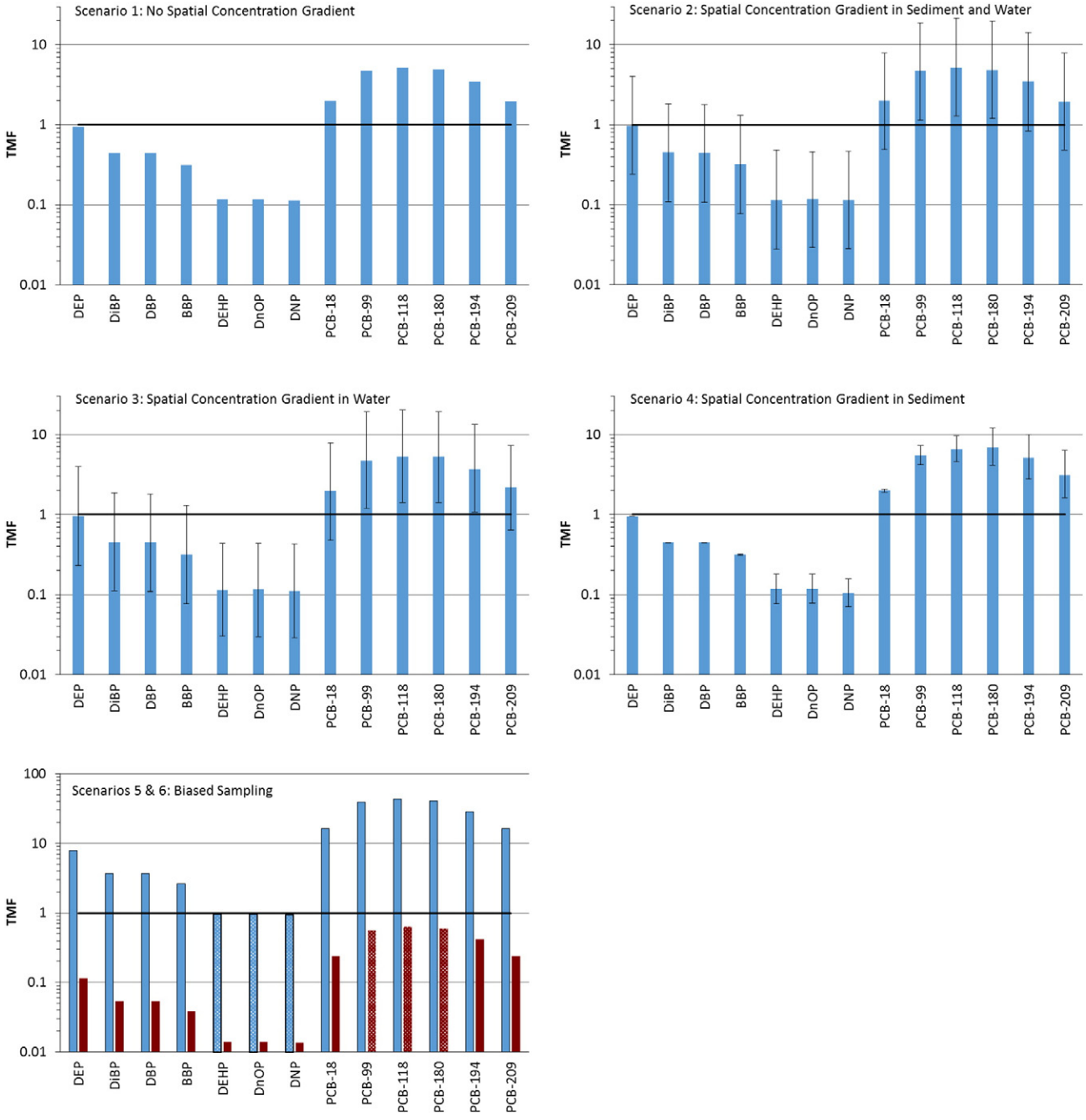

Fig. 3. Model calculated mean TMFs of 7 phthalate esters (PEs) and 6 polychlorinated biphenyls (PCBs) in the defined False Creek ecosystem. Systematic random sampling (n = 10,000 Monte Carlo simulations) was used to sample each species in the food web for the defined Scenarios 1–4. Error bars indicate 95% confidence intervals of the mean TMF for the 10,000 model simulations. Scenario 1 is the control or reference scenario which contains no concentration gradients. Scenario 2 depicts modeled TMFs when gradients are present in both sediment and the water column. Scenarios 3 and 4 depict modeled TMFs when gradients are present in the water column or the sediment, respectively. Modeled TMFs from the two biased (judgment) sampling designs (Scenario 5, blue bars; Scenario 6, red bars) are also shown.

the study area, even if systematic random sampling is followed for species collection. In other words, field TMFs may be systematically biased in study locations where spatial concentration differences exist. For example, DiBP exhibited a median modeled TMF = 0.45 with a 95% confidence interval that ranged from 0.11 to 1.8, indicating that individual TMF studies may produce statistically significant TMFs that are either less than or greater than a value of 1 (i.e., TMF < 1.0 or TMF > 1.0).

The confounding effect of spatial concentration differences on the calculation of field TMFs was further illustrated by results from the biased sampling scenarios (Fig. 3; Scenarios 5 and 6), which were used to imitate judgment sampling designs that may occur in field studies. The judgment sampling designs produced biased TMFs for the PCBs and the PEs that were greater than or less than a value of 1, depending upon the modeling scenario. For example, the biased sampling scenarios resulted in model calculated TMFs for PCB-180 of 0.87 and 38. Similarly, the biased sampling scenarios resulted in model calculated TMFs for DEP of 0.11 and 7.8. These results demonstrated that widely different TMF values can be found in areas where spatial concentration differences are present and a biased sampling design is used. Thus sample collection design and the location where samples are collected may

