Tools for Evaluating the Fate and Bioaccumulation of Organic Compounds in Aquatic Ecosystems.

Erick Nfon
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Erick Nfon
Department of Applied Environmental Science (ITM)
Stockholm University
S-10691 Stockholm
Sweden.
erick.nfon@itm.su.se
This work is dedicated to my parents for their love, endless support and encouragement.
Abstract

The bioaccumulation of organic contaminants in aquatic ecosystems has been a key focus in environmental toxicology over the last decades. Bioaccumulation is a key concept in ecological risk assessments since it controls the internal dose of potential environmental contaminants. Information on the bioaccumulation of contaminants is used by regulatory authorities in the development of water quality standards, categorizing substances that are potential hazards and quantifying the risk of chemicals to human health. A basis for identifying priority chemicals has been the use of the octanol-water partition coefficient (K\text{ow}) as a criterion to estimate bioaccumulation potential. However, recognizing that the bioaccumulation process is not controlled by the hydrophobicity of a chemical alone, this thesis proposes a set of tools, incorporating chemical properties, environmental characteristics and physiological properties of organisms, to study the bioaccumulation of contaminants in aquatic ecosystems.

In striving to achieve this objective, a tool based on an equilibrium lipid partitioning approach was used in Paper I to evaluate monitoring data for bioaccumulation of organic contaminants. In Papers II and III, mechanistic based modelling tools were developed to describe bioaccumulation of hydrophobic compounds in aquatic food webs. In Paper IV, the bioaccumulation of organic compounds in aquatic food chains was studied using stable isotopes of nitrogen. The mechanistic fate and food web models developed in this thesis provide regulators and chemical manufacturers with a means of communicating scientific information to the general public and readily applicable mechanistic fate and food web models that are easily modified for evaluative assessments purposes.
List of Papers

This thesis is based on the following papers and manuscript which will be referred to by their Roman numerals.

I. Interpreting time trends and biomagnification of PCBs in the Baltic region using the equilibrium lipid partitioning approach.

Nfon, E., Cousins, I.T. Environmental Pollution 2006 (144), 994–1000.
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II. Modelling PCB Bioaccumulation in a Baltic Food Web.

Nfon, E., Cousins, I.T. Environmental Pollution 2007 (148), 73–82.
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III. Influence of submerged aquatic vegetation on the fate and food web transfer of pesticides in small freshwater systems.


IV. Biomagnification of organic pollutants in benthic and pelagic marine food chains from the Baltic Sea.

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### Abbreviations

<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ATSDR</td>
<td>Agency for Toxic Substances and Disease Registry</td>
</tr>
<tr>
<td>BAF</td>
<td>Bioaccumulation factor</td>
</tr>
<tr>
<td>BCF</td>
<td>Bioconcentration factor</td>
</tr>
<tr>
<td>BMF</td>
<td>Biomagnification Factor</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>CHEM1</td>
<td>Hypothetical pesticide with log K\textsubscript{OW} = 3</td>
</tr>
<tr>
<td>CHEM2</td>
<td>Hypothetical pesticide with log K\textsubscript{OW} = 5</td>
</tr>
<tr>
<td>CHEM3</td>
<td>Hypothetical pesticide with log K\textsubscript{OW} = 7</td>
</tr>
<tr>
<td>[cCHL]</td>
<td>cis-Chlordane</td>
</tr>
<tr>
<td>[tCHL]</td>
<td>tran-Chlordane</td>
</tr>
<tr>
<td>DDT</td>
<td>Dichlorodiphenyltrichloroethane</td>
</tr>
<tr>
<td>ELP</td>
<td>Equilibrium lipid partitioning</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>f</td>
<td>Fugacity</td>
</tr>
<tr>
<td>FWMF</td>
<td>Food Web Magnification Factor</td>
</tr>
<tr>
<td>HCH</td>
<td>Hexachlorocyclohexanes</td>
</tr>
<tr>
<td>H</td>
<td>Henry's Law constant</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>K\textsubscript{OW}</td>
<td>Octanol water partition coefficient</td>
</tr>
<tr>
<td>K\textsubscript{OA}</td>
<td>Octanol air partition coefficient</td>
</tr>
<tr>
<td>K\textsubscript{OC}</td>
<td>Organic carbon water partition coefficient</td>
</tr>
<tr>
<td>K\textsubscript{AW}</td>
<td>Air water partition coefficient</td>
</tr>
<tr>
<td>lw</td>
<td>Lipid weight</td>
</tr>
<tr>
<td>LRAT</td>
<td>Long range Atmospheric Transport</td>
</tr>
<tr>
<td>P</td>
<td>Persistence</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>PCB</td>
<td>Polychlorinated Biphenyls</td>
</tr>
<tr>
<td>PCN</td>
<td>Polychlorinated Naphthalene</td>
</tr>
<tr>
<td>PBDE</td>
<td>Polybrominated diphenyl ethers</td>
</tr>
<tr>
<td>POPs</td>
<td>Persistent Organic Pollutants</td>
</tr>
<tr>
<td>REACH</td>
<td>Registration, Evaluation, Authorization and Restriction of Chemical substances</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>TL</td>
<td>Trophic level</td>
</tr>
<tr>
<td>TMF</td>
<td>Trophic Magnification Factor</td>
</tr>
<tr>
<td>TP</td>
<td>Trophic Position</td>
</tr>
<tr>
<td>UNECE</td>
<td>United Nations Economic Commission for Europe</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environmental Programme</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>Z</td>
<td>Fugacity capacity</td>
</tr>
</tbody>
</table>
Swedish Summary

Många organiska föroreningar har tillverkats avsiktligt med användningsområden inom industriella processer, som jordbruks kemikalier eller som aktiva substanser i hushålls- och konsument produkter. Produktionen av dessa ämnen har stadigt ökat och resulterat i vidspred och förrorening av miljön. Vissa av dessa ämnen såsom PCB och DDT föreningar är svårnedbrytbara, hydrofoba och kan bioackumuleras i akvatiska organismer till nivåer som kan resultera i negativa effekter och/eller skada normala biologiska funktioner. Dessutom, transporterar dessa ämnen upp i näringskedjan via födointag så att organismer på högre trofinivåer blir mer förrorenade än sina byten.

Denna avhandling förordrar ett antal verktyg som integrerar kemiska egenskaper, miljö faktorer och organismers fysiologiska egenskaper för att studera bioachumulationen av förroreningar i akvatiska ekosystem. Ett verktyg baserat på jämviktsfördelning till lipider användes för att utvärdera miljöövervakningsdata för bioackumulation av organiska förroreningar. Mekanistiska modelleringsverktyg utvecklades för att beskriva bioackumulationen av hydrofoba ämnen i akvatiska näringsvävar. En metod baserad på stabila kväveisotoper användes för att studera bioackumulationen av organiska ämnen i akvatiska näringskedjor. Verktygen som utvecklades i denna avhandling erbjuder ett förbättrat tillvägagångssätt för att identifiera substanser som kan bioackumuleras utan att vara hydrofoba och på så sätt utgöra en ekologisk risk.
Contribution by the author:

Paper I
I was primarily responsible for searching the literature and extracting useful data, developing the monitoring database, evaluating results, statistical analysis and writing the manuscript.

Paper II
I was primarily responsible for the modelling work, performing simulations, evaluating the model output and writing the manuscript.

