



# Essential Biomolecules in Food Webs

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We here review the ecological role of essential nutritional biomolecules [fatty acids (FA), amino acids (AA), sterols, vitamins] in aquatic and terrestrial food webs, encompassing the forces behind their environmental distribution. Across ecosystems, mutualistic relationships frequently ensure exchanges of vitamins between producer and demander, especially between B<sub>12</sub> and other B vitamins as well as the AA methionine. In contrast, FA, sterols and most AA are transferred up the food chain via classical predator-prey interactions, and therefore have good biomarker potential for trophic interactions. As biomass-flow depends on the absolute amounts of potential limiting resources, considering solely the relative share in the respective biochemical group may under- or overestimate the availability to consumers. Moreover, if not accounted for, “hidden” trophic channels, such as gut symbionts as well as metabolic conversion of precursor molecules, can hamper food web analyses. Fundamental differences exist between aquatic and terrestrial ecosystems: Vitamin B<sub>12</sub> produced by ammonium oxidizing Archaea is essential to many aquatic algae, whereas terrestrial plants escaped this dependency by using B<sub>12</sub> independent enzymes. Long-chain ω<sub>3</sub> polyunsaturated FA (LC-ω<sub>3</sub>PUFA) in aquatic systems mainly originate from planktonic algae, while in terrestrial systems, belowground invertebrates can well be a source, also supporting aboveground biota. Interlinks from terrestrial to aquatic ecosystems are of a biochemically totally different nature than *vice versa*. While biomass rich in proteins and LC-ω<sub>3</sub>PUFA is transferred to land, e.g., by trophic relationships, the link from terrestrial to aquatic ecosystems provides recalcitrant plant carbon, mainly devoid of essential nutrients, fuelling detrital food chains. Recent global changes influence food webs via altered input and transfer of essential biomolecules, but separating the effects of nutrients, CO<sub>2</sub>, and warming is not trivial. Current evolutionary concepts (e.g., Black Queen, relaxed selection) considering the costs of metabolic production partly explain food web dynamics, especially for vitamins, whereas adaptations to potential oxidative stress seem to be more important for LC-PUFA. Overall, the provision with essential biomolecules is precious for both heterotrophs and auxotrophs. These nutritional valuable molecules often are kept unaltered in consumer metabolism, including their stable isotope composition, offering a great advantage for their use as trophic markers.

**Keywords:** food web, essential biomolecules, fatty acids, amino acids, sterols, vitamins, trophic transfer, environmental distribution

## INTRODUCTION

Despite the importance for trophic interactions and consumer fitness, a general comprehension of essential biomolecules structuring food webs and driving consumer adaptations is still lacking to date. For example, little is known about the environmental distribution of essential FA, AA, sterols and vitamins, and how ecosystem functions are constrained by their bioavailability. Essential biochemical resources can directly influence consumers' growth and reproduction, and in turn trophic relationships, including food intake or metabolic requirements. Thus, their availability can act as selection pressure on the evolution of consumer populations.

This paper conceptually summarizes current knowledge and potential implications of essential biomolecules on ecosystem dynamics, i.e., their biochemistry and functionality, their availability and transfer within food webs, and their use as trophic markers. A major focus is set on the forces behind environmental distributions, interlinks between ecosystems and alterations due to anthropogenic impacts. Further, evolutionary aspects in the provision of biomolecules and metabolic adaptations are highlighted.

