Lipids in Aquatic Ecosystems

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Pages 93 to 114

Chapter 5
Integrating Lipids and Contaminants in Aquatic Ecology and Ecotoxicology

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5.1 Introduction

Heterotrophic organisms in marine and freshwater food webs ingest a wide range of essential and xenobiotic compounds. *Essential* compounds are physiologically required by consumers, yet cannot be synthesized de novo, or cannot be synthesized in quantities sufficient to meet an organism's need for somatic growth, reproduction, and survival (*see* Goulden and Place 1990, for daphnids; Tocher 2003, for teleost fishes). For example, some polyunsaturated fatty acids (PUFA) and trace elements such as zinc (Zn), iron (Fe), calcium (Ca) are considered essential, and if inadequate amounts are available in the diet, the health and fitness of an organism can be reduced. *Xenobiotic* compounds have no physiological value for organisms, but can be accumulated by consumers and can be toxic in cases were concentrations are sufficiently high (Watson et al. – Chap. 4). Xenobiotic compounds include many of the classic contaminants, such as PCBs, DDT, and mercury (Hg), and more recently recognized contaminants, such as estradiol, and can also be accumulated from non-dietary sources. It should be noted that essential compounds can also be toxic if concentrations are high enough or if they are converted to other molecules. For example, it has been suggested that PUFA in diatoms can be converted to unsaturated aldehydes, which reduce egg hatching rates in marine herbivorous copepods (Miralto et al. 1999).

Lipids are recognized to be amongst the most important nutritional factors that affect the fitness of aquatic organisms, supplying energy and essential compounds for general metabolic functioning, somatic growth and reproduction (Müller-Navarra et al. 2000), and enhanced immunocompetency (Kiron et al. 1995). Among lipid classes, storage lipids, such as triacylglycerols, serve as high-energy sources, whereas structural lipids, such as phospholipids, are essential building blocks for cell membranes. Essential lipids are of particular nutritional importance for aquatic consumers as they support physiological development and health of organisms and, in a larger

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sense, strengthen the nutritional status of aquatic food webs. Although de novo synthesis of omega-3 (n-3) PUFA in aquatic ecosystems is generally restricted to algae, it has been reported that some heterotrophic nanoflagellates (Bec et al. 2006; and see Devilettes and Bec – Chap. 2) and protozoans (Klein Breteler et al. 1999) have the enzymatic ability to produce n-3 PUFA, as well as sterols, from their respective precursors. Thus, such key organisms from lower trophic levels can be involved in *trophically upgrading* their food for their own physiological benefit as well as, inadvertently, for the benefit of consumers at higher trophic levels (Fig. 5.1). In aquatic consumers, such conversion may occur when there is conditional dietary need for long-chain polyunsaturates (Cunnane 2003). It is, however, important to note that biosynthesis of fatty acids (FA) is greater in organisms at the base of the aquatic food chain, whereas higher trophic organisms such as zooplankton and fish are not likely to biosynthesize highly unsaturated fatty acids (HUFA) de novo to any significant extent (Tocher 2003; Chap. 9). Thus, the *trophic transfer* of essential

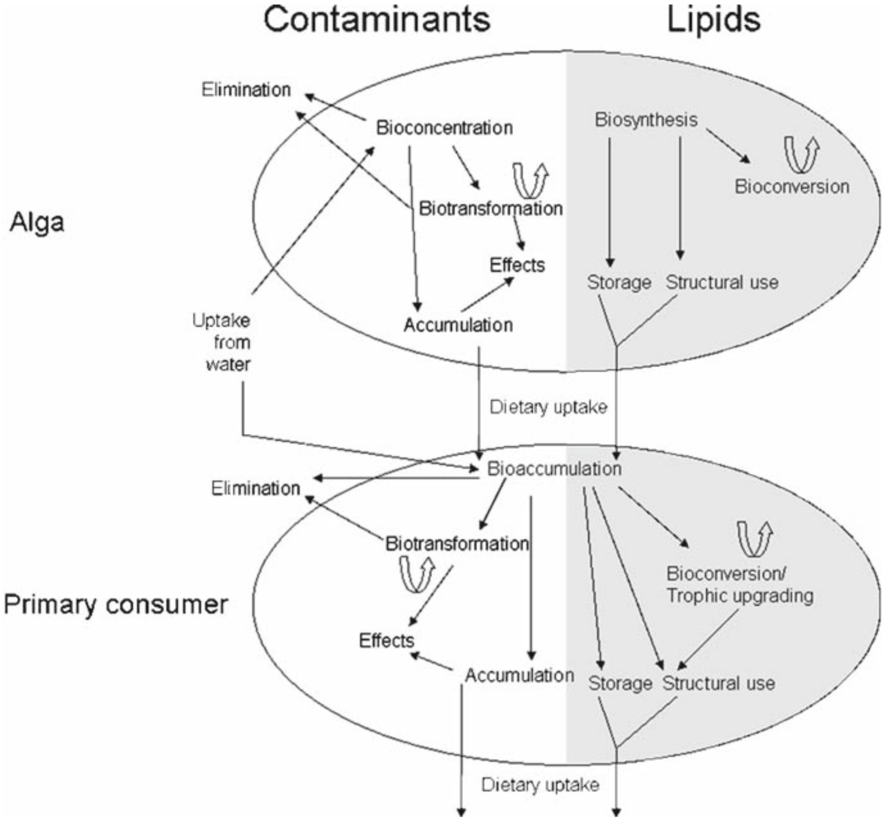

Fig. 5.1 Schematic of the relevant processes controlling the movement of lipids and contaminants through aquatic food webs. The relative importance of various processes and mechanisms can vary widely with the contaminant or lipid and organisms in question. Processes and pathways in the primary consumer are similar in secondary and higher level consumers

lipids from primary producers to upper trophic levels is critical for the health of higher trophic level organisms. Trophic transfer is also commonly used when discussing contaminants, and refers to the movement of a contaminant from resource to consumer (Borgå et al. 2004). The presence of organisms capable of trophically upgrading FA within the food web is often crucial for supplying a diet rich in nutritionally beneficial PUFA and sterols and changes to food web structure and components may alter this important process.