have a large impact (by a factor of up to 100 in this example) on the determination of the TMF when spatial concentration differences exist. Comparison of Scenario 2 to Scenarios 3 and 4 (Fig. 3 and Fig. S1 of the SI) indicated that model calculated TMFs in the defined False Creek ecosystem were most sensitive to spatial gradients in water (Scenario 3) relative to spatial gradients in sediment (Scenario 4).

Fig. 4, which illustrates the results of Monte Carlo simulations within the constraints of Scenario 2, where spatial concentrations in water and sediments vary from 10 to 100 fold, shows that the influence of spatial concentration differences on TMF bias was not the same across all substances. Fig. 4 shows that for substances which exhibited a greater degree of trophic dilution or biomagnification, there was a greater probability for a study to "correctly" determine the occurrence of trophic dilution (i.e., TMF < 1.0) or biomagnification (i.e., TMF ≥ 1.0) when spatial concentration differences were present. For example, for PCB-180 with a reported field TMF of 6.5 or a median model calculated TMF of 4.9 (based on Scenario 2), there was a >99% probability that a TMF ≥ 1.0 would be determined at a site with 10–100 fold differences in concentration across the study area. This may explain why field TMFs of PCB-180 and PCB-153, which are often used as reference chemicals for TMF studies, are determined to be >1 in almost all studies. Likewise, for DEHP with a reported field TMF of 0.34 or a median model calculated TMF of 0.12, which are equivalent to trophic dilution factors (1/TMF) of 2.9 and 8.3, respectively, there was >99% probability that a TMF < 1.0 would be determined under the conditions of Scenario 2. For DiBP with a median model calculated TMF of 0.45 there was a 14% probability that a TMF ≥ 1.0 or an 86% probability that a TMF < 1.0 would be determined.