## THE ROLE OF ESSENTIAL BIOMOLECULES IN THE FOOD WEB

### Fatty Acids

#### Biochemistry and Functionality

Among FA,  $\omega$ 3- and  $\omega$ 6PUFA are essential for many animals. Unlike plants and higher fungi, whose methyl-end desaturases introduce double bonds in  $C_{16}$ - and  $C_{18}$ FA at the  $\omega$ 3 and  $\omega$ 6 position, animal desaturases work toward the carboxyl-end beyond the  $\omega$ 6 position (Sprecher et al., 1995; Monroig and Kabeya, 2018). This results in characteristic " $\omega$  families," i.e.,  $\omega$ 3,  $\omega$ 6,  $\omega$ 9 (Figure 1). For animals the primary essential dietary derived PUFA of the  $\omega$ 6 family is linoleic acid (LA: 18:2 $\omega$ 6), and of the  $\omega$ 3 family  $\alpha$ -linolenic acid (ALA: 18:3 $\omega$ 3). LA and ALA are the precursors for the respective LC-PUFA, also called highly-unsaturated fatty acids (HUFA), obtained by chain elongation and further desaturation (Figure 1). Conversion rates among PUFA, especially from ALA to eicosapentaenoic acid (EPA: 20:5 $\omega$ 3) or docosahexaenoic acid (DHA: 22:6 $\omega$ 3), are low (Stanley-Samuelson et al., 1987; Bell and Tocher, 2009). For instance, only around 5% of ALA are converted to EPA in omnivorous vertebrates, including humans (Davis and Kris-Etherton, 2003). Dietary provision with EPA and DHA can directly enhance consumers' growth, health and fitness (e.g., humans—Hulbert et al., 2014; Nwachukwu et al., 2017; insectivorous birds—Twining et al., 2016; soil microarthropods—Menzel et al., 2018). Therefore, LC- $\omega$ 3PUFA are classified as semi-essential (Müller-Navarra, 1995a), and LC- $\omega$ 3PUFA supplementation, e.g., produced via metabolic engineering (Gong et al., 2014), is recommended for humans.

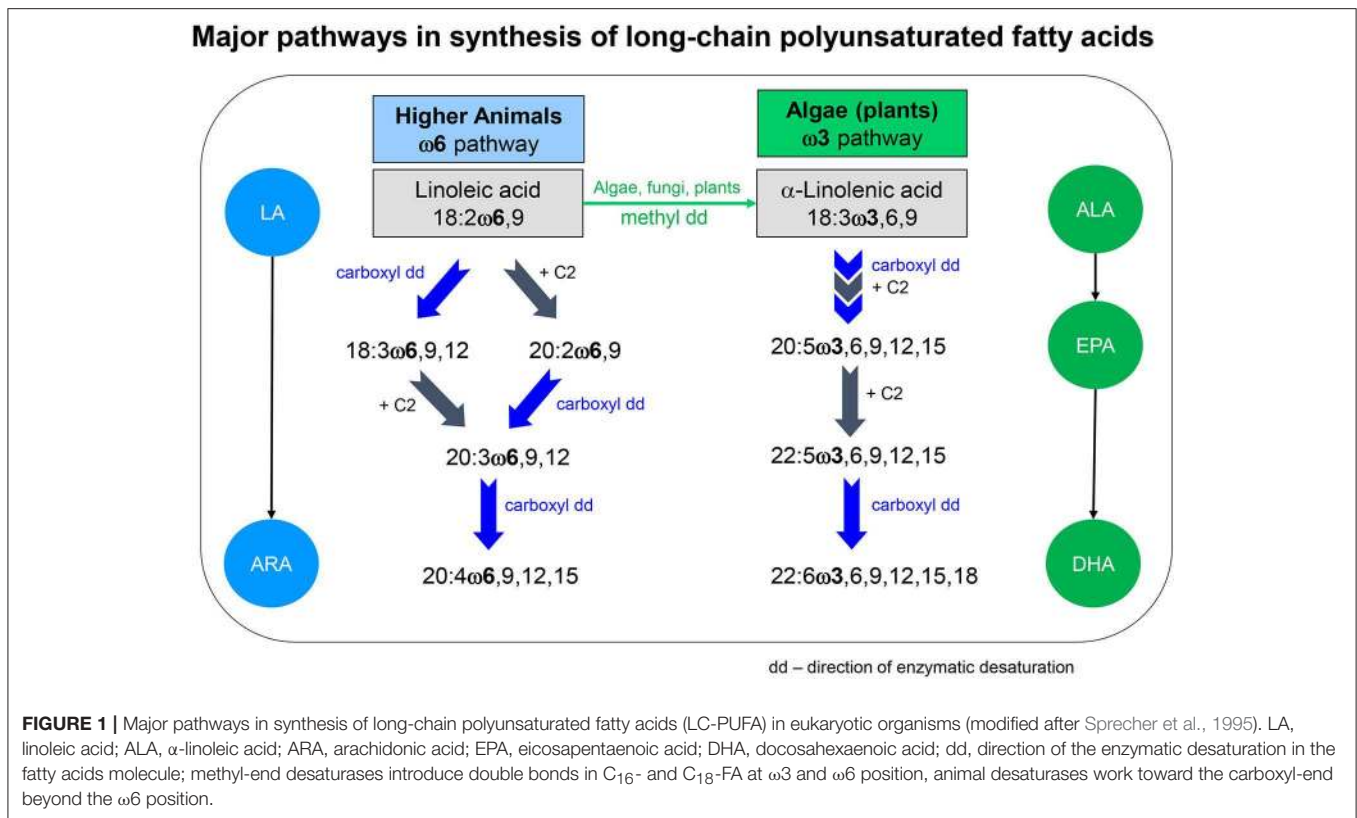
LC-PUFA have several key physiological functions in animals. They are an integral part of biological membranes and maintain their adequate viscosity and selective permeability (Vance and Vance, 2002). Further,  $\gamma$ -linolenic acid (GLA:

18:3 $\omega$ 6), arachidonic acid (ARA: 20:4 $\omega$ 6) and EPA serve as precursor for tissues hormones such as eicosanoids, which mediate inflammatory processes, immune response or cell growth (Stanley and Kim, 2019). Moreover, EPA and DHA are concentrated in nervous tissue, being the dominant FA of brain lipids (Wiktorowska-Owczarek et al., 2015). Differences in PUFA requirements exist depending on the consumer taxonomic affiliation, its ontogenetic stage and especially egg production (for zooplankton: Brett et al., 2009), which can affect trophic interactions (Müller-Navarra, 2008). Overall, the dietary LC-PUFA content is critical for growth, reproduction, and neural development for many aquatic and terrestrial invertebrates as well as vertebrates, including humans (e.g., Stanley-Samuelson et al., 1988; Parrish, 2009; Hulbert and Abbott, 2012).

### Main Producers

The main  $\omega$ 3- and  $\omega$ 6PUFA producer in aquatic systems are eukaryotic algae (Table 1). In particular, the synthesis of LC- $\omega$ 3PUFA in algae is tightly connected to photosynthesis, because they are part of the glycolipids in thylakoid membranes of chloroplasts (Guschina and Harwood, 2009). Similar to accessory pigments, LC-PUFA play a role in the light harvesting process. Systematic affiliation seems to be the strongest determinant of PUFA distribution in seston (Müller-Navarra et al., 2004), a finding also reported from cultures (Cobelas and Lechado, 1989; Ahlgren et al., 1992; Galloway and Winder, 2015; Taipale et al., 2016a). However, environmental factors including nutrients, temperature, salinity and light also directly affect the PUFA pattern of algae (Guschina and Harwood, 2009). While LC- $\omega$ 3PUFA compositions in algae based on relative proportions already assigns group specific pattern (Galloway and Winder, 2015; Peltomaa et al., 2017), differences based on absolute amounts are much more pronounced (data by Cobelas and Lechado, 1989; Ahlgren et al., 1992; Müller-Navarra, 1995b; Jónasdóttir, 2019) and important for the availability to consumers.

Due to their high absolute EPA content, diatoms are the greatest EPA supplier, both in most marine and freshwater (except dystrophic) systems, followed by chryptophytes, haptophytes, dinophytes and eustigmatophytes (Table 1). From their absolute DHA content, dinophytes are the main supplier, followed by haptophytes. However, certain diatoms as well as most dinophytes are too big to be ingested by most zooplankton. Moreover, heterotrophic stramenopiles (e.g., thraustochytrids) used in pharmaceutical DHA production (Gupta et al., 2012) may be a so far underestimated DHA provider. Heterotrophic eukaryotes can also contribute to sestonic EPA (e.g., ciliates—Bec et al., 2010; Hartwich et al., 2012), converting ALA mainly supplied by chlorophytes and cryptophytes to EPA, i.e., trophically up-grading sestonic food quality for zooplankton. Cyanobacteria generally do not contain LC-PUFA, although some taxa comprise  $C_{18}$ -PUFA (e.g., ALA) but at low absolute concentrations (Table 2). Prokaryotes are usually not a source of LC-PUFA, although they occur in bacteria in deep-sea isolates, which is probably an adaptation to low temperature and high pressure in the habitat (DeLong and Yayanos, 1986). Macro-algal chlorophytes display a FA



pattern similar to their micro-algal counterpart, while marine rhodophytes have an especially high share of EPA (but none or low DHA) and phaeophytes comprise intermediate levels of LC-PUFA (Fleurence et al., 1994; Pereira et al., 2012).