Xenobiotic chemicals, which we will also refer to as contaminants, in the diet of animals come from a variety of sources, with those of anthropogenic origin that bioaccumulate in aquatic organisms of particular concern and the focus of this chapter. Contaminants that are a concern for aquatic food webs include: metals and metalloids (such as Al, Ar, Cd, Cr, Cu, Ni, Pb, Hg, Se); organic contaminants including polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), polybrominated biphenyls (PBB), chlorinated phenols, pesticides, polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF), and other industrial chemicals (e.g., perflourinated alkanes); and organometallic compounds such as the potentially powerful neurotoxin methyl mercury (MeHg). Contaminants that bioaccumulate have the potential to counteract the mostly favorable physiological effects of essential dietary nutrients, particularly at higher trophic levels, and eventually in humans, because their dietary pathways, or trophic transfer, may follow similar pathways as those of lipids (Newman 1998; for essential fatty acids, see Kainz et al. 2006, 2008).

Most lipid ecologists have focused on increasing our understanding of lipid synthesis and distribution (Hagen and Auel 2001; Graeve et al. 2005; Guschina and Harwood 2006), the trophic relationships of lipids (Dalsgaard et al. 2003; Iverson et al. 2004; Kainz et al. 2004), and the physiological effects of different lipid classes and their constituent FA on aquatic organisms (Müller-Navarra et al. 2000; Tocher 2003; Martin-Creuzburg and von Elert 2004). Similarly, most aquatic ecotoxicologists focus their research on how contaminants move through aquatic food webs (Campfens and MacKay 1997; Russell et al. 1999; Borgå et al. 2004) and how they affect the physiological performance of organisms (Wang and Fisher 1999; Tanabe 2002; Scott and Sloman 2004). Since most FA and contaminants are trophically transferred through aquatic food webs, but potentially have very different effects and relevance, there is a need to understand how the fate of these two chemical groups varies across food webs and amongst different aquatic ecosystems. It is, therefore, important to investigate sources, biological uptake, biotransformation, physiological implications, accumulation and elimination of both lipids and contaminants within aquatic food webs. For example, changes in food webs associated with increasing stress from climate change, invasive species, and habitat destruction may result in significant changes in contaminant and lipid dynamics within ecosystems (Kelly et al. 2006). Furthermore, differences in FA and contaminant trophic transfer in food webs have the potential to provide novel insights on ecological function and the influence and effects of stress. Thus, the main objectives of this chapter are to evaluate and contrast trophic transfer of dietary lipids and contaminants in aquatic food webs. In doing so we will examine their dynamics in aquatic ecosystems and demonstrate their potential for assessing and predicting aquatic food web health, structure, and function.

5.2 Trophic Transfer of Contaminants in Aquatic Food Webs

The bioaccumulation and trophic transfer of contaminants is well studied and has been summarized in a number of recent reviews (e.g., Morel et al. 1998; Gobas and Morrison 2000, Borgå et al. 2004). Here, we summarize some major factors that influence contaminant bioaccumulation that are relevant to the goals of this review.

A key point regarding the accumulation of contaminants is that they can be accumulated by aquatic organisms, (a) directly from the water, called *bioconcentration* (the net process by which the chemical concentration in an aquatic organism achieves a level that exceeds that in the water, as a result of chemical uptake through chemical exposure in water) or (b) via food and water, defined as *bioaccumulation* (the net process by which the chemical concentration in an aquatic organism achieves a level that exceeds that in the water, as a result of chemical uptake through all possible chemical exposure, i.e., water or food, and elimination from all possible routes) (Gobas and Morrison 2000). This differs from dietary lipids, which can only be acquired from the diet. While lipids can by synthesized by aquatic organisms, contaminants cannot, although some can be modified via biotransformation (e.g., Konwick et al. 2006). The relative importance of food or water as a source of contaminant accumulation is highly dependent on the contaminant and organism in question, and for metals/elements the characteristics of the water, and is discussed below. The accumulation of organic contaminants and elements/metals are very different and are dealt with separately.

5.2.1 Trophic Transfer of Organic Contaminants

Most organic contaminants (OCs), such as PCBs and pesticides, are hydrophobic, and this drives their accumulation by aquatic organisms (Mackay 1982). Accumulation of OCs is generally considered to be a passive process, driven by diffusion and differences in fugacities of a chemical when in different matrices (e.g., water and aquatic organisms; Mackay and Paterson 1981). The fugacity of a chemical can be defined as a molecule's urge to escape or flee a system and is based on the differences in chemical potentials of a contaminant between matrices (Mackay and Paterson 1981). Contaminants will flow from high to low fugacity, with fugacity based on a combination of the properties of the contaminant and matrix. For example, at equal concentrations in water and lipid, contaminants that are hydrophobic (e.g., PCBs) will have a much higher fugacity in the water and thus will diffuse from water to lipids until the fugacities in each matrix are equal. Concentrations of PCBs can be as much as 7 orders of magnitude greater in the lipids than in the water when fugacities are equal. Even when OCs are not in equilibrium between matrices, which is the most common case, their concentrations are in general much higher in aquatic organisms than water, which is consistent with their hydrophobic and lipophilic characteristics.

Passive diffusion of contaminants into organisms can also occur in the gastrointestinal (GI) tract of an organism, although it is somewhat different than accumulation from water. As lipids are broken down in the GI tract, they form micelles that diffuse across the intestinal wall (Gobas et al. 1993; Kelly et al. 2004). Hydrophobic contaminants in the stomach contents are often transported along with the micelles or may diffuse into the cell walls directly (Burreau et al. 1997). Regardless of the mechanism, the movement of contaminants from the GI contents to the organism is, for the vast majority of contaminants of concern, a passive process.