Paper III
I was primarily responsible for the modelling work, performing simulations and preparing the manuscript.

Paper IV
I was primarily responsible for transforming the raw data into a usable form, performing calculations, statistical analysis, evaluating the results and writing the manuscript.
1. Introduction

1.1 Contamination of the aquatic environment

The general public, regulatory authorities and the media have been interested in the contamination of the environment by chemical substances over the last decades. This is reflected in the growing influence of environmental movements and the increasing number of regulatory instruments available to local and international environmental authorities (e.g. REACH in the EU). Scientists, especially analytical chemists have been at the forefront in improving our understanding of the effects of chemical substances and the levels present in the environment. The rapid improvement in analytical capability arising from the development of methods such as Inductively Coupled Plasma (ICP), advanced chromatographic methods and mass spectrometry (e.g. Harris 1999) has made analysis and detection of inorganic and organic compounds present at extremely low levels more routine. The widespread availability of analytical data has encouraged ecotoxicologists to undertake both short term and lifecycle studies on the effects of very low and/or lethal concentrations on a population. For example the USEPA has undertaken a series of studies on the toxicity of a variety of organic compounds (e.g. PAHs, chlordane compounds and PCB mixtures) and inorganic compounds (mercury, nickel and nickel compounds and silver compounds (ATSDR, 2007). Environmental chemists, on the other hand, are interested in elucidating and understanding the sources, fate (transport and reactions) and the impacts of human activities on these processes (Baird, 1995; Manahan, 2003; Schwarzenbach et al., 2003). These impacts may be felt on a local scale, e.g. the presence of urban air pollutants such as PAH in Stockholm (e.g. Prevedouros et al., 2004) or on a global
scale, e.g. global distillation of pollutants in Polar Regions (Wania and Mackay, 1993; Wania and Mackay, 1996).

1.2 Chemicals of concern, sources and environmental occurrence

Chemicals that were studied in this thesis include persistent organic pollutants (POPs), other less persistent organic pollutants including pesticides and hypothetical organic compounds. POPs of interest include organochlorine pesticides and industrial chemicals listed in the Stockholm convention (e.g. chlordane compounds (e.g., trans-chlordane [tCHL], cis-chlordane [cCHL]), DDT, dieldren, PCB congeners).

Many organic pollutants have been intentionally produced by man and are used as/in chemical products, in industrial applications (e.g. PCBs in transformers), in agriculture (e.g. DDT as pesticides) and as household (consumer) and commercial applications. Sources of environmental contamination include both intentional, controlled releases (pesticides and insecticides) and unintentional releases (combustion processes, leakages from products and industrial discharges such as waste water). As a consequence of the resistance to natural decomposition processes and the ability to undergo long range atmospheric transport (LRAT) (e.g. Wania and Mackay, 1995; Gouin et al., 2000; Wania, 2003; Czub and McLachlan, 2004), some of these compounds have become widely distributed in the environment.
Adverse effects such as uterine lesions and sterility in seals, reproductive failure of several species including raptors in the Baltic Sea region, the peregrine falcon and the double crested cormorants in North America have been attributed to contamination by organic compounds such as DDT, PCBs and PCNs (e.g. Norstrom et al., 1981; Helander et al., 1994). Exposure to toxic organic compounds (e.g. PAHs, dioxins, furans) through the consumption of contaminated food items is also thought to pose a significant risk to human health especially with respect to birth defects, developmental disorders, cancer and cardiovascular effects (e.g. Llobet et al., 2006; Domingo et al., 2006; Stern, 2007). A matter of concern is the strong evidence that suggests certain organic compounds may act as endocrine disrupting compounds that may interfere with biological mechanisms and function (Colborn et al., 1993; UNECE, 1995; USEPA, 1997).

A situation of vital importance is the progressive accumulation of contaminants from environmental matrices such as water and sediments by organism such as invertebrates, fish, mammals and birds that inhabit these matrices. Many POPs fall into this category and migrate from the water column into the lipid phases of biota and accumulate to high levels. Furthermore, these compounds are transferred between organisms occupying different trophic levels via ingestion such that organisms at higher trophic levels are more contaminated than their prey (Clark et al., 1990; Gobas et al., 1993; Sharp and Mackay, 2000).
2. *Fate and bioaccumulation processes*

The predominant processes used to describe the uptake and elimination of contaminants by a fish (or likewise any aquatic “water-breathing” species) are depicted in Figure 1.

![Diagram of fish with uptake and loss processes labeled](image)

**Figure 1.** A conceptual diagram of the major uptake and loss process of contaminants by a fish expressed in terms of fugacity and D-values and concentrations and rate constants *(Courtesy of Mackay 2001)*.

Uptake may occur by respiration (from overlying water column and sediment pore water) and/or through the consumption of contaminated food. Key pathways of contaminant elimination include respiration, egestion and metabolic transformation. Growth dilution, which acts to reduce the concentration of contaminant in biota, is also included here as a pseudo-elimination process. Other uptake and elimination pathways such as dermal absorption and reproductive losses (lactation, egg laying, and birth) were not considered in the models.
presented in this thesis but will in any case be mentioned here for the sake of completeness.

The mechanistic description that follows is based on exposure and uptake from the aquatic environment, but the approach can be similarly applied with some minor modifications to terrestrial species as well (e.g. Kelly and Gobas, 2001, 2003; Armitage and Gobas, 2007).

The uptake and elimination mechanisms of contaminants in water by aquatic organisms as described by Spacie and Hamelink, (1982) is thought to occur by (a) a direct partitioning of chemical between the gill surfaces and overlying water at a rate directly proportional to the dissolved concentration in water and (b) elimination through the gills, body fluids and biotransformation at a rate proportional to the concentration in the organism. This so called “one compartment model” is described using two equations, namely

\[
\begin{align*}
\text{For uptake:} & \quad \frac{dC_F}{dt} = k_1 C_W \\
\text{For elimination:} & \quad \frac{dC_F}{dt} = -k_2 C_F
\end{align*}
\]

Where \( k_1 \) and \( k_2 \) are uptake and elimination rate constants (time\(^{-1}\)), \( C_F \) is the concentration in fish (mg of contaminant/kg of organism) and \( C_W \) is the dissolved concentration in water (mg of contaminant/L water). A mass balance equation can be written to track the change in concentration of the fish which takes the form:

\[
\frac{dC_F}{dt} = k_1 C_W - k_2 C_F
\]
At steady state (uptake = elimination, \(dC_r/dt = 0\)), the concentration in the fish can be determined as

\[ C_f = \frac{k_1}{k_2} C_w \]  

(4)

For hydrophobic compounds that have a high affinity for lipid phases, uptake through the respiratory surfaces may result in a slow build-up of chemical in the organism such that \(C_f\) is much greater than \(C_w\). The term bioconcentration is used to describe the increase in concentration of a contaminant in an organism as a result of uptake through the respiratory surfaces and this phenomenon is expressed as a bioconcentration factor (BCF).

\[ BCF = \frac{C_f}{C_w} = \frac{k_1}{k_2} \]  

(5)

However, organisms in field conditions are exposed to contaminants from different sources, and uptake may also occur through consumption of contaminated prey, dermal absorption as well as across respiratory surfaces. Bioaccumulation is used to describe the total uptake and a bioaccumulation factor (BAF) is used to describe the bioaccumulation process

\[ BAF = \frac{C_f}{C_w} \]  

(6)

A related phenomenon is the ability of organisms at higher trophic levels in food webs to accumulate non-metabolizing compounds to higher concentrations than in the diet. (e.g.
This phenomenon, referred to as biomagnification, occurs between trophic levels as a result of the transfer of contaminants via ingestion of food. The biomagnification of a contaminant between organisms at adjacent trophic levels is usually expressed by a biomagnification factor (BMF):

\[
\text{BMF} = \frac{C_f}{C_D}
\]  

(7)

\(C_f\) (mg of contaminant/kg of the organism) and \(C_D\) (mg of contaminant/kg of food) are the contaminant concentrations in the organism and the diet, respectively. Furthermore, the biomagnification of a contaminant in a food web as a whole is referred to as food web magnification. The food web magnification of contaminants is characterized using a food web magnification factor (FWMF) or trophic magnification factor (TMF) (e.g. Broman et al., 1992; Hop et al., 2002) that expresses the average increase in contaminant concentration per trophic level in a food web.