Vascular plants are considered as the major source for PUFA in terrestrial food webs and predominantly contain  $C_{18}$ -PUFA, i.e., ALA and LA. Herbivores such as ruminants can acquire LC- $\omega 3$ PUFA via ciliates as gut symbionts (Veira, 1986; Newbold et al., 2015), which may be able to convert ALA to EPA, like certain ciliates in aquatic systems. Primary producers in biological soil crusts (green algae and cyanobacteria) synthesize ALA, with green algae additionally comprising the PUFA  $16:3\omega 3$  as a potential precursor (Buse et al., 2013; **Table 2**). However, the role of biological soil crusts as  $\omega 3$ PUFA supply for terrestrial food webs has not been explored yet. Among heterotrophs higher fungal taxa commonly synthesize ALA (Ruess and Chamberlain, 2010), moreover lower soil fungi can supply LC- $\omega 3$ PUFA, predominantly Chytridiomycetes and Oomycetes (Lösel, 1988), and arbuscular mycorrhiza fungi (Gladyshev et al., 2013). Further, there is evidence that many soil invertebrates provide LC- $\omega 3$ PUFA (see **Figure 3**, and chapter  $\omega 3$ PUFAs—aquatic vs. terrestrial food webs).

### Trophic Transfer and Biomarkers

The importance of EPA and DHA for food quality affects biomass trophic transfer in aquatic ecosystems (Müller-Navarra, 1995a; Brett and Müller-Navarra, 1997; Müller-Navarra et al., 2000). PUFA itself can be as twice as efficiently transferred from the first

to the second trophic level compared to bulk carbon (Gladyshev et al., 2011; Mayor et al., 2011). LC- $\omega 3$ PUFA are particularly retained and accumulated in consumer lipids of aquatic food webs (Strandberg et al., 2015; Guo et al., 2016), which is also a central issue in aquaculture (e.g., Navarro et al., 2014). Generally, fatty acids from the diet can be incorporated into consumer body tissue without major modification, a fact called “dietary routing” (Stott et al., 1997). Based on this,  $\omega 3$ PUFA were used as qualitative markers for trophic interactions in freshwater plankton (Desvillettes et al., 1997), and semi-quantitatively in food webs in marine pelagial (Dalsgaard et al., 2003) and benthos (Kelly and Scheibling, 2012). By applying metabolic conversion factors, dietary routing was traced quantitatively (Iverson et al., 2004) in vertebrates connected to the marine food chain, e.g., for arctic mammals (polar bears—Thiemann et al., 2008) or sea birds (Williams and Buck, 2010). Further, Galloway et al. (2015) employed a Bayesian approach (FA source-tracking algorithm) comparable to the use of stable isotopes in food web ecology. This wide application of lipids as trophic markers in aquatic habitats has benefitted from the frequent occurrence of  $\omega 3$ PUFA in primary producers at the food web base.

In contrast, the use of FA biomarker in terrestrial food webs has lagged behind. First trophic transfer of fatty acids was assigned in detrital food chains in soils from bacteria and fungi to microbial grazers (nematodes—Ruess et al., 2002; Collembola—Haubert et al., 2006) and further up to omnivores and predators (Collembola—Ruess et al., 2004; spiders—Pollierer et al., 2010). Opposite to aquatic ecosystems, this was based on the dietary