In study areas where spatial concentration differences are present, the likelihood of a study finding a TMF < 1.0 for a material that has a TMF ≥ 2.0 in the absence of spatial concentration differences, or conversely, a TMF > 1.0 for a material that has a TMF ≤ 0.5 in the absence of spatial concentration differences, was <20% (Fig. 4). For example, the likelihood of finding a TMF < 1.0 was small (<20% for PCB-18 and PCB-209), very small (<5% for PCB-194), or negligible (<1% for PCB-99, PCB-118, and PCB-180) for the False Creek ecosystem when spatial gradients were present. Similarly, the likelihood of obtaining a TMF >1.0 was very small (≤5% for BBP) or negligible (<1% for DEHP, DnOP, and DNP) when spatial gradients were present. However, for substances like DEP, DiBP, and DBP, which exhibit a relatively low degree of trophic dilution (median model TMF = 0.45 to 1.0), there was a substantial probability ranging from 13% to 47% that a study would determine a TMF ≥ 1.0. Once again, for substances that exhibit a greater degree of trophic dilution or biomagnification, there is a greater probability that studies conducted in systems where spatial concentration differences exist will "correctly" identify the occurrence of trophic dilution (i.e., TMF < 1.0) or magnification (i.e., TMF ≥ 1.0).

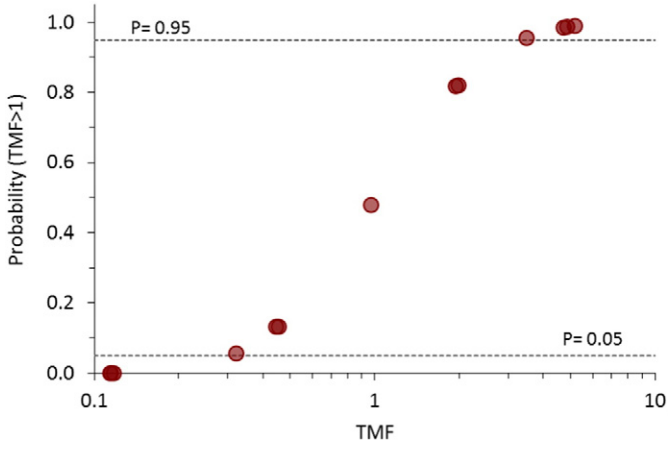

Fig. 4. The probability that a model calculated TMF > 1 will be obtained for the defined False Creek ecosystem when spatial concentration gradients exist (Scenario 2) as a function of the model calculated TMF that was obtained when spatial concentration gradients did not exist (Scenario 1).

Reducing spatial differences in sediment and water concentrations within a study area reduces the confounding influence of spatial concentrations on the TMF and thus increases the probability that a study will correctly identify the inherent trophic magnification capacity of a substance (i.e., the TMF in absence of spatial concentration differences). Also, as demonstrated by the similarity between the median model TMF in the presence of spatial concentration gradients and the median model TMF in absence of spatial concentration gradients, an increase in the number of TMF studies considered in the determination of the TMF may be expected to provide better estimates of the inherent TMF of a chemical. Bayesian inference as applied here has been demonstrated to reduce the uncertainty of estimated trophic level assignments and by extension increase the precision of field TMFs (McGoldrick et al., 2014; Powell et al., 2010; Powell et al., 2009; Starrfelt et al., 2013). Nonetheless, increased precision does not lead to decreased variability or systematic bias of TMF that may result from spatial differences in concentration.