The potential for bioaccumulation increases with increasing levels of hydrophobicity and slower elimination rates. Increasing hydrophobicity eventually results in diet being a much more important exposure route for heterotrophic aquatic organisms when compared with water (Thomann 1981). For phytoplankton, bioconcentration is the only mechanism of contaminant accumulation. In bioaccumulation studies, the hydrophobicity of OCs is most often evaluated using the log octanol–water partition coefficient (log K_{ow}). This coefficient measures how hydrophilic ("water loving") or hydrophobic ("water fearing") a chemical is using octanol as a surrogate for lipids (Finizio et al. 1997). Differences in K_{ow} between OCs are generally due to changes in water solubility; most OCs are highly octanol soluble, and hence highly lipid soluble, but differ substantially in their water solubility (Mackay et al. 2000). However, log K_{ow} and water solubility correlations are rarely 1:1 and can vary substantially among groups of contaminants (Schwarzenbach et al. 2003). Log K_{ow} also provides a fairly accurate quantitative prediction of bioconcentration; relationships between log K_{ow} and log bioconcentration factors (BCF; $[\text{organism}]_{\text{lipid}}/[\text{water}]$) for recalcitrant compounds are generally 1:1 (Mackay 1982; Fox et al. 1994; Finizio et al. 1997; Fig. 5.2a). Log K_{ow} values have also been used to evaluate other parameters such as biomagnifications factors (BMF = $[\text{predator}]_{\text{lipid}}/[\text{prey}]_{\text{lipid}}$) (Fisk et al. 1998, 2001) (Fig. 5.2b). The log K_{ow} of most OCs range from 3 to 8 (Mackay et al. 2000), and OCs with a value of ≥5 are accumulated almost completely via the diet (Thomann 1981).

Once an OC is assimilated by an organism, its fate, or bioaccumulation potential, is determined largely by a combination of its hydrophobicity and susceptibility to biotransformation. OCs can be eliminated either via diffusion, which is passive and controlled by the physico-chemical properties of the chemical, or via biotransformation by the organism, which is active and varies with the organism and environmental conditions (particularly temperature; Buckman et al. 2007). The more hydrophobic an OC is, the longer it is retained (i.e., longer half-life) and the greater its bioaccumulation (Fisk et al. 1998), but if the chemical is biotransformed it will be eliminated more quickly (i.e., short half life) and will have lower bioaccumulation (Fisk et al. 2000). However, the metabolite of the contaminant may itself bioaccumulate; sometimes to a greater extent than the parent compound (Konwick et al. 2006). These concepts are demonstrated by examining the bioaccumulation of PAHs and PCBs. Both of these contaminant groups have similarly high hydrophobicities (log K_{ow} range from 5 to 8) (Mackay et al. 2000). PCBs are highly bioaccumulated by fish because most congeners cannot be biotransformed (Kwon et al. 2006; Wong et al. 2004); however, PAHs do not achieve high concentrations in fish because they are readily biotransformed (D'Adamo et al. 1997). PAHs are also readily bioaccumulated

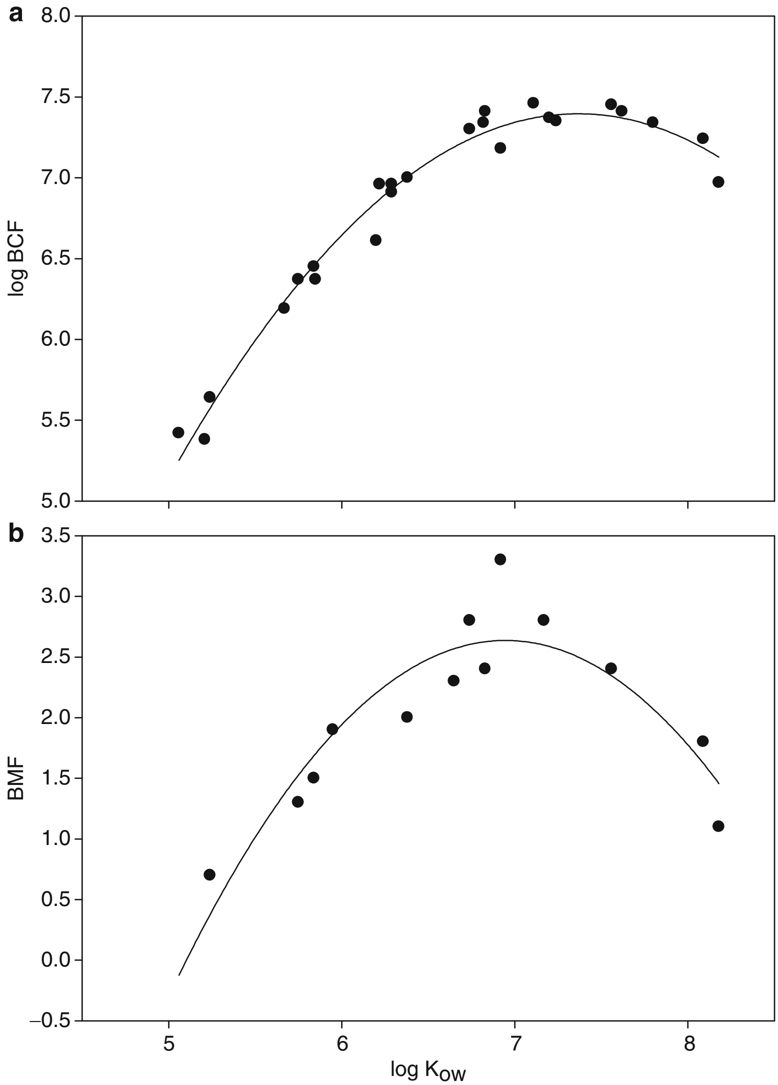

Fig. 5.2 Relationships between log K_{ow} and log BCF (**a**; log BCF = −14.5 + 5.9 * log K_{ow} – 0.4 log K_{ow}^2, $r^2 = 0.99$, $p < 0.0001$) and BMF (**b**; BMF = −34.8 + 10.0 * log K_{ow} – 0.8 log K_{ow}^2, $r^2 = 0.91$, $p < 0.001$) from laboratory studies. BCF data is from Fox et al. (1994) for zebrafish (*Brachydanio rerio*), BMF data from Fisk et al. (1998) for juvenile rainbow trout (*Oncorhyncus mykiss*) and K_{ow} from Hawker and Connel (1988)