**TABLE 1** | Essential biomolecules within the groups of fatty acids, sterols, vitamins, and amino acids.

Molecule	Habitat	Main producer	Predominantly affected consumers	Biomarker potential	Limitation (When and where?)	Reference
$\omega$ 3 poly-unsaturated fatty acids	Aquatic	EPA <sup>1</sup> : diatoms, cryptophytes, dinophytes, haptophytes, eustigmatophytes DHA <sup>1</sup> : dinoflagellates, haptophytes, cryptophytes ALA: green algae, cryptophytes	Herbivores (zooplankton), fish (esp. juveniles)	+	(hyper)eutrophic systems; summer	Cobelas and Lechado, 1989; Ahlgren et al., 1992; Müller-Navarra et al., 2004; Galloway and Winder, 2015; Jónasdóttir, 2019
	Terrestrial	Algae, higher plants (ALA as precursor for EPA and DHA)	Herbivores (plant feeders)	+ (16:3 $\omega$ 3; 18:3 $\omega$ 3)	Continuously	Ruess and Chamberlain, 2010; Buse et al., 2013
Sterols	Aquatic	Eukaryotic algae (phytosterols), fungi, vertebrates (cholesterol)	Arthropods, other invertebrates	$\pm$ /+ (e.g., dinosterol, gorgosterol, oxysterols)	Cyanobacterial bloom conditions	Goad, 1981; Von Elert et al., 2003; Krauss et al., 2011; Santos et al., 2015
	Terrestrial	Fungi (ergosterol, sitosterol), vertebrates (cholesterol), plants (phytosterols)	Arthropods	+ (ergosterol)	Some pollen feeding insects	Burden et al., 1989; Pilorget et al., 2010; Vučić and Cvetkovi, 2015; Moreau et al., 2018
Vitamin B <sub>1</sub> (Thiamin)	Aquatic	(cyano)bacteria, algae (78% are B <sub>1</sub> autotrophs)	Animals, auxotrophic algae	-	Unknown (connection to other B-vitamins)	Provasoli and Carlucci, 1974; Croft et al., 2006
	Terrestrial	Bacteria, plants	Herbivores, grannivores, frugivores, fungi	-	Plant dormancy, ectomycorrhizal fungi without plant host	Grayston et al., 1996; Roje, 2007; Aseni-Fabado and Munné-Bosch, 2010; Vranova et al., 2013
Vitamin B <sub>7/8</sub> (Biotin)	Aquatic	Certain bacteria, algae (95% are biotin autotrophs)	Animals	-	Unknown (connection to other B-vitamins)	Croft et al., 2006
	Terrestrial	Plants	Herbivores, grannivores, frugivores, fungi	-	Plant dormancy, ectomycorrhiza fungi without plant host	Grayston et al., 1996; Roje, 2007; Aseni-Fabado and Munné-Bosch, 2010; Vranova et al., 2013
Vitamin B <sub>9</sub> (Folates)	Terrestrial	Plants, soil bacteria (streptomycetes), endosymbionts of invertebrates	Herbivores, grannivores, frugivores, fungi	-	Plant dormancy, ectomycorrhiza fungi without plant host	Baya et al., 1981; Roje, 2007; Taylor et al., 2012; Hunter et al., 2015
Vitamin B <sub>12</sub> (Cobalamin)	Aquatic	Thaumarchaeota (cobalamin), cyanobacteria (pseudo-cobalamin)	Auxotrophic algae, animals, fungi	+ (as gene transcripts)	Summer/fall, coastal/high nitrogen low chlorophyll areas	Croft et al., 2006; Doxey et al., 2015; Helliwell et al., 2016
	Terrestrial	Gut symbionts, soil bacteria, certain green algae, higher plants	Animals		Cobalt deficient soils	Croft et al., 2006; Roje, 2007; McCutcheon et al., 2009; Taylor et al., 2012
"Source" amino acids	Aquatic	Bacteria, algae	Animals	+ (combined with stable isotopes)	Allochthon/detrital impacted systems (protein limitation)	Bleakley and Hayes, 2017; Choi et al., 2017
	Terrestrial	Higher plants, bacteria, gut symbionts	Animals	+ (combined with stable isotopes)	Detrital systems (protein limitation), nematophagous fungi (N limitation)	Steffan et al., 2015; Larsen et al., 2016; McMahon and McCarthy, 2016; Takizawa et al., 2017

Given are molecules with known ecological impact in aquatic and terrestrial food webs. ALA,  $\alpha$ -linolenic acid; EPA, eicosapentaenoic acid; DHA, docosahexaenoic acid.

<sup>1</sup>For the specific differences between freshwater and marine ecosystems see section "main producers" in the text.

routing of non-essential FAs, e.g., methyl-branched and cyclic forms derived from bacteria (Ruess and Chamberlain, 2010). The achievement of comparable results in the herbivore food chain was hindered by the lack of LC- $\omega$ 3PUFA in terrestrial

primary producers, resulting in ALA as major biomarker for plant feeding (Ruess and Chamberlain, 2010) and C<sub>16</sub>- $\omega$ 3PUFA for algal feeding (Buse et al., 2013). However, this drawback of lower diversity in FA markers can be overcome by applying stable



**TABLE 2** | Proportion of polyunsaturated fatty acids (PUFA in % of total fatty acids) in the neutral lipids of photoautotrophic microbiota dominant in terrestrial soil crusts.