It is worth mentioning that \(C_W\) is the dissolved concentration and not the total concentration (\(C_T\)). The dissolved concentration can be estimated for water containing particulate and dissolved organic carbon using correlations relating \(C_W\) and \(C_T\) (e.g. Gobas and Morrison, 2000). However, such simplifications do not account for the slow sorption/desorption kinetics of some organic compounds and the presence of other phases (e.g. soot carbon) with a stronger sorption capacity than organic carbon (e.g. Pignatello and Xing, 1996; Qiu and Davis, 2004). Equations have been derived for estimating the sorption of organic compounds to soot carbon,
and to date have only been validated experimentally for the polycyclic aromatic hydrocarbons (PAHs) (Cornelissen et al., 2005).

2.1 Modelling uptake and loss processes

The uptake and elimination pathways shown in Figure 1 can be described in terms of fugacity (f) or concentrations (C). The fugacity approach has been thoroughly described by Mackay, (2001) and is only briefly described here. Fugacity expresses the fleeing or escaping tendency of a chemical from a compartment, and at dilute concentrations, fugacity is linearly related to concentration by the expression

\[ C = Zf \]  

(8)

Where \( C \) is the chemical concentration in mol/m\(^3\), \( f \) is the fugacity (Pa) and \( Z \) is the fugacity capacity of the chemical in a compartment (mol/m\(^3\) Pa). Thus equation 5 can be re-written in fugacity format by replacing the concentration terms with the corresponding fugacity (\( C_f = Z_f f_f \) and \( C_w = Z_w f_w; \) \( f_f = f_w \) at equilibrium). Simple empirical relationships are used to calculate \( Z \) for different environmental compartments (Table 1).
Table 1. Equations used to estimate Z values (mol /Pa m$^3$)

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Expression</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$Z_{AIR} = 1/RT$</td>
<td>$R$ - gas constant</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T$ - temperature (K)</td>
</tr>
<tr>
<td>Water</td>
<td>$Z_W = 1/H$</td>
<td>$H$ - Henry’s law constant (Pa m$^3$/mol)</td>
</tr>
<tr>
<td>Sediment</td>
<td>$Z_S = f_{oc} \cdot 0.41 \cdot K_{OW} \cdot \rho Z_W$</td>
<td>$f_{oc}$ - fraction of organic carbon</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\rho$ - sediment solid density</td>
</tr>
<tr>
<td>Lipid (octanol)</td>
<td>$Z_L = K_{OW} Z_W$</td>
<td>$K_{OW}$ - octanol water partition coefficient</td>
</tr>
<tr>
<td>Biota</td>
<td>$Z_F = L_f \cdot K_{OW} Z_W$</td>
<td>$L_f$ - lipid content of organism</td>
</tr>
<tr>
<td>Food</td>
<td>$Z_A = L_A Z_O$</td>
<td>$L_A$ - lipid content of food</td>
</tr>
</tbody>
</table>

Furthermore, the rate of uptake and loss processes ($N$, mol/h) can be expressed as the product of the fugacity and transport and transformation parameters referred to as D-values (mol/Pa h).

A comprehensive review of the determination and use of D-values to express uptake and loss processes in organisms is presented in Mackay, (2001). For example, a D-value for uptake by respiration ($D_W$) and food ($D_A$) can be expressed as

$$D_W = G_{WEW} Z_W$$  \hspace{1cm} (9)

$$D_A = G_{EAZ_A}$$  \hspace{1cm} (10)
Where $G_W$ and $G_A$ (m$^3$/h) are the gill ventilation rate and the food consumption rate, $Z_W$ and $Z_A$ (mol/m$^3$/Pa) are fugacity capacities of water and food, respectively, $E_W$ (%) is the gill uptake efficiency of chemical absorption from water and $E_A$ (%) is the gut absorption efficiency of chemical absorption from food. Similarly, the uptake by respiration and dietary uptake can be expressed using concentration and rate constants and it can be shown that both approaches are equivalent algebraically (e.g. Sharpe and Mackay, 2000; Mackay, 2001).

A mass balance equation can be assembled to track the dynamics of the chemical in the organism as

$$V_F Z_F \frac{df_f}{dt} = \text{total uptake rate} - \text{total elimination rate}$$

$$= D_W f_W + D_A f_A - f_f (D_W + D_A + D_M + D_G + D_E) \quad \text{(11)}$$

$V_F$ and $Z_F$ are the volume and fugacity capacity for the fish, $D_M$, $D_G$ and $D_E$ are the D-values for metabolism, growth dilution and excretion. Equation 11 can be solved using a steady state approximation (Paper II) or by numerical integration to follow changes in the fugacity in the organism over time (Paper III). For example, at steady state (uptake = loss rate)

$$f_f = f_W \frac{D_W}{(D_M + D_G + D_E + D_W)} + f_A \frac{D_A}{(D_M + D_G + D_E + D_W)} \quad \text{(12)}$$

Equation 12 can be simplified by separating the different terms in the numerator and expressing them as a ratio of D-values of the denominator.
\[ f_F = f_W W + f_A A \] (13)

W and A are defined as fugacity factors for respiration and diffusive uptake from water and food respectively and clearly indicates the contribution of the different uptake routes to the fugacity of the organism (e.g. Campfens and Mackay, 1997). For example, if \( D_W \) is very large as is the case for chemicals with \( \log K_{OW} \leq 4 \), the fugacity in the organism \( f_F \) equals \( Wf_W \) and the BCF \( (f_F/f_W) \) approximates to \( W \). However for chemicals of high \( \log K_{OW} \) \( (\geq 5) \), the \( D_A \) term dominates and the fugacity \( f_F \) equals \( Af_A \) and the BMF \( (f_F/f_A) \) approximates to \( A \). Equation 13 expresses the total fugacity in the organism as a result of bioconcentration and biomagnification of the contaminant (Mackay, 2001). Gobas, (1993, 1999) used a fugacity approach to describe the biomagnification process. Hydrolysis and gut absorption results in a decrease in the fugacity capacity \( (Z) \) of the food (or an increase in the fugacity of the food) relative to the fugacity of the gastrointestinal tract. This fugacity difference provides a gradient for diffusion of chemical from the food into the organism. Furthermore, the decrease in the fugacity capacity of the food in the digestive tract also causes a decrease in the \( D \) value for egestion \( D_E \) relative to the \( D_A \) and the ratio \( D_A/D_E \) is termed a limiting or the maximum biomagnification factor \( Q_D \). Generally, \( Q_D \) has a typical value of 3–5 for aquatic invertebrates (Conolly and Pedersen, 1988; Campfens and Mackay, 1997) and is much larger for mammals and birds (Drouillard and Norstrom, 2000; Fraser et al., 2003). Observe that if \( Q_D \) is substituted in equation 13, the fugacity in the organism \( f_F \) equals \( Q_D f_A \) and the BMF approximates to \( Q_D \).
3. **Aim of this thesis**