by many classes of invertebrates, notably mussels, because they lack the enzymes that biotransform PAHs (D'Adamo et al. 1997). Note, although not accumulated, PAHs and their metabolites can, nonetheless, influence the health of fish (see e.g., Incardona et al. 2006).

Finally, if a chemical is sufficiently hydrophobic (log $K_{ow} > \sim 4$; Fisk et al. 2001) and recalcitrant (i.e., cannot be biotransformed), it will have a tendency to biomagnify through food webs. *Biomagnification* is the increase in chemical concentration with each trophic level transformation in the food web (Gobas and Morrison 2000), resulting in the highest concentrations in the upper trophic levels (Fisk et al. 2001). It should be stressed that even if a contaminant does not biomagnify, dietary exposure may still be the most important exposure route for aquatic organisms (Borgå et al. 2004).

5.2.2 Factors that Influence Organic Contaminant Bioaccumulation

A number of biological factors influence bioaccumulation and trophic transfer of OCs, and detailed reviews on this subject have been previously published (e.g., Borgå et al. 2004). These are briefly summarized here because many of these factors will also influence the trophic transfer of individual lipid compounds, although in different ways, and assessments of lipid and contaminant dynamics need to account for the fact that differences between food webs or organisms within the food webs may result in variation in contaminant and lipid behavior.

Most OCs of interest in aquatic food webs are highly lipid soluble, and water insoluble, and significantly influenced by the organism's lipid dynamics. In fact, comparative studies on OC levels in aquatic biota often account for the influence of lipids by either (a) lipid normalizing the concentration ([OC]/lipid content) (Thomann 1989), (b) using total lipid content as a covariate in statistical models (Hebert and Kennleyside 1995), or (c) using the residuals of the regression of OC levels on lipids for further analysis (Hebert and Kennleyside 1995, Hop et al. 2002). All of these approaches assume that the accumulation of OCs is linearly correlated with the organism's total lipid content, although in phytoplankton organic carbon can be used (see e.g., Swackhamer and Skoglund 1993). However, the types of lipids in the organism are rarely considered, even though this can influence contaminant uptake dynamics. For example, marine zooplankton store energy as dense wax esters in addition to triacylglycerols (Hagen and Auel 2001; Scott et al. 2002). In general, linear relationships between total lipid content and OC concentrations can be found within a population, although this can vary seasonally (Greenfield et al. 2005). Most parameters that quantify lipophilic OC bioaccumulation (e.g., BMFs) or trophic transfer (food web studies, see below) use lipid normalization to remove the influence of variable lipid contents (e.g., Fisk et al. 2001). This is particularly important in food web studies as total lipid concentrations can vary substantially between organisms at different trophic levels (Kidd et al. 1998).

For OCs that bioaccumulate and biomagnify, concentrations generally increase with body size and age in aquatic invertebrates and fish (Fisk et al. 2003; McIntyre and Beauchamp 2007). Age and size of fish are often highly correlated within a fish population (Johnston et al. 2002) but can often vary among populations, ecosystems, or temporally, even for the same species. The relationship between age or size and OC concentration will also vary with the contaminant. Very hydrophobic OCs (log $K_{ow} > 6$) are generally found to increase throughout a fish's life; that is, they may never achieve equilibrium between the fish and its environment (Paterson et al. 2006). Whereas, more moderately hydrophobic OCs (log $K_{ow} < 6$) may reach an equilibrium between fish and the environment and not increase in concentration once a specific age or size is reached (Paterson et al. 2006). Hidden within the age or size and OC relationships, but rarely acknowledged, is the influence of growth rate (*but see* Trudel and Rasmussen 2006, Paterson et al. 2006). The high growth rates commonly seen in the early spring and summer periods in temperate aquatic systems will generally decrease the observed OC concentrations per unit biomass (Paterson et al. 2006). During the late summer, autumn, and winter, when feeding decreases, growth rates decline or even stop and OC concentrations will increase because body mass decreases and slow OC elimination rates lag behind (Paterson et al. 2007).

Temperature and reproduction may also have an important influence on observed OC concentrations in aquatic organisms. As temperatures decrease, elimination rates of OCs in aquatic organisms decrease (Buckman et al. 2007). Decreasing temperature will also reduce feeding and growth rates, as discussed above, resulting in lower exposure to contaminants. Thus, contaminant dynamics can vary among systems that have different climatic regimes, such as tropical (Kidd et al. 2001) or arctic (Kidd et al. 1998). Reproduction by female aquatic organisms provides an opportunity to eliminate OCs through lipid rich eggs (Fisk and Johnston 1998), although the influence of this is much less important in fish (Johnston et al. 2002) than in mammals, where lactation provides an efficient means of eliminating lipophilic OCs (Fisk et al. 2001).

Another important factor that influences observed OC concentrations in aquatic organisms is trophic position (Rasmussen et al. 1990; McIntyre and Beauchamp 2007). Since many OCs biomagnify, higher trophic level organisms will have greater OC concentrations. The influence of trophic position is often more important than body size, age, or reproductive state (Borgå et al. 2004), although trophic position and body size are highly correlated in aquatic ecosystems.