In the absence of the confounding effects of spatial gradients (Scenario 1), TMFs for chemicals that have a relatively low K_{OW} (i.e., log K_{OW} < 5.5) appear to be insensitive to the existence of a sediment-water non-equilibrium, as expressed by the sediment-water fugacity ratio (i.e., $f_{S/W} \neq 1$), in the defined False Creek ecosystem (Fig. 5). These substances, which include DEP, DiBP, DBP, BBP and PCB-18, are predominantly absorbed from the water by many aquatic species such that the diet contributes only a small fraction of the organisms' total chemical intake. Thus $f_{S/W}$ and, by extension trophic transfer, does not play a significant role or have an impact on the TMF for these substances. In contrast, chemicals with higher K_{OW} (i.e., log K_{OW} ≥ 5.5), which are absorbed by organisms via the diet to a greater degree than the lower K_{OW} substances, exhibit increasing sensitivity of TMF to the increasing magnitude of $f_{S/W} > 1$ (Fig. 5), especially for substances with slower rates of biotransformation (i.e., $k_M \leq 0.01\ d^{-1}$; equivalent to a transformation rate of 1% per day or biotransformation half-life of about 70 days). For example, an increase in $f_{S/W}$ from 1 to 100 increases the TMF for a non-biotransforming substance such as PCB-180 (log $K_{OW} = 7.7$; $k_M = 0.0004\ d^{-1}$) from TMF = 5 to TMF > 10. In contrast, TMF ≤ 1 would result over the same 100-fold increase in $f_{S/W}$ for a biotransforming substance such as DEHP (log $K_{OW} = 8.2$; $k_M = 0.31\ d^{-1}$). The sediment-water fugacity ratio exerts its effect on trophic transfer through the dietary route. Thus an increase in $f_{S/W}$ elevates concentrations in sediments relative to those in water thereby increasing concentrations in benthic invertebrates relative to organisms in the water column. An increase in concentrations in benthic invertebrates causes an increase in dietary uptake of animals feeding on benthic invertebrates at the base of the food web and in turn increased uptake in their predators. The increase in relative importance of the diet as a route of uptake compared to respiratory uptake elevates both the trophic magnification and trophic dilution effects. The net effect being that TMFs for slowly biotransforming substances (e.g., PCBs) increase as sediment-water fugacity ratios increase above a value of 1, whereas the TMF of biotransforming substances (e.g., PEs) remains comparatively unchanged (Fig. 5).

4.2.2. Biotransformation rate

Chemical space diagrams were developed for the False Creek ecosystem to graphically represent median modeled TMFs for chemicals across wide ranges in K_{OW} and $k_{M,N}$ (Fig. 6 and Fig. S2 of the SI). These figures illustrate the sensitivity of model calculated TMFs to K_{OW} and $k_{M,N}$. For reference, PCBs occupy chemical space at the bottom of the figures (i.e., $k_{M,N}$ is very slow) where biotransformation is predicted to have negligible impact on the relationship between K_{OW} and TMF. In contrast, PEs are expected to occupy chemical space at the top of the figure or beyond (i.e., $k_{M,N}$ is relatively fast) where biotransformation is predicted to have significant impact on the relationship between K_{OW}