The general objective in this thesis was the development and application of tools to study the fate and bioaccumulation of organic pollutants in aquatic ecosystems. Three separate kinds of tools were developed/applied:

i) Equilibrium lipid partitioning approach (ELP approach) *(Paper I)*

ii) Steady-state/dynamic bioaccumulation models based on the fugacity approach *(Paper II-III)*

iii) Stable nitrogen isotope approach for studying trophic magnification *(Paper IV)*

All three approaches were applied to study the fate and bioaccumulation of organics in the Baltic Sea ecosystem *(Papers I, II and IV)*. A dynamic food web model was also used to study the fate and bioaccumulation of pesticides in small aquatic ecosystems (i.e. ponds, streams and ditches; *Paper III*).

While the quantification of contaminants in single components of ecosystems is important, it is also necessary to understand intermedia transfer processes, and the parameters that influence these processes. Thus, an emerging consensus in environmental research is a shift from the narrower goal of understanding pollutant dynamics in a single media to the much broader goal of using multimedia approaches. The later approach offers more powerful and complete insights into the overall fate of a contaminant and more studies are needed to help the field
acquire greater influence with regulatory agencies and the public in general. This thesis is a contribution to this endeavour and applies a multimedia approach to study the bioaccumulation of organic contaminants. As a result of extensive monitoring activities, a large set of data exist on contaminants in the Baltic Sea region, however little effort has been made to carry out a system wide interpretation or analysis of the collected data. Furthermore, the only previously published mechanistic food web model available for the Baltic (Czub and Mclachlan, 2004) describes the uptake and bioaccumulation of organic contaminants in a short marine food chain consisting of 3 pelagic species at different life stages. The tools developed in Paper I and Paper II addresses these deficits by (a) presenting an ecosystem wide assessment and interpretation of contaminant data collected from the Baltic Sea ecosystem, using a well tested methodology, (b) developing a food web bioaccumulation model for a large Baltic food web comprising both pelagic and benthic species at different life stages, which to the best of my knowledge is the most extensive mechanistic food web model ever attempted for the Baltic Sea ecosystem.

Paper III describes a novel approach for evaluating the food web transfer of pesticides in small-scale ecosystems (e.g. ponds, streams, ditches or mesocosms) which means (a) aquatic macrophytes are included as a component of the aquatic ecosystem, and as a food item for food web species (b) the transfer of pesticide residues, between environmental compartments and biota is explicitly calculated using the fugacity concept, (c) uptake/elimination of pesticide residues, are described using similar approaches used in large-scale steady state food web models. A particularly important feature in this approach is the applicability to legacy as well as
current use pesticides in commerce and the relative ease in which simulation scenarios may be
generated to suit particular evaluative or regulatory contexts. For example, input data can be
easily modified to evaluate data sets generated during pesticide registration or to evaluate
different combinations of physical-chemical properties in the design of pesticide formulations.

The bioaccumulation of the POPs has been evaluated individually in separate Baltic food chain
studies. However, Paper IV presented an opportunity to simultaneously evaluate the
bioaccumulation of persistent and metabolizable compounds in a benthic and pelagic food
chain and to examine relationships between chemical properties and bioaccumulation
potential. This is particularly important since differences in bioaccumulation potential of
organic compounds are often related not only to variation in chemical properties but also to
interactions with the environment (e.g. respiration of sediment pore-water versus overlying
water) and the composition of the food chain.

3.1 Why we need tools to study bioaccumulation of contaminants

Bioaccumulation is of interest to the general public and especially to legislative agencies in
terms of setting limitations for current and future emissions and/or discharges from industrial
facilities; setting water quality criteria and providing information that may form the basis of
future ecosystem assessments (remediation, risk assessments, hazard evaluation programs
etc). Generally, legislative authorities develop water quality criteria and water quality standards
based on raw data and/or results from scientific investigations. These are then used to devise
for example, total maximum loadings of a pollutant a facility may discharge or emit without exceeding water quality standards. However, scientific studies are not available for the over 100 000 chemicals of commerce listed in the European Inventory of Existing Commercial Chemical substances (EINECS) database (Nordberg and Ruden, 2007). Bioaccumulative organic chemicals are often identified on the basis of their hydrophobicity; hence most decisions on bioaccumulation have been based on the use of the octanol-water partition coefficients ($K_{ow}$) as criteria to estimate bioaccumulation (Lerche et al., 2002). Many expressions relating bioaccumulation to the $K_{ow}$ have been formulated especially for aquatic organisms (e.g. Neely et al., 1974; Veith et al., 1979; Mackay, 1982). However, the bioaccumulation process is controlled by the balance of absorption, dilution, metabolism and excretion processes in an organism and not just the hydrophobic character of the chemical alone (e.g. Connolly and Pedersen 1988; Connell, 1990). An alternative approach is the development of tools incorporating information on the chemistry and fate of contaminants in the environment and a mechanistic understanding of the bioaccumulation process. Such tools will probably provide a better approach to identify substances that may bioaccumulate but are not hydrophobic and access the bioaccumulation potential and ecological risks from chemicals.
4. Tools for Evaluating Bioaccumulation

4.1 The equilibrium lipid partitioning approach

The ELP approach is based on equilibrium partitioning model (EqP) and describes the distribution of hydrophobic compounds between compartments or phases in contact with each other (DiToro et al., 1991). The tool does not involve a mechanistic description of the bioaccumulation or biomagnification process, rather monitoring data are converted to equilibrium lipid concentrations (i.e., the concentration in a lipid/octanol that would be equilibrium with the concentration in a given medium) which have common units (method explained below). This is analogous to converting concentrations to fugacities (which are directly proportional to equilibrium concentrations; Mackay, 2001), but more readily understandable for the layperson who may find the fugacity concept unfamiliar. Once monitoring data has been converted to ELP concentrations it facilitates the identification of time trends, and establishment of the equilibrium, bioaccumulation and biomagnification status of the ecosystem. Therefore, the ELP approach is best applied in situations were monitoring data is readily available for contaminants in the different abiotic compartments and biota in an ecosystem (e.g. Webster et al., 1999). This happens to be the case for the Baltic Sea region where monitoring for organic contaminants has been going on at least during the last decades.

The application of the ELP tool involves the collection and screening of monitoring data and the subsequent analysis of the data using linear regression techniques. Usually monitoring data are reported for a variety of environmental matrices (e.g. air, water, sediment and biota) at
different locations in an ecosystem and analyzed at different laboratories. It is important to devise criteria to ensure homogeneity as much as possible. For example, it may be necessary to eliminate data collected close to or from obvious point sources or hotspots such as urban areas. This eliminates the large spatial variations in concentrations near to point sources and urban areas compared to data collected at background sites. And most importantly, the sampling and analytical methods needs to be checked to make sure standard protocols were used. In most cases, value judgements such as placing more confidence in data from accredited laboratories or data reported in peer-reviewed publications are used.