5.2.3 Trophic Transfer of Elements/Metals

The bioaccumulation of elements/metals[1] by aquatic organisms is in several regards more complicated than OCs and involves the interaction of chemically, physically,

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[1] The term elements is considered more appropriate than the more commonly used terms metals or heavy metals because modern analytical methods provide data for a wide suite of elements, which include both metallic and non-metallic members (Duffus 2002).

and biologically mediated processes. Elements enter aquatic environments through both natural and anthropogenic sources, and human activity can result in high levels of elements in aquatic environments. Elements differ from most OCs in that they occur naturally in the environment and are classified as either essential (e.g., copper, zinc, manganese), because they are necessary to an organism for life, or nonessential (e.g., arsenic, cadmium, mercury), which may be present in an organism, but serve no known positive biological role. Essential elements are regulated by organisms to specific internal levels, although information on these ranges for most elements and aquatic organisms is limited. It has, however, been suggested that levels in a species should not vary widely among systems (McMeans et al. 2007). Nonessential elements can sometimes behave like essential elements if regulated through the same processes, but are generally assumed to be regulated less efficiently than essential elements (Kraemer et al. 2005) and can thus reflect local levels and vary spatially within the same species (McMeans et al. 2007).

Elements are accumulated by aquatic organisms from either the surrounding water or from food with the relative importance of these exposure routes varying amongst the different elements, and even the forms of the element. Elements can occur as ions (cations or anions) or as complexes (with inorganic ligands, chelates with organic ligands, or sorbed onto particle surfaces) with each different form referred to as an element species. The species of an element that is observed in an aquatic ecosystem will vary with the physio-chemical characteristics of that ecosystem (Gundersen et al. 2001), in particular pH and redox state, and thus element bioaccumulation can vary widely among ecosystems.

Most elements do not biomagnify (Newman 1998), and if differences in metal concentrations among animal species are accounted for, generally do not show patterns related to food web structure. For example, Cd and Ag concentrations in marine copepods were 3× higher than in ingestible (>0.2 μm), suspended particles, whereas Co and Se concentrations were 4× lower in copepods than in suspended particles (Fisher et al. 2000). In fact, many elements have been found to be *biodiluted*, i.e., decreased in concentration with increasing trophic level (Campbell et al. 2005a). This results in greater accumulation in lower trophic level organisms (e.g., some invertebrates) due to a combination of greater physiological need (essential elements), greater accumulation from water (surface-to-volume ratio) and/or poorer elimination capacity (Fig. 5.3). The exception is Hg, which has been widely shown to biomagnify in aquatic food webs (Kainz et al. 2006; Campbell et al. 2005a; Cabana and Rasmussen 1994) and can reach concentrations in some biota that warrant concern for both the wildlife and humans who consume them (Fisk et al. 2003) (Fig. 5.3). The biomagnification of Hg is driven by the species MeHg, which bonds with sulphur-containing amino acids. This differs from other OCs in that hydrophobicity and lipid content do not explain the behavior of MeHg in food webs. Cesium, zinc, thalium, and rubidium have also been shown, in some but not in all studies, to biomagnify (Campbell et al. 2005a,b; Dietz et al. 1996), although to a much lower extent than mercury.