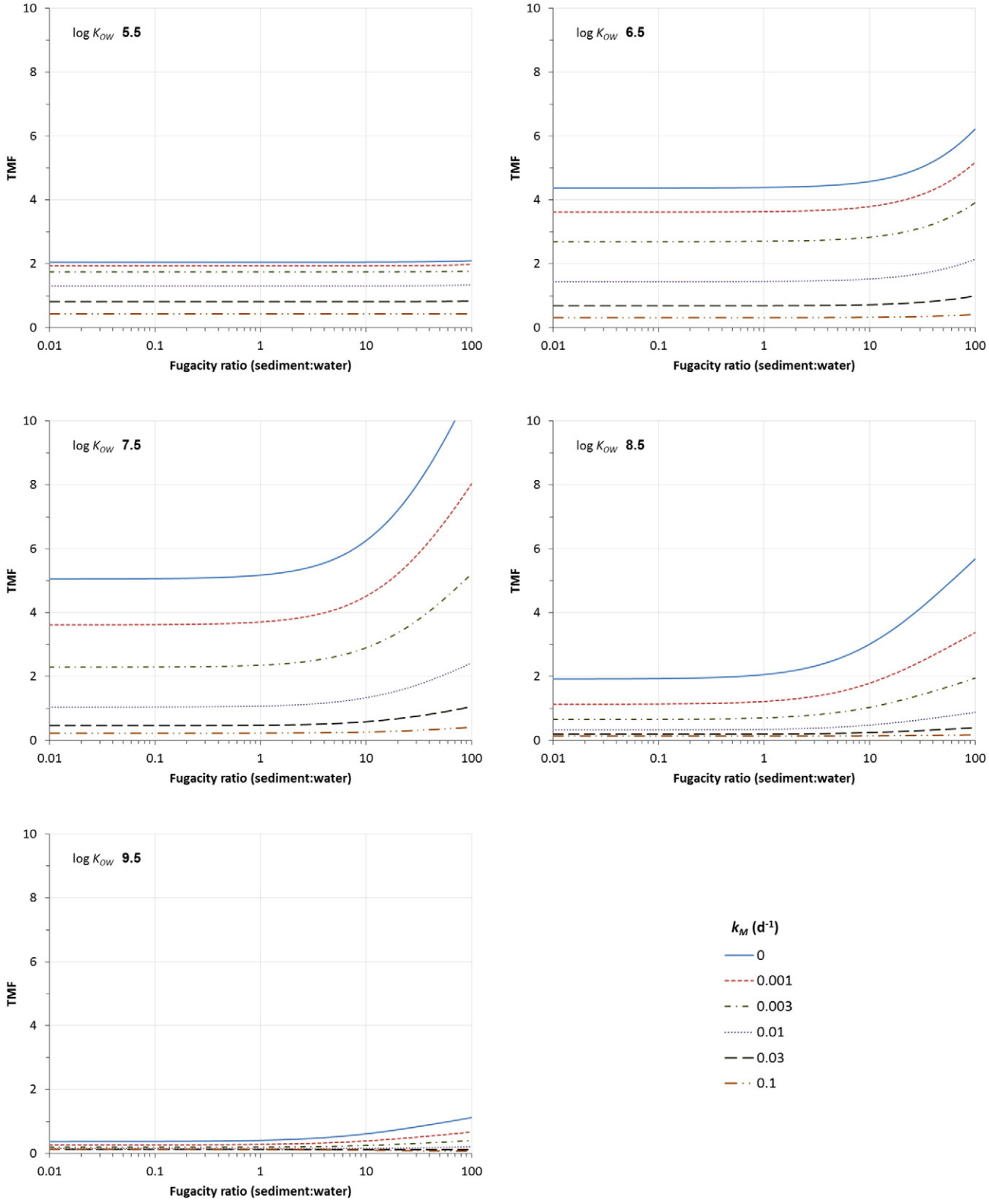

Fig. 5. Sensitivity of the model calculated TMF to the sediment-water fugacity ratio ($f_{S/W}$) in the absence of spatial concentration gradients (Scenario 1) for the defined False Creek ecosystem. Each plot shows the impact of $f_{S/W}$ on TMF at a specified log K_{OW} (range 5.5–9.5; shown as individual plots) for a specified range of biotransformation rate ($k_M = 0$ to 0.1 d^{-1}; shown as individual lines in each plot).

and TMF. There are many permutations for K_{OW} and $k_{M,N}$ that potentially occupy the presented chemical space, theoretically representing thousands of chemicals. Substances with log $K_{OW} < 4$ are not represented in the diagrams because this area defines the chemical space where dietary exposure and uptake from food is <15% of the respiratory exposure and uptake from water.

Model calculations indicate (Fig. 6) that in the absence of concentration gradients (Scenario 1), TMFs for substances that are not subject to

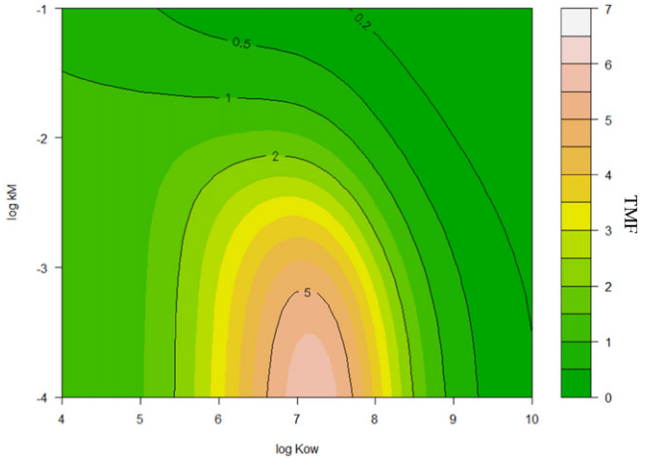

Fig. 6. Chemical space of model calculated TMFs for the False Creek food web in the absence of concentration gradients (Scenario 1). The biotransformation rate constant ($k_{M,N}$) was normalized for a 10 g fish. Colors in contours represent a scale of TMF ranging from 0 to 7, as shown in the side bar.