The data collection and screening results in a database of concentrations in conventional units (e.g. μg/l for water samples, g/g for sediments or ng/g lw for biotic samples). A possible method of addressing this difficulty is to express all concentrations on a common basis. Webster et al, (1999) used an equilibrium lipid partitioning concentration approach to analyze monitoring data collected from the Great Lakes in North America. The concentration of a contaminant in a medium \( (C_M) \) can be converted to the ELP concentration \( (C_M^{ELP}) \) using equation 14

\[
C_M^{ELP} = K_{LM} C_M
\]  

(14)

\( K_{LM} \) is the lipid to media partition coefficient. Partition coefficients are usually expressed as ratios of fugacity capacities or by combining groups of known partition coefficients (e.g. \( K_{OW} = Z_O/Z_W \) and \( K_{AW} = K_{OW}/K_{OA} \)). Concentrations reported in conventional units can be easily converted to ELP concentrations using the expressions in Table 2.
Table 2. Expressions used to convert concentrations reported in conventional units to ELP \((g/m^3)\).

<table>
<thead>
<tr>
<th>Medium</th>
<th>Conventional units</th>
<th>g/m(^3)</th>
<th>Conversion equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>ng/m(^3)</td>
<td>(10^{-9})</td>
<td>(C_{ELP_{air}} = C_{air} K_{OA})</td>
</tr>
<tr>
<td>Water</td>
<td>ng/L</td>
<td>(10^{-6})</td>
<td>(C_{ELP_{water}} = C_{water} K_{OW})</td>
</tr>
<tr>
<td>Sediment</td>
<td>µg/g</td>
<td>1.5(*)</td>
<td>(C_{ELP_{sed}} = C_{sed} K_{OSED}^{+})</td>
</tr>
<tr>
<td>Biota</td>
<td>µg/g</td>
<td>1(**)</td>
<td>(C_{ELP_{biota}} = C_{biota} / l_{biota})</td>
</tr>
<tr>
<td>Lipid</td>
<td>µg/g</td>
<td>1(**)</td>
<td>(C_{ELP_{lipid}} = C_{lipid})</td>
</tr>
</tbody>
</table>

* The bulk density for sediments was assumed to be 1500 kg/m\(^3\).
** The density of biota and lipids was assumed to be 1000 kg/m\(^3\).
\(^{+}K_{OSED}\) is the “octanol-sediment” partition coefficient \((Z_{O}/Z_{SED})\).

ELP concentrations of contaminants in different media can be easily evaluated for bioaccumulation using linear regression techniques (Paper I). Alternatively, an average biomagnification factor (TMF or FWMF) can be determined from the ELP concentrations and trophic positions (TP) of the components of the ecosystem derived from the known feeding relationships (e.g. Mackintosh et al., 2004 and Paper II) or using nitrogen isotopes techniques (Rolff et al., 1993 and Paper IV). In this case the regression of ELP and TP is expressed as a linear equation of the form

\[
\ln (ELP) = A + B \times TP \quad (15)
\]
Where $B$ is the slope of the regression and $A$ is the intercept. The TMF can then be calculated using equation

$$\text{TMF} = e^B$$  \hspace{1cm} (16)

TMF $> 1$ indicating biomagnification of the contaminant across the food web, TMF $< 1$ indicating biodilution and TMF $= 1$ indicates no change in concentration of the contaminant across the food web.

**4.2 Steady state and dynamic modelling**

The development of the steady state modelling tool involves expanding equation 11 to cover not just one species but different species comprising a food chain or a food web in an aquatic ecosystem. For example for a food chain or food web consisting of $n$-organisms, $n$-equations of the form of equation 11 can be derived for each species, and the $n$-equations can then be linked together through dietary relationships to define the uptake of contaminants directly from the environment and indirectly through the consumption of contaminated prey. Thus equation 11 can be rewritten as

$$V_i z_i \frac{df_i}{dt} = \Sigma(D_{Aji} f_j) + D_{Wi} (f_w x_{wi} + f_s x_{si}) - D_{Ti} f_i$$  \hspace{1cm} (17)
Where $i$ is a species in the food web ($i = 1$ to $n$), $V$, $Z$ and $f_i$ are the volume, the $Z$-value and the fugacity of the species. $D_{Aji}$ is the food uptake $D$-value to species $i$ occurring from consumption of species $j$ in the food web, $D_{Vi}$ is the respiration $D$-value, $f_W$ is the fugacity of water, $x_{Wi}$ is proportion of water column water respired by species $i$; $f_S$ is the fugacity of sediment, $x_{Si}$ is the proportion of sediment pore-water respired by species $i$ and $D_{Ti}$ is the sum of the loss $D$-values for species $i$ (includes respiration, egestion, metabolism and growth dilution). The set of equations are readily solved by assuming steady state (Paper II) or unsteady state (Paper III) framework were conditions change with time. The steady state framework assumes that the environmental characteristics of the compartments change relatively slowly with time and is generally applicable to modelling the fate and bioaccumulation of contaminants in large ecosystems (e.g. Clark et al., 1990; Thomann et al., 1992; Gobas, 1993; Morrison et al., 1996; Campfens and Mackay, 1997). In this context the approximation is extended to include the following characteristics: (a) growth rates are linear and all processes are first order with respect to the chemical concentration (b) the species in the food web have maintained constant $D$-values for a period of time which is long relative to the clearance time of the contaminant. Thus at steady state, the general expression for a species $i$, which may respire in water column and sediment pore water and consume multiple prey is written as

$$D_{Ti} f_i = \Sigma (D_{Aji} f_j) + D_{Wi} (f_W . x_{Wi} + f_S . x_{Si})$$

$$f_i = \Sigma (A_{ji} f_j) + W_i (f_W . x_{Wi} + f_S . x_{Si})$$

(18)

(19)
The set of equations can be transformed into a matrix containing terms representing dietary relationships, organism fugacities and a respiration vector of the form

\[
A f = E
\]  

(20)

Where \( A \) is a food preference matrix, \( f \) is the vector of organism fugacities \((f_i - f_n)\) and \( E \) is a respiration vector (with terms of the form \( W_i (f_{wi} x_{wi} + f_{si} x_{si}) \)). For a food chain consisting of 3 species, equation 20 becomes

\[
\begin{bmatrix}
(1 - A_{11}) & -A_{12} & -A_{13} \\
-A_{12} & (1 - A_{22}) & -A_{23} \\
-A_{13} & -A_{23} & (1 - A_{33})
\end{bmatrix}
\begin{bmatrix}
f_1 \\
f_2 \\
f_3
\end{bmatrix}
= \begin{bmatrix}
W_1 (x_{1w} f_w + x_{1s} f_s) \\
W_2 (x_{2w} f_w + x_{2s} f_s) \\
W_3 (x_{3w} f_w + x_{3s} f_s)
\end{bmatrix}
\]

(21)

The coefficients in the \( A \) matrix represent the consumption of each organism by another. The vector of fugacity values is solved using a Gaussian elimination routine to quantify the fugacities (or concentrations), amounts, and chemical fluxes resulting in a complete steady-state mass balance throughout the entire food web. The bioaccumulation of contaminants in the food web can then be deduced by evaluating the fugacity of the species in the food web relative to the fugacity of the abiotic environment. For example, if the fugacity of species 2 \( f_2 \) > fugacity in water \( f_w \), then species 2 is bioaccumulating the contaminant. Furthermore, if \( f_2 > f_1 \) (fugacity of species 1 at a lower trophic level), then the contaminant is biomagnified.
Aside from the mechanistic description of the bioaccumulation process, this tool also offers the possibility of quantifying the D-values for the different processes and deducing for each species the important processes contributing to the observed fugacity. Furthermore, such a modelling tool can be subjected to a systematic sensitivity or uncertainty analysis to identify the input parameters that significantly influence the predicted fugacities in the species of the food web. The steady state approximation has been shown to be consistently successful for modelling the fate and bioaccumulation of a range of organic contaminants in aquatic ecosystems (Mackay et al., 1983; Mackay et al., 1989; Gobas, 1993; Campfens and Mackay, 1997; Morrison et al., 1997).