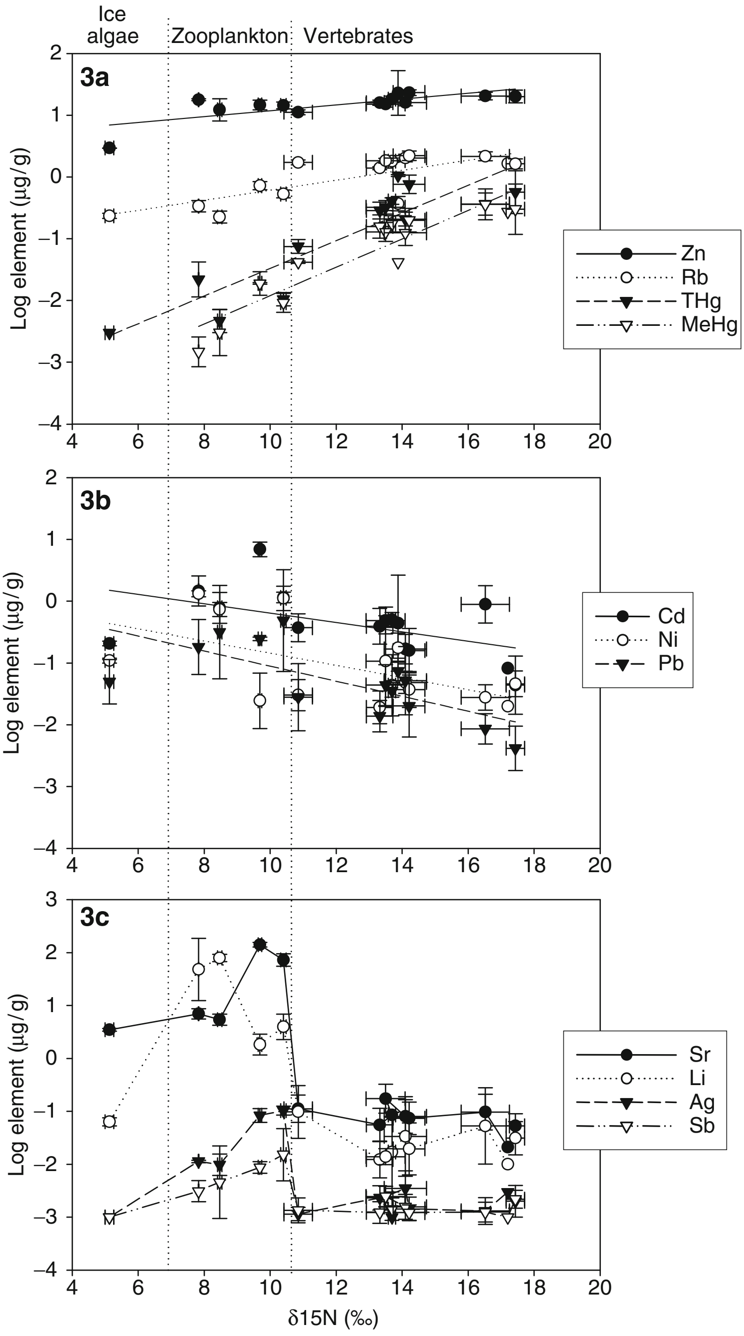

Fig. 5.3 Mean ± S.D. of log-transformed elements versus $\delta^{15}N$ and regressions of various metals versus $\delta^{15}N$ values of individual biota (from Campbell et al. 2005a). The vertical dotted lines indicate which data points represent ice algae, zooplankton and vertebrates (seabirds, fish and seals). Part (**a**) shows the metals that are biomagnifying through the food web with regression lines; (**b**) indicates the metals that are biodiluting through the food web with regression lines; while (**c**) indicates selected metals that are higher in zooplankton than in vertebrates by at least an order of magnitude

5.3 Trophic Transfer of Lipids

In addition to containing dietary energy for organisms at higher trophic levels, lipids provide structural (i.e., phospholipids and sterols) and storage (i.e., triacylglycerols and wax esters) functions, both of which are important when evaluating the ecological condition of food webs and ecotoxicological influence of contaminants on them. Although lipids are ecotoxicologically important for determining the extent to which lipophilic OCs are bioaccumulated in aquatic organisms (see above), there is physiological evidence that lipids, including PUFA and sterols (see Martin-Creuzberg and von Elert – Chap. 3), provide a nutritionally stabilizing function for aquatic organisms. However, the retention of dietary lipids is not driven directly, as the case with contaminants, by the biochemical properties of the lipids, but rather by the organism's specific lipid requirement and/or its ability to directly gain physiological benefits. For example, the cyanobacterium *Spirulina platensis* and the eukaryotic microalgae *Chlorella vulgaris* and *Botryococcus braunii* increase their relative content of unsaturated FA with decreasing temperature ("FA plasticity of algae"; e.g., Sushchik et al. 2003), indicating that algal thermoadaptation can directly affect the quality of FA transferred to consumers. When feeding on the eicosapentaenoic acid (20:5n-3; EPA)-containing marine diatom *Thalassiosira weissflogii* the copepod *Acartia tonsa* had 10× higher egg production rate than when feeding on the EPA-impoverished ciliate *Pleuronema* spp. (Ederington et al. 1995). Moreover, concentrations the n-6 PUFA arachidonic acid (20:4n-6; ARA) and the EPA increased 10.8× and 4.2×, respectively, from lacustrine seston to macrozooplankton (Kainz et al. 2004), which lends support to the argument that these PUFA are physiologically important for zooplankton.

However, not all "essential fatty acids" (see Parrish – Chap. 13) are retained similarly in aquatic organisms. For example, while docosahexaenoic acid (22:6n-3; DHA) is the most highly retained PUFA in most freshwater fish (Ahlgren et al. 1994), there is a significant difference in DHA concentration between copepods and cladocerans (e.g., Persson and Vrede 2006). Bioaccumulation patterns of essential fatty acid concentrations between macrozooplankton (>500 μm) and planktivorous rainbow trout (*Oncorhynchus mykiss*) showed that linoleic acid (LIN; 18:2n-6), α-linolenic acid (ALA; 18:3n-3), ARA, and EPA were 31%, 60%, 29%, and 65% lower, respectively, in dorsal muscle tissues of rainbow trout than in cladocera-dominated macrozooplankton prey (Kainz et al. 2006). Furthermore, while concentrations of bacteria-derived FA, including odd-numbered saturated and branched-chain FA (Kaneda 1991), increased 5.8× from seston to macrozooplankton (Kainz and Mazumder 2005), the ecological significance of such bacterial FA retention is still unclear. These divergent FA concentration patterns suggest that the transfer of nutritionally important lipids is dependent on the organism's physiological requirements as well as the taxonomic structure of aquatic food webs and displays conceptual differences to bioaccumulation patterns of contaminants. Such conceptual differences are explained by the organism's ability to selectively retain specific nutrients, but its inability to exert control over bioaccumulation of OC.

5.4 Concurrent Flow of Lipids and Contaminants

As detailed earlier, lipids and contaminants are accumulated by aquatic organisms and transfer through trophic levels. The major difference between contaminants, particularly OCs, and lipids, is that contaminants are passively bioaccumulated and concentrations are not regulated, whereas physiologically required lipids are selectively regulated. These differences have a direct bearing on the dynamics of lipophilic OCs and are of particular importance when examining the concurrent flow of lipids and weakly lipophilic contaminants. This is because the ecotoxicological fate of weakly lipophilic contaminants, such as MeHg, is not related to selective lipid metabolism in aquatic organisms, a feature that may result in higher bioaccumulation of some contaminants than lipids (Kainz et al. 2006). To increase our understanding of flow dynamics of lipids and contaminants and to subsequently evaluate the nutritional value of aquatic food web components, it is necessary to investigate concurrent pathways of dietary chemicals (nutrients and contaminants) in natural communities under realistic exposure conditions.