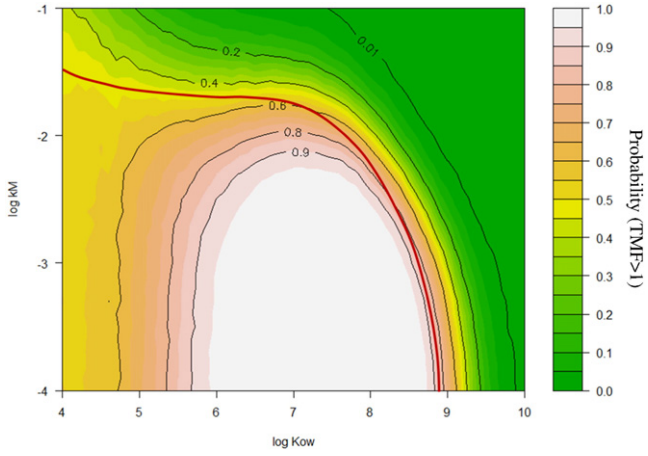

Fig. 7. The probability that a model calculated TMF ≥ 1 will be obtained for the defined False Creek ecosystem when spatial concentration gradients in water and sediment were both present (Scenario 2). The biotransformation rate constant ($k_{M,N}$) was normalized for a 10 g fish. Colors in contours represent a scale of probability of TMF ≥ 1, shown in the side bar. The solid red line represents the contour of TMF = 1 from the chemical space diagram of Fig. 6 (i.e., probability of 1 that TMF ≥ 1 in the absence of concentration gradients, Scenario 1).

significant rates of biotransformation (i.e., $k_{M,N} < 0.0001\ d^{-1}$) may be expected to increase with increasing K_{OW} from approximately 1, for substances with log K_{OW} of about 4, to values of approximately 5 or greater for substances with log K_{OW} between 6.5 and 7.5 (maximum TMF = 5.8 at log K_{OW} = 7.2). For substances with log K_{OW} > 7.5, the TMF drops with increasing K_{OW} to values below 1 for substances with a log K_{OW} of about 8.8 or greater. Fig. 6 illustrates that an increase in $k_{M,N}$ reduces the TMF, and that even slow rates of $k_{M,N} \leq 0.01\ d^{-1}$ (i.e., transformation rate of 1% per day or biotransformation half-life of 70 days) may reduce the TMF substantially, especially for substances of high K_{OW}. A $k_{M,N}$ of approximately 0.025 d^{-1}, representing a loss of only 2.5% of the chemical in the organism per day through this process, is sufficient to eliminate trophic magnification for all substances explored in this study. The model calculations suggest that the TMF is very sensitive to the rate at which chemicals are biotransformed, particularly over the log K_{OW} range from 5 to 8 (Fig. 6).

The chemical space diagrams also showed that median TMFs for the defined False Creek ecosystem were essentially the same regardless if spatial concentration gradients were present or not (Fig. S2 of the SI). However, the 95% confidence intervals about the mean TMFs were large when spatial concentration gradients were present (Fig. 3, Scenario 2), indicating that individual field TMF values may be biased when spatial gradients exist, especially in water (Fig. 3, Scenario 3). In contrast to that depicted when spatial gradients were absent (Fig. 6), the probability of observing a field TMF ≥ 1.0 (or conversely a field TMF < 1.0) was substantially decreased when spatial gradients were present (Fig. 7). For example, the probability of observing a field TMF ≥ 1.0 when spatial gradients were present was >80% only for substances with slow to intermediate rates of biotransformation (i.e., $k_{M,N} < 0.01\ d^{-1}$) and having log K_{OW} ranging from 5.4 to 8.8. Similarly, the probability of observing a field TMF ≤ 1.0 when spatial gradients were present was >80% only when rates of biotransformation were relatively fast (i.e. $k_{M,N} > 0.04\ d^{-1}$) or for substances having log K_{OW} > 8.5.