PUFA	<i>Chlorella vulgaris</i>	<i>Klebsormidium flaccidum</i>	<i>Nostoc commune</i>	<i>Saccharomyces cerevisiae</i>	ANOVA	
					F <sub>(3,8)</sub>	P
16:2 ω6,9	6.9a	8.9b	0.4c	-c	260	<0.001
16:3 ω3,6,9	19.4a	16.4b	-c	-c	1519	<0.001
18:2 ω6,9	11.2a	27.5b	6.3c	0.2d	1964	<0.001
18:3 ω3,6,9	36.7a	22.0b	36.4a	0.3c	541	<0.001
18:3 ω6,9,12	0.2a	1.1b	1.0b	-a	23	<0.001
Total fat in mmol g <sup>-1</sup> (fresh weight)	22.1a	10.9b	3.4c	4.3c	121	<0.001

Compared are the green algae *Chlorella vulgaris* and *Klebsormidium flaccidum*, and the cyanobacterium *Nostoc commune* to the common yeast *Saccharomyces cerevisiae*. Given are ANOVA F and P values; data within a row with the same letters are not significantly different according to Tukey HSD (P < 0.05). Modified after Buse et al. (2013); -, not detected.

isotope fingerprints, tracing FA dietary routing via their δ<sup>13</sup>C signal. Here, main approaches are <sup>13</sup>CO<sub>2</sub> pulse-labeling of plants (Pausch et al., 2016) or using natural differences in <sup>13</sup>/<sup>12</sup>C ratios of C3 and C4 plants (Haubert et al., 2009; Ngosong et al., 2011) (Figure 2). However, a broader application of FA in food web ecology of vertebrates, as common in marine systems, is still lacking, except of the usage of FA markers in food chemistry (Molketin and Giesemann, 2007). For an overview on trophic transfer and biomarkers in terrestrial systems see reviews of Ruess and Chamberlain (2010) and Traugott et al. (2013).

## Sterols

### Biochemistry and Functionality

Sterols are an important lipophilic part of cell membranes in eukaryotic organisms, embedded within the membrane phospholipids. Moreover, they are frequently esterified to membrane LC-PUFA. The central sterol synthesized in animals is cholesterol, a C<sub>27</sub> sterol. However, not all animals are capable of *de novo* sterol synthesis. For example, arthropods lack this ability (Goad, 1981; Martin-Creuzburg and von Elert, 2009), and many insects and crustaceans prefer Δ<sup>5</sup> and Δ<sup>5,7</sup> over Δ<sup>7</sup> and Δ<sup>22</sup> sterols (e.g., Teshima, 1971; Behmer and Nes, 2003). Known from herbivorous insects and crustaceans, dietary phytosterols are typically altered by de-alkylation and saturation, e.g., of C<sub>24</sub> methyl and ethyl sterols, to form cholesterol (Svoboda and Thompson, 1985). Despite this, sterol limitation was shown for crustaceans feeding on laboratory cultures of heterotrophic and autotrophic bacteria (e.g. Martin-Creuzburg et al., 2011 for *Daphnia*) or diatoms (Hassett, 2004 for *Acartia*, *Calanus*). However, interacting effects of sterols with the provision of EPA (Martin-Creuzburg et al., 2009 for *Daphnia*) or AA (Wacker and Martin-Creuzburg, 2012 for a rotifer) were also demonstrated. Nevertheless, a minor part of sterols (less than 1%) is required as precursor for molting hormones in arthropods (e.g., ecdysteroids; Svoboda and Thompson, 1985).

In vertebrates, 7-dehydrocholesterol is converted to cholecalciferol (vitamin D<sub>3</sub>) under UV irradiation and functions as steroid hormone in the Ca-metabolism, with special importance for skeleton structures, e.g., in humans (DeLuca, 1998). Except for hormone production, sterol requirements

of many organisms seem not to be specific. Additionally, the metabolic modification of dietary sterols widens sources for organisms with a low or lost ability of *de novo* synthesis.