However, the steady state approximation does not account for the effects of temporal differences in contaminant levels and thus exposure due to changes in emissions and environmental conditions. Thus the steady state modelling tool cannot be used evaluate the fate and bioaccumulation properties of contaminants such as pesticides that are emitted periodically into small scale ecosystems such as ponds, streams, ditches or mesocosms (e.g. Crossland, 1982; Rand and Clark, 2000; Dekissa et al., 2004). Such time varying conditions are expected to influence the fate and bioaccumulation and hence dynamic models are more appropriate in such instances (Paper III). The philosophy used in development of the dynamic modelling tool is similar to that in the steady-state modelling tool but equation 17 is solved either by iteration or by integration assuming initial conditions to track changes in fugacity (or concentration) of the contaminant in the species with time. Thus it is possible to evaluate the bioaccumulation of contaminants by a species in the food web at the different developmental stages (e.g. juvenile or adult stages) and the changes in the dynamics of the contaminant in the
ecosystem as a result of changes in emissions or food web structure with the dynamic modelling tool.

4.3 Stable nitrogen isotopes approach

The theoretical background in the present approach is based on the differences in the assimilation of isotopes of nitrogen ($^{14}$N and $^{15}$N) by aquatic and terrestrial biota. Generally, the fate of contaminants in a food web depends on the food web structure as well as flows of material and energy (e.g. carbon flow, nitrogen flow). The flow of nitrogen isotopes has been used as a variable to describe food web interactions (e.g. trophic positions and length of food webs) as well as to study the biomagnification of contaminants in marine systems (Rolff et al., 1993; Hobson, 1995; Abend and Smith, 1997; Fisk et al., 2001). Generally, predators at the top of aquatic food webs enrich the heavier isotope of nitrogen ($^{15}$N) relative to their prey due to the preferential excretion of the lighter isotope ($^{14}$N) (Peterson and Fry, 1987; Hansson et al., 1997; Wada and Hattori, 1991; Vander Zanden and Rasmussen, 2001). This finding is not limited to nitrogen isotopes, as it has also been observed that the relationship between the different isotopes of other elements (e.g. carbon, sulfur, oxygen) change once they are exposed to natural processes in the biosphere. Specifically the relationship between ($^{12}$C/$^{13}$C) expressed as $\delta^{13}$C (‰) provide a time integrated measure of assimilated diet as well as information on carbon sources that can be used to differentiate between consumption of pelagic and benthic prey (France, 1995; Hecky and Hesslein, 1995; Newman and Unger, 2003). Trophic levels as well as the structure of food webs can be derived from feeding relationships or by classifying the
species as producers, consumers and predators based on stomach contents or interspecies relationships (Oliver and Niimi, 1988; Burreau et al., 2004). However, consumers may show varying dietary composition due to the availability or shortage of a prey item or may prey on both animal and plant matter (i.e. consumers may be omnivorous, e.g. Ruus et al., 2002).

The stable isotopes tool combines the analysis of stable isotopes and POP concentrations to quantitatively describe the biomagnification of contaminants in food webs (e.g. Broman et al., 1992; Rolff et al., 1993). The fundamental equation relating changes in isotopic composition (isotopic abundance) in a species in a food web relative to that in a standard substance (atmospheric nitrogen for nitrogen) takes the form:

\[
\delta^{15}N(\%) = \left( \frac{^{15}N/^{14}N}_{\text{sample}} - \left( ^{15}N/^{14}N \right)_{\text{air}} \right) \times 1000
\]

(22)

Where \( \delta^{15}N \) is the stable isotope composition expressed in (‰). The determined \( \delta^{15}N \) of the species are then applied to (a) calculate the trophic levels assuming a fractionation of 3–5 ‰ between a predator and prey (e.g. Minagwa and Wada, 1984; Cabana and Rasmussen, 1994) and (b) in the regression describing the trophic transfer of contaminants through the entire food web. The slope of this regression represents the biomagnification potential (B) of a contaminant in a food web and gives the TMF (or FWMF) when substituted into equation 16. Furthermore, biomagnification factors (BMFs) adjusted for trophic levels based on \( \delta^{15}N \) values
can be calculated as the ratio of the lipid normalized contaminant concentrations (for lipid soluble contaminants, otherwise wet weight) in the predator and prey species.

\[
BMF = \frac{\frac{[\text{predator}]}{[\text{prey}]}}{\left( \frac{TL_{\text{predator}}}{TL_{\text{prey}}} \right)}
\]  

(23)
5. Summary of Papers

5.1 Summary of Paper I

In Paper I, the time trends, bioaccumulation and biomagnification of five PCB congeners (IUPAC 28, 101, 138, 153 and 180) in the Baltic Sea was studied. A comprehensive dataset of concentrations in air, water, sediment and biota including phytoplankton, zooplankton, pelagic macrofauna, herring, cod, salmon and guillemots from background sites was selected for case study. The temporal trends in biomagnification were evaluated by linear regression of the ELP concentrations for the years 1987–2001.

Results and discussion

The analysis showed declining PCB congener concentrations in air, water, some fish species and guillemots with calculated half lives ranging from 3 to 11 years for all PCB congeners and in all media. These results are consistent with the expectations that the decline in abiotic exposure concentrations as a result of emission reductions would be reflected in biotic concentrations in the ecosystem. TMFs (FWMFs) > 1 were obtained for all 5 PCB congeners indicating biomagnification in the food web. Additionally, TMFs were observed to increase with log $K_{OW}$ of the congeners. The study shows that the ELP approach can be used to evaluate large amounts of monitoring data that have been collected in the Baltic Sea region for biomagnification of PCB congeners (and other organic contaminants) and could potentially be applied to monitoring data collected from other ecosystems.
5.2 Summary of Paper II

The goal of Paper II was to develop a mechanistic model to study the bioaccumulation of organic contaminants in a large Baltic food web. The chemicals modelled included 5 PCB congeners, selected to span a range of physical and chemical properties and hence environmental behavior. The food web included 14 pelagic and benthic aquatic species and is a representative large Baltic food web. The model developed is capable of predicting the ELP concentrations (and/or fugacities), and generating the rates of uptake, loss and transformation processes of PCB congeners by the different species in the food web. The model was evaluated by comparing the predicted ELP concentrations against monitoring data and by sensitivity analysis in which the influence in variation in input data on the model predictions was monitored.