5.4.1 Lipids as Chemical Tracers in Ecotoxicology

When diet is the major conveyor of contaminants to aquatic consumers, ecotoxicologists often use tracers to indicate dietary sources of these contaminants. For example, stable isotopes of naturally occurring elements (Broman et al. 1992) and specific contaminants of concern (e.g., stable isotopes of Hg; Orihel et al. 2006) are applied to quantify bioaccumulation of contaminants to specific trophic levels within the aquatic food web. The application of stable isotopes, $\delta^{15}N$ as an indicator of consumer trophic position (Campbell et al. 2005a; Cabana and Rasmussen 1994) and $\delta^{13}C$ as an indicator of the dietary source (Campbell et al. 2000), in ecotoxicology is widespread (Borgå et al. 2004). As some essential fatty acids bioaccumulate along aquatic food webs, they have also been used as an index of MeHg bioaccumulation with increasing trophic position of zooplankton (Kainz et al. 2006). These authors found that MeHg concentrations were significantly correlated with ARA ($R^2 = 0.80$) and EPA concentrations ($R^2 = 0.65$). In a study on herring gull trophodynamics from sites across the Laurentian Great Lakes, Hebert et al. (2006) showed that egg EPA concentrations and n-3/n-6 FA ratios correlated significantly with egg $\delta^{15}N$ values (and contaminant levels; Hebert, pers. comm.) providing further information on how food web structure influences lipid dynamics in aquatic ecosystems.

Fatty acids are useful as source-specific biomarkers because it is often possible to quantify algal, bacteria, and allochthonous-derived FA compounds. Napolitano (1999) described PUFA in plankton as markers to assess algal-derived FA and odd-saturated and branched-chain FA as bacterial biomarkers. In zooplankton, it is assumed that most FA are largely dietary in origin and can thus be used as diet indicators (see Brett et al. – Chap. 6). Hence, Kainz et al. (2002) suggested that measuring the contributions of algal, bacterial, and allochthonous matter contributions to zooplankton diets by looking at group specific FA provides more detailed information on how the bioaccumulation of MeHg in zooplankton is related to the retention of specific diet sources. It was shown that MeHg concentrations in freshwater zooplankton were significantly ($p < 0.01$) associated with concentrations of bacterial ($R^2 = 0.50$) and, to a lesser degree, with algal ($R^2 = 0.35$) FA (Kainz and Mazumder 2005).

In an effort to shed more light on transport and chemical reactivity of PAH concentrations in a river estuary, Countway et al. (2003) found that PAH, except perylene, were correlated with allochthonous sterols (i.e., campesterol, stigmasterol, and β-sitosterol) during the fall/winter sampling and concluded that specific sterols play an important role in the fate and transport of PAHs. Correlations between the saturated long-chain lignoceric acid (24:0), used as allochthonous organic matter indicator (Sun and Wakeham 1994), and MeHg concentrations in zooplankton (Kainz et al. 2002) and lake sediments (Kainz et al. 2003) were not significantly associated, indicating that MeHg and this allochthonous organic matter indicator follow different uptake pathways. Although such source-specific FA biomarkers provide more detailed information than bulk organic matter analyses (e.g., total organic carbon concentrations, atomic C/N ratios, and $\delta^{13}C$), it is critical to know how such lipid compounds are retained and bioconverted in aquatic organisms when using them as biomarkers for ecotoxicological studies.

5.4.2 Implications for Aquatic Food Web Health

The biochemical composition and concentrations of lipids and contaminants largely determine the nutritional value of aquatic food organisms for their consumers. Most FA, PUFA in particular, in marine and freshwater systems are primarily of autochthonous origin, where primary producers at the base of the food web supply FA to organisms at higher trophic levels (see Gladyshev et al. – Chap. 8). Metals, however, can be taken up by algae from the ambient water and subsequently passed on to consumers. Because aquatic consumers can take up metals directly from the water (Pickhardt and Fisher 2007; Wang and Fisher 1998) as well as from their food, there are more entry routes for metals into consumers than for lipids. Although it has not yet been clearly demonstrated, metals, such as MeHg, may negatively affect pathways of lipid synthesis in algae. This could occur because MeHg accumulates in the cell cytoplasm of algae (Mason et al. 1996) where enzymes required for FA synthesis are located (Rangan and Smith 2004).

Algae play a central role in determining the health of aquatic food webs as they provide varying levels of both dietary nutrients and contaminants to upper trophic levels. Algal lipid composition varies among taxa (Guschina and Harwood – Chap. 1; Viso and Marty 1993; Volkman et al. 1998; Pereira et al. 2004) and with productivity of aquatic systems; Müller-Navarra et al. (2004) demonstrated that dietary supply of n-3 PUFA declined with increasing lake productivity (i.e., n-3 PUFA-poor cyanobacteria) at the plant–animal interface. Moreover, access to algal-derived FA may be constrained by food limitation (DeMott et al. 2001), taxa size-related FA composition, as well as by the presence of toxic algae (Jüttner 2005). Dietary lipid retention strongly depends on the physiological requirements of consumers for individual FA. For zooplankton, there is laboratory and field evidence that cladocerans are clearly impoverished in DHA (Persson and Vrede 2006), whereas copepods (Evjemo et al. 2003) and rotifers (Parrish et al. 2007) are generally DHA-enriched. The availability of dietary n-3 PUFA is important for the somatic growth of marine (Copeman et al. 2002), freshwater (Engstrom-Ost et al. 2005), and anadromous fish (Sargent et al. 1999), and DHA is the most highly retained PUFA in a variety of freshwater fish (Ahlgren et al. 1994). Therefore, the taxonomic composition of the lower aquatic food web clearly affects the dietary supply of FA to higher consumers.