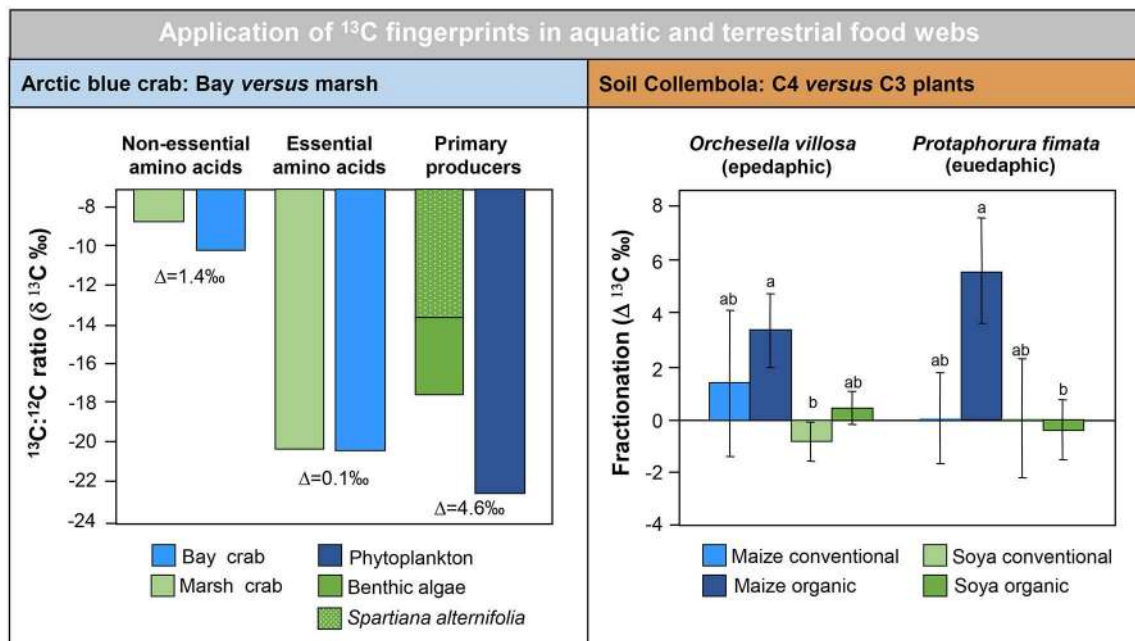
### Main Producers

In planktonic food webs, eukaryotic macro- and micro-algae are very variable sources of over 250 different sterols (mainly C<sub>28</sub> phytosterols) (Santos et al., 2015) (Table 1). However, their distribution within an algal class is not as uniform as for PUFA (e.g., Volkman, 1986, Martin-Creuzburg and Merkel, 2016; Taipale et al., 2016a). Prokaryotic planctomycetes and poribacteria have the genetic infrastructure for sterol synthesis (Pearson et al., 2003) but their role in dietary sterol supply is unknown. Eukaryotic fungi are potentially an important resource in aquatic ecosystems, especially in streams (Krauss et al., 2011). The same applies to chytrids, ubiquitous fungal parasites in aquatic ecosystems, providing a sterol source to their grazers even in absence of their phytoplankton hosts (Gerphagnon et al., 2019). Cyanobacteria as prokaryotes do not produce sterols at all (Volkman, 2003).

In terrestrial ecosystems, higher plants deliver mainly C<sub>28</sub> and C<sub>29</sub> sterols (Moreau et al., 2018) e.g., by leaves, fruits, roots and bulbs to herbivores, both in above- and belowground food webs (Table 1). Fungi are also frequent sterol producers in soil systems (Burden et al., 1989), contributing ergosterol as a major component of their cell membranes (Joergensen and Wichern, 2008). If and how these fungal sterols can act as a nutrition source for soil animals has yet to be explored. Finally, symbiotic fungi in the gut may provide a substantial part of sterols to their insect host (reviewed by Douglas, 2009).

### Trophic Transfer and Biomarkers

Phytosterols are metabolically converted by several herbivorous consumers to suit specific physiological requirements, hampering their trophic biomarker usage. Above, many animals—especially vertebrates—are capable of *de novo* sterol synthesis, which makes sterol limitation further up the food chain unlikely, especially in the 3RD and 4TH trophic level of both, aquatic and terrestrial food webs. However, a comprehensive understanding is still lacking.