Results and discussion

The model predictions indicated bioaccumulation and biomagnification of PCB congeners in the Baltic food web as indicated by the increase in ELP concentrations from the base of the food web to organisms at higher trophic positions. The most dominant uptake process of PCB congeners at lower trophic levels was respiration, while dietary uptake was the dominant uptake pathway for fish species. Model predicted ELP concentrations in all species and for all PCB congeners were a factor of 2-5 lower than ELP estimated from monitoring data.
Model sensitivity analysis indicated the log $K_{ow}$ and the annual average temperature were the most important parameters affecting the predicted ELP concentrations. Organism specific parameters became important for higher trophic level species (e.g. cod and salmon), and the fractional respiration from water and pore water was a crucial parameter especially to the benthic species. A steady state model appears to capture the bioaccumulation behavior of PCB congeners in the Baltic ecosystem. Model improvement efforts should be on better describing the fractional respiration in water and pore water which is currently an uncertain parameter.

### 5.3 Summary of Paper III

The goal of Paper III was to develop a dynamic combined fate and food web model that can be used as a tool to study the influence of submerged aquatic vegetation on the fate and food web transfer of pesticides in small-scale ecosystems such as ponds, streams, ditches or microcosms. Submerged vegetation play a vital role as primary producers in food webs and may also play a role in reducing the dispersion of pesticides and thus limiting exposure of the aquatic species.

The developed model consists of an abiotic fate model with three compartments including water, sediment and submerged aquatic vegetation (macrophytes), linked to a pond food web of 11 target species representing different trophic levels and guilds. A group of three hypothetical pesticides of varying hydrophobicity (log $K_{ow}$ of 3 to 7) were selected as model compounds, and the fate of these compounds in a pond with varying macrophytes density was investigated. In selecting the physical-chemical properties of the pesticides we assumed that all
three compounds were very persistent (half-life of 55000 h) in all media. This assumption ensures that differences in fate is due to the differences in hydrophobicity as indicated by log \( K_{\text{OW}} \) and avoids the uncertainty and the controversy associated with selecting degradation rate constants which are variable in field conditions.

Results and discussion

The model output indicated the fate and food web transfer of highly hydrophobic compounds with \( \log K_{\text{OW}} \geq 5 \) were affected by the assumed macrophytes density. The fate and food web transfer of compounds with \( \log K_{\text{OW}} \leq 4 \), which is a more representative hydrophobicity of the majority of current-use pesticides, were not significantly affected by the inclusion of aquatic macrophytes in the pond environment. The increased importance of macrophytes for the highly hydrophobic compounds is a result of the dominance of particle deposition in the mass transfer from water to macrophytes. Chemicals with \( \log K_{\text{OW}} \leq 4 \) were not significantly influenced by particle deposition, nor were they bioconcentrated by macrophytes. These results enabled us to conclude that the fate and food web transfer of many current use pesticides will not be influenced by the presence of submerged vegetation in a pulse exposure since \( \log K_{\text{OW}} \leq 4 \).

The model predicted peak concentrations in the top predator, which is a relevant metric in aquatic risk assessment were consistently lower than peak concentrations estimated using the EU guidelines for risk assessment. It is recommended that the mechanistic model could be used as a tool for interpreting laboratory, mesocosms and field measurements as well as for
providing realistic estimates of dynamic food web accumulation of pesticides in aquatic systems.

**5.4 Summary of Paper IV**

In Paper IV, the stable nitrogen isotope method was used to study the trophic transfer and biomagnification of a number of organic pollutants, including chlorinated pesticides (e.g. PCBs, PAHs, DDTs, PCNs and chlordane compounds) in benthic and pelagic food chains in the Baltic Sea. The structures of the food chains were characterized using $\delta^{15}N$ and linear relationships between lipid-normalized contaminant concentrations and trophic level (based on $\delta^{15}N$) were used to estimate food web magnification factors and biomagnification factors in the pelagic and benthic food chains.

**Results and discussion**

The mean $\delta^{15}N$ ranged from 3.0–8.4 ‰ in the pelagic food chain and 8.4–12.02 ‰ in the benthic food chain. The higher $\delta^{15}N$ in the benthic species than in the pelagic species was probably a result of the close association and feeding of these species on benthos which is enriched in $^{15}N$.

The variation in $\delta^{15}N$ indicated a pelagic food chain structure of four trophic levels of the form phytoplankton-zooplankton-mysis-herring, which is consistent with what is previously known about the dietary habits of the species. However, the structure of the benthic food chain as
indicated by the variation in $\delta^{15}$N is probably in error due to a higher $^{15}$N for monoporeia than for Saduria.

BMF $> 1$ and TMF $> 1$ were obtained for PCB congeners, DDT metabolites, dieldrin and chlordane compounds with $\log K_{OW} > 6$, indicating biomagnification in the food chains. Furthermore, enantiomers of the same compound (e.g., $trans$-chlordane [tCHL] and $cis$-chlordane [cCHL]; and $trans$-nonachlordane [tNCHL] and $cis$-nonachlordane [cNCHL]) showed differing biomagnification properties. The PAHs with comparable hydrophobicity to PCBs were not biomagnified as a result of metabolism and elimination by higher trophic level species in marine food chains. The results for the PCNs indicated BMFs $> 1$ and TMFs $> 1$ for pentachlorinated and hexachlorinated PCN congeners (e.g. PCN 54, PCN 59 and PCN 68), and TMFs $< 1$ for the lower chlorinated homologue groups (e.g. tetrachlorinated PCN congeners) indicating trophic dilution. HCH isomers with $\log K_{OW} \sim 3.8$ showed a low bioaccumulation potential, consistent with the expectation that biomagnification will not occur for compounds with $\log K_{OW} < 5$ due to a combination of decreased uptake and increased excretion (Russell et al., 1999; Borgå et al., 2004; Thomann, 1989; Thomann and Connolly, 1992).
6. **General conclusions and achievements**

The papers presented in this thesis and the research undertaken has demonstrated the application of a series of tools to assist in the evaluation of the fate and bioaccumulation of organic contaminants in aquatic ecosystems.

By generating a database of monitoring data where all concentrations are expressed as ELP, the research in **Paper I** presents scientific information in a simple and understandable form to the public and policy makers. The research complements the huge efforts that have been deployed towards monitoring organic contaminants in the Baltic Sea environment. The generated database provides a wealth of information on pollutants in the Baltic Sea and has been made available to other researchers.

The research in **Paper II** represents a novel approach in Baltic food web modelling by proposing an extensive mechanistic model of several trophic levels of pelagic and benthic aquatic species that complements previous studies on the bioaccumulation of organic contaminants in short Baltic food chains. The steady state approach appeared to capture the general bioaccumulation behavior of PCB congeners in the Baltic food web. By evaluating the model against monitoring data it was possible to conclude that the model provides a reasonable mechanistic and quantitative understanding of the fate of PCB congeners in a large Baltic food web. Additionally, by subjecting the model to a rigorous sensitivity analysis we also identified the important parameters that should help focus future model improvement options and application. The
mechanistic model could be utilized by regulators in the assessment of the potential hazards of non-ionic organic compounds in the Baltic Sea.

The research in Paper III also proposed a novel approach in pesticide fate and food web modelling. Aquatic macrophytes are included as abiotic compartment and as food for food web species, and a fugacity approach was used to describe the interactions between the different components in the pond food web and the emitted pesticide. The model predictions indicated different response times by food web species to changes in water phase concentrations and a clear influence of aquatic macrophytes on the fate and food web transfer of highly hydrophobic compounds. In Paper III it is concluded that the model predicted maximum concentrations are more representative of the true exposure of fish-eating birds and terrestrial mammals than a worst-case scenario currently used in the EU guidelines for regulating pesticides. Accordingly, the pesticide fate model proposed in Paper III has potential application in improving the current practices in exposure and risk assessment of pesticides.