5. Model application

The MBAW model calculations and evaluations show that rates of biotransformation may lower TMF. The model calculations also illustrated that spatial concentration gradients may confound and systematically bias the calculation of TMF. The impact of concentration gradients on whether a TMF is determined to be either >1 or <1 appears to be greatest for substances that are subject to a low degree of biomagnification or trophic dilution (Fig. 4). Such chemicals have unbiased TMFs (in the absence of concentration gradients) that are close to a value of 1. High K_{OW} chemicals, which biotransform relatively slowly, belong in this class of chemicals. For substances that do not strongly biomagnify or dilute in food webs, variability in exposure concentrations can obscure the chemical's true bioaccumulation behavior. For such substances, it can be expected that studies conducted in locations where spatial concentration differences are present will produce TMFs, including TMF values for the same chemical that may be substantially >1 or substantially <1. One may perhaps view spatial variability in concentrations as the noise that competes with the signal (i.e., the chemical's bioaccumulation behavior). If there is more noise (i.e., greater spatial concentration differences), then the biomagnification or trophic dilution signal needs to be proportionally greater to be correctly recognized.

The model may be able to play a useful role in a priori design of studies that minimize the "noise" (i.e. spatial concentration differences) and hence increase the probability that a TMF is correctly characterized. For example, in study locations where spatial concentrations differences are suspected or known to exist, the model can help to assess which sampling design has the greatest likelihood of detecting a chemical's inherent trophic distribution in the sampled food webs. The model may also be useful in the a posteriori evaluation of measured TMFs in study areas subject to spatial concentration differences. An example application of the model to an a posteriori situation would be using the model to assess the likelihood that reported field TMFs for substances in a defined study area can be expected to represent the biomagnification or trophic dilution capacities implied by the model calculated TMFs.

Because of the effect of spatial concentration differences on the determination of the TMF and the frequent presence of concentration gradients at study sites, the application of a spatial modeling approach should be an important consideration in the planning of food-web bioaccumulation studies. Spatial modeling should go hand in hand with a detailed analysis of the chemical exposure conditions when conducting field based TMF studies. If concentration gradients cannot be avoided, then a characterization of the spatial concentration differences across a field study site is essential to derive a TMF that can reveal a chemical's trophic magnification behavior. The model illustrates how field data may be evaluated retrospectively by accounting for concentration gradients in TMF evaluation, when water/sediment monitoring data are

available. In addition, the model also has a potential application in developing sampling designs for field TMF studies to be conducted in areas where spatial concentration differences are likely to be significant. Finally, it can be recommended that the true trophic magnification properties of chemicals are more likely to be revealed in study locations where spatial chemical concentration differences are absent or small compared to locations where spatial concentration differences are significant.

Acknowledgements

We thank Professor Donald Mackay (Trent University) for his contributions to this work. We also thank Dr. Peter Fisk and Claire Gibson (Peter Fisk Associates), and Dr. Charles Staples (Assessment Technologies, Inc.) for their helpful reviews of an early draft of the manuscript. Graphical abstract artwork was prepared by Christopher Sushynski (Dow Corning Corporation) and is used here with permission. This work was conducted by Dow Corning Corporation as a member of CES - Silicones Europe (CES). Dow Corning Corporation manufactures and sells silicon-based chemical products. CES is a non-profit sector group of the European Chemical Industry Council (Cefic) that represents all major producers of silicones in Europe. Project funding and open access publication were provided by CES, with additional funding provided by Dow Corning Corporation as the employer of Dr. Jaeshin Kim, Dr. David Powell, Dr. Rita Seston, and Dr. Kent Woodburn. Professor Frank Gobas (Simon Fraser University) and Dr. Jon Arnot (ARC Arnot Research and Consulting Inc.) acknowledge funding support by Dow Corning Corporation that was provided in compensation for their time spent working on development of the model and assistance with preparation of this manuscript. The Authors affirm that the submitted Work is original, does not contain any statements or information that is intentionally misleading or inaccurate, and does not infringe any duty of confidentiality which the Authors may owe to another party or violate any contract, expressed or implied, that the Authors may have entered into. All of the institutions where the submitted Work was performed have authorized publication. The authors affirm that to the best of our knowledge all potential and/or relevant competing financial or other interests that might be affected by publication of the submitted Work are disclosed herein. A beta version of the Multibox-AQUAWEB (MBAW) model described in this manuscript is under evaluation. The MBAW model will be made freely available to all interested individuals, pending completion of beta testing and evaluation.