Bioaccumulation patterns of metals are strongly determined by metal-specific predator–prey enrichment factors and appear to be independent of lipid bioaccumulation processes (see Sect. 5.2.3). Phytoplankton classes clearly differ in their ability to synthesize and retain various FA (Sushchik et al. 2003; Guschina and Harwood – Chap. 1), sterols and other lipids (Volkman et al. 1998), whereas Pickhardt and Fisher (2007) reported no appreciable differences of MeHg uptake by three eukaryotic algal groups. Differences in specific lipid synthesis but similar contaminant uptake patterns by different algae species have important implications for their consumers. This is evident for zooplankton taxa that differ in their ability to retain dietary FA (Persson and Vrede 2006), but do not differ in their ability to bioaccumulate contaminants such as MeHg (Kainz et al. 2006). Such discordant concentration patterns of essential nutrients and contaminants in zooplankton confirm that food web structure is functionally important for understanding the quantity and quality of lipids as well as contaminants flowing to organisms at higher trophic levels.

5.4.3 Lipid Composition and Contaminants

The ecotoxicological role of lipids in aquatic organisms is important, but the influence of lipids on hydrophilic and hydrophobic contaminants is different. As presented above, the term "lipophilic" is applied for chemicals with log K_{ow} values ≥5 (Borgå et al. 2004). The K_{ow} value is a measure of total lipid solubility and does not refer to any specific lipid class or compounds. Although the term lipid solubility in the contaminant literature is generally not related to specific lipid classes or compounds, the biochemical composition of lipids in aquatic organisms is, nonetheless, important for the bioaccumulation of lipophilic contaminants. For example, it has been reported that chlorobenzenes preferentially bind to storage lipids in African catfish (*Clarias gariepinus*; van Wezel and Opperhuizen 1995) and, total PCB concentrations in ribbed mussels (*Geukensia demissa*) correlated best with triacylglycerol concentrations (Bergen et al. 2001). Moreover, although it is still unclear whether PCBs at the concentrations found in aquatic ecosystems cause physiological damage to biota, phospholipids (structural lipids) in gonads and muscles of the eastern oyster (*Crassostrea virginica*) were shown to decrease following PCB exposure (Chu et al. 2003). Such findings show that bioaccumulation patterns of

Table 5.1 Ecological and ecotoxicological relevance of lipids and contaminants for aquatic food webs (with references where appropriate)

	Lipids	Contaminants
Source	Fatty acid synthesis	Geological
	SAFA – plants[a], animals[b]	Anthropogenic
	MUFA – plants[a], animals[b]	Biological (e.g., methylation)[c]
	PUFA – plants[a]	
Uptake	Dietary[d]	Dietary and via water[e]
Physiological relevance	Structural lipids[f]	Benign if concentrations are below toxicity threshold
	Support/enhance somatic growth[g–i]	
	Support/enhance reproduction[g]	Toxic if concentrations are above toxicity threshold, effects include:
	Storage lipids	Bind to lipid classes (PCBs – storage lipids[j])
		Reduce reproduction[k]
Bioaccumulation	Organism dependent[l]	Organism[m] (e.g., lipid content, size, age, etc.), trophic position[n] and environment dependent (e.g., temperature)[o]
Trophic status of aquatic ecosystem	Decreasing nutritional quality of fatty acids with eutrophication[p]	Decreasing bioaccumulation with eutrophication[q]

[a] Guschina and Harwood 2006;
[b] Tocher 2003;
[c] St. Louis et al. 2004;
[d] Brett et al. 2006;
[e] Wang and Fisher 1998;
[f] E.g., temperature adaptation, Dey et al. 1993;
[g] Martin-Creuzburg and von Elert 2004;
[h] Ravet et al. 2003;
[i] von Elert 2002;
[j] For ribbed mussels (*Geukensia demissa*): Bergen et al. 2001;
[k] Rohr and Crumrine 2005;
[l] Persson and Vrede 2006;
[m] Kainz et al. 2006;
[n] Cabana and Rasmussen 1994;
[o] Borgå et al. 2004;
[p] Müller-Navarra et al. 2004;
[q] For methyl mercury: Pickhardt et al. 2002

lipophilic OCs are linked to selective lipid class dynamics, but also indicate the scientific need to further identify how contaminants affect the production and bioconversion of essential lipids in aquatic organisms (Table 5.1).

5.5 Conclusions

Lipids play a major role in the accumulation of lipophilic contaminants in aquatic organisms. To further "eco"-toxicological understanding of lipids and contaminants in aquatic food webs, future research will need to investigate concurrent flows of contaminants and lipids, at concentrations relevant to aquatic ecosystems, and their effects on proper physiological functioning from cell to whole organism levels. Such approaches require detailed identification of the spatial positioning of contaminants and lipid compounds within cells, tissues, and organs. Because recent research has strongly advanced our knowledge on how some PUFA and sterols positively affect the physiological development of aquatic organisms (Martin-Creuzberg and von Elert – Chap. 3; Ahlgren et al. – Chap. 7), it is equally important to understand how the concurrent presence of contaminants affect aquatic organisms and eventually food webs.

From a management perspective, it is clear that the maintenance, protection, and where possible, improvement in the flow of essential lipids along aquatic food webs is desirable. It is also clear that management strategies should simultaneously strive to limit the bioaccumulation of contaminants. Integrating our knowledge of contaminant bioaccumulation and the beneficial effects of certain dietary lipids is necessary and promising; for example, increased dietary supply of PUFA, in particular EPA, as a clear somatic growth-enhancing nutrient for daphnids (Müller-Navarra et al. 2000, von Elert 2002), may result in lower dietary contaminant concentrations per unit biomass of zooplankton and possibly organisms at higher trophic levels. Such approaches, driven by diet quality rather than quantity, could alter our interpretation of the phenomenon of "growth dilution" of contaminants that has thus far been attributed to high algal biomass (Pickhardt et al. 2002). It is furthermore expected that increased dietary access to PUFA increases the health of aquatic ecosystems because organisms would be able to enhance their immuno-competency (see Arts and Kohler – Chap. 10). Ultimately, the goal is to identify, maintain, protect, and, where possible, improve those food web structures (including food–fish interactions in aquaculture) that provide an optimal supply of essential lipids with limited contamination to aquatic organisms and eventually humans.

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