The research in Paper IV presented an opportunity to study the biomagnification, trophic transfer and food web magnification of a wide range of persistent and metabolizable contaminants in two Baltic food chains. This study integrated differences in exposure of aquatic species due to position in the water column, variation in physical chemical properties and food web structure and produces a reasonable explanation to concentration patterns that have been previously reported in the literature. Despite uncertainty in the structure of the benthic food chain studied it was possible to conclude that trophic transfer and biomagnification of
contaminants is influenced by the variation in chemical properties and differences in metabolic capabilities of the food chain species. While the data used for this study has been available since 1994, this is first time that all data have been collated, plotted and properly interpreted. Aside from the results reported in Paper IV, we have also made available historical data that could be compared to more recent results to gain a better picture of the changing contaminant status in the biotic environment of the Baltic Sea.
7. Future research needs

Recommendations for further research arising from this thesis include:

- Extending the application of the ELP approach in Paper I to other pollutants such as PAHs, HCH, PBDE’s and HCB for which an extensive amount of monitoring data is already available. Converting measured concentrations to ELP concentrations or fugacities provides valuable information about the behavior of different contaminants in an ecosystem: it can be used to determine if a contaminant is trophically magnifying or diluting, it can be used to identify and compare time trends in different media and it can determine if certain media are acting as sources/sinks (e.g. if there is an enhanced fugacity in a particular media).

- The food web model developed in Paper II should be evaluated for a wider range of organic contaminants (e.g. emerging pollutants such the brominated flame retardants).

- It would be challenging but interesting exercise to adapt the model presented in Paper II for estimating the bioaccumulation of perfluorinated compounds as biomonitoring data are beginning to emerge for the Baltic Sea region (e.g. Holmström et al., 2005; Bignert et al., 2008).

- A dynamic version of the food web model in Paper II could be developed and compared to the steady-state model. This would facilitate the extension of the model to other species including birds, seals and humans. Steady-state models are probably not appropriate for estimating the bioaccumulation of POPs given the long time taken to achieve steady-state in these species. The model could further be extended to provide
an estimate of human exposure from the consumption of fish. In a risk assessment perspective this exposure could be compared to terrestrial exposure (from consumption of meat and dairy products).

- The dynamic model, if developed, could further be coupled either to a bioenergetics model (e.g. models developed at the Baltic Nest Institute for describing nutrient dynamics) capable of predicting changing populations and dietary preferences with time or to a dynamic fate model such as the POPCYCLING Baltic model (Wania et al., 2000) capable of predicting the effect of temporal changes on uptake in the food web.

- The dynamic combined fate and food web model presented in Paper III was evaluated using hypothetical compounds. Future evaluation with datasets generated during pesticide registration by pesticide manufacturers is highly recommended. Such evaluation will strengthen the approach outlined and identify areas of weakness that needs improvement.

- The $^{15}$N approach applied in Paper IV is limited by a number of assumptions some of which are the assumption of similar fractionation of $^{15}$N amongst trophic levels and dietary exposure as the main exposure route of aquatic species. However, the validity of these assumptions is currently under debate (e.g. Borgå et al., 2005; Paterson et al., 2006) and improved methods for applying these isotope methods may be suggested. It is also important that researchers tackle questions such as the dependence of TMFs determined using $^{15}$N on temperature, intrinsic environmental characteristics, DOC fluctuations, food web composition and long range transport. As long as these questions
remain unresolved it will limit the application of trophic magnification factors in regulatory contexts (Muir 2009).

- We recommend extending the stable isotope approach to other Baltic species. It would be interesting to compare the trophic magnification of air breathers and water breathers within the Baltic as has been done in other ecosystems (e.g. Kelly et al., 2007).

- The results in Paper III suggested a benthic food chain inconsistent with the known dietary patterns of the species. The reason(s) for this discrepancy is currently unknown thus more work is needed on comparing benthic and pelagic food webs.

- The growing evidence to support climate change may have important implications for chemical fate and bioaccumulation processes. For example, important partitioning properties controlling the fate and bioaccumulation of pollutants in the environment are susceptible to changes in temperature. Climate change may also change salinity in the Baltic, the intensity of primary production and nutrient loading, as well as the food web structure due to the eradication of local species or introduction of alien species due to changing conditions. It would be an interesting research exercise to couple future predicted changes in climate, meteorological, biogeochemical and ecosystem changes to chemical fate and bioaccumulation models so that future changes in chemical fate and bioaccumulation resulting from climate change can be better estimated.

Finally, I insert a few words of caution. Generating the tools presented in this thesis, required the collection of data to describe the environment, the chemicals of interest and the food web species. Average or median values were used for some parameters together with other
simplifying assumptions. While such simplifying assumptions have the merit of reducing complex environmental processes into simple processes they are also associated with uncertainties and limitations that must be appreciated and understood. Elmgren’s assertion (Elmgren, 2000) that environmental management decisions can hardly wait for scientific certainty but should be viewed as experiments, to be monitored, learned from and then modified was one of the guiding principles in the development of the tools described in this work.
8. Acknowledgements

This work was made possible by funding from The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning through grant number 21.0/2003-0206 and The Swedish International Development Agency (SIDA) through research grant SWE-2005-451. I would like to thank the following people for their help and support throughout my program at ITM. First of all, I would like to especially thank Associate Prof. Ian T Cousins, my supervisor, for his endless and excellent guidance and encouragement that helped me during this work. Words cannot be good enough to express my gratitude toward him. I like to thank Professor Dag Broman, my assistant supervisor who provided material and excellent advice on nitrogen isotopes and Baltic food webs.

My gratitude also goes to Dr. Johan Persson of The Swedish Chemicals Agency (Kemi) and Associate Professor Magnus Breitholtz at ITM for their guidance, helpful comments and time spent serving on my Ph.D. review committee. I am also grateful to Dr. Costas Prevedouros who provided valuable comments and advice on the scientific content of the manuscripts and shared his knowledge of environmental modelling with me. I must give special thanks to the many friends and colleagues at ITM and especially to past and current members of the fate modelling group (Amaya Franco, James Armitage, and Robin Vestergren). ITM has always been a friendly and comforting environment for me and I feel very fortunate to have met all the friends and colleagues, with whom I shared so much together. I am grateful to the ITM review committee members for the critical review and constructive comments on this dissertation.
I owe great debts of gratitude to Ginger, Robin, Tyrese and Nikki for their love and encouragement over these years. My mother and father deserve special recognition for it would have been impossible to have an education without them. I also wish to convey my profound gratitude to Ulf and Anna Söderberg, Mats and Katarina Vigebo, Anne Britt and Robert Gabrielson in Umeå for the help, guidance and support they provided when I came to Umeå. I want to acknowledge my sisters, Patience (RIP), Mary, Gwen and Anne-Marie, my brother Chris and my friends, Harry B, Epanti R, Asima M, Ebongue C, Pagou A, Ambe M, Ngwa E, Adamu S, Lifongo L, Loyal N, Nkongho F, Bell E, Benda N, Ekema S, Kembi E, Adamu S, Mayah J and Mayah S. To all of you, thanks for the encouragement and support!!!
9. References


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