Appendix A. Supplementary data

Supplementary data, tables, and figures discussed in this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.02.013.

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List of symbols

$\overline{C_{B,s}}$: weighted average of chemical concentrations in species s [g/kg wet weight]
$C_{B,r,i,j}$: chemical concentration in prey species r in compartment (i,j) [g/kg wet weight]
$C_{B,s,i,j}$: chemical concentration in species s in compartment (i,j) [g/kg wet weight]
$C_{S,i}$: total chemical concentration in sediment in compartment $(i,3)$ [g/kg dry weight]
$C_{WD,i,j}$: dissolved chemical concentrations in water in compartment (i,j) [g/L]
$C_{WT,i,j}$: total chemical concentrations in water in compartment (i,j) [g/L]
$f_{S/W,i,j}$: sediment/bottom water compartment fugacity ratios [−]
$H_{s,i,j}$: home range factor in compartment (i,j) [−]
$k_{1,s,i,j}$: chemical uptake rate constant via respiration of species s in compartment (i,j) [d^{-1}]
$k_{2,s,i,j}$: rate constant for chemical elimination via respiration of species s in compartment (i,j) [d^{-1}]
$k_{D,s,i,j}$: rate constant for uptake via ingestion of food by species s in compartment (i,j) [d^{-1}]
$k_{E,s,i,j}$: rate constant for elimination via excretion of contaminated feces by species s in compartment (i,j) [d^{-1}]
$k_{G,s,i,j}$: growth rate constant of species s in compartment (i,j) [d^{-1}]
K_{LW}: lipid-water partition coefficient [−]
$k_{M,N}$: biotransformation rate normalized for a 10 g fish at 15 °C
$k_{M,s}$: rate constant for biotransformation by species s [d^{-1}]
K_{OC}: organic carbon–water partition coefficient [L/kg organic carbon]
K_{OW}: octanol–water partition coefficient [−]
$m_{0,s,i,j}$: fraction of respiratory ventilation by species s of water from compartment (i,j) [−]
MB: mean model bias [−]
$M_{P,s,i,j}$: fraction of respiratory ventilation of sediment pore-water in compartment (i,j) for sediment dwelling species s [−]
$OC_{W,i,j}$: organic carbon content in water compartment (i,j) [−]
$ø_{S,i,j}$: volume fraction of solids in sediment [−]
$ø_{oc,i}$: fraction of organic carbon in bottom sediment solids (kg oc/kg sediment dw) [−]
P_r: fraction of diet containing prey r [−]
$R_{r,i,j}$: presence factor for prey species r in compartment (i,j) [−]
T: water temperature [°C]
TMF: trophic magnification factor [−]
$TMF_{C,i}$: modeled TMF for chemical i [−]
$TMF_{O,i}$: observed TMF for chemical i [−]
TP_r: trophic position of prey species r in the diet of species s [−]
TP_s: mean trophic position of the predator species s [−]
T_{ref}: reference temperature = 15 °C
W_B: wet weight of organism [g]
$W_{B,N}$: reference wet weight of organism = 10 g
$X_{POC,i,j}$: concentration of particulate organic carbon in water compartment (i,j) [kg OC/L]
Z_L: fugacity capacity of lipid [mol/Pa/m^3]
Z_O: fugacity capacity of octanol [mol/Pa/m^3]