**FIGURE 2 |** Carbon stable isotope fingerprinting in aquatic and terrestrial food webs based on differences in  $\delta^{13}\text{C}$  of primary producers. Left— $\delta^{13}\text{C}$  content in bulk tissue of major resources and in non-essential and essential amino acids of Atlantic blue crabs (*Callinectes sapidus*) in bay and marsh habitats (data from Fantle et al., 1999). The difference in  $\delta^{13}\text{C}$  between primary producers or amino acid fractions is expressed as  $\Delta^{13}\text{C}$ . Right—fractionation ( $\Delta^{13}\text{C}$ ) in linoleic acid (18:2 $\omega$ 6,9) between Collembola (*Orchesella villosa*, *Protaphorura fimata*) and soil fungi in a C3 (soya) and C4 (maize) arable system with different farming practice (data from Haubert et al., 2009). No fractionation indicates dietary routing of linoleic acid and hence fungal-feeding. Values with the same letters are not significantly different according to Tukey HSD ( $P < 0.05$ ).

Metabolic sterol processing was reported, e.g., for heterotrophic protists feeding on macro-algae (Chu et al., 2009), soil nematodes feeding on plant roots (Chitwood and Lusby, 1991; Chitwood, 1999), millipedes feeding on terrestrial plant litter (Rawlins et al., 2006), and crustaceans feeding on phytoplankton (Martin-Creuzburg and Merkel, 2016 for *Daphnia*). Additionally, biochemical sterol modulation generally occurs in herbivore insects (Svoboda and Thompson, 1985). However, the suitability of phytosterols may differ (Martin-Creuzburg et al., 2014 for *Daphnia*; Gergs et al., 2015 for gammarids), and not all zooplankton consumers do convert those (Wacker and Martin-Creuzburg, 2012 for rotifers). Although the less group-specific occurrence of phytosterols in algae and their conversion in many herbivores are hampering their sole application as trophic markers in pelagic food webs, sterols together with FA as markers seem promising to track food intake, as shown for dwelling ophiurids and holothurians in a deep-sea environment (Drazen et al., 2008). In general, sterols are widely used as biomarkers in sediments due to their chemical persistence, e.g., separating allochthonous and autochthonous produced biomass (Bianchi and Canuel, 2011).

## Vitamins

### Biochemistry and Functionality

Vitamins are a diverse class of rather complex compounds, and from the two major groups only the most important in food web ecology are considered here:

### Lipid soluble vitamins (A, D, E)

Vitamin A is essential for animals and primarily needed for vision. Carotenoids (provitamin A) are synthesised in chloro- and chromoplasts of photoautotrophic organisms as photoprotecting agent (Saini et al., 2015; Huang et al., 2017). Vitamin E is an anti-oxidant protecting susceptible LC-PUFA, and requirements in animals are connected to PUFA provision (Zhang et al., 2017). This protective function may also be related to the transition from parthenogenetic to sexual reproduction, male fertility (spermatogenesis) and enhanced growth of the mictic offspring as shown for the rotifer *Asplanchna* by Gilbert (1980). Vitamin D is a derivative from cholesterol and considered in the chapter on sterols above.

### Water soluble vitamins (B-group)

$\text{B}_1$  (thiamin) is a cofactor of several core enzymes, e.g., in the transfer of  $\text{C}_2$ -groups (dehydrogenases, decarboxylases) in the carbohydrate metabolism. Requirements of external  $\text{B}_1$  are mostly due to the lack of either synthesis of the pyrimidine or the thiazole moiety in algae (Lewin, 1961). If capable of biosynthesis, thiamin is only produced on demand via riboswitches, both in prokaryotes and eukaryotes (McRose et al., 2014), making the process very efficient. Physiological interconnections exist with other vitamins, e.g., folic acid ( $\text{B}_9$ ) deficiency influences  $\text{B}_1$  adsorption and metabolism (Wolak et al., 2017). Further, supply in  $\text{B}_1$  can alter the FA pattern towards EPA and DHA, e.g., in the algae *Rhodomonas baltica* (Chi et al., 2018).

B<sub>7</sub> (biotin) requirements are known for some crysophytes, dinophytes, and euglenoid algae (Provasoli and Carlucci, 1974). Folic acid (B<sub>9</sub>) is synthesized by plants, including algae (Baker et al., 1981), but is essential to animals as a cofactor of thymidyl-synthase, catalyzing nucleotide syntheses, which governs DNA repair and replication.

B<sub>12</sub> (cobalamin) is a cofactor in enzymes carrying activated methyl groups or providing carbon-based free radicals for reactions removing non-acid hydrogen atoms (Marsh, 1999). It is involved in the synthesis of AA and DNA, and in shuffling C<sub>1</sub>-groups into the citrate circle. Two synthesis pathways exist, i.e., the more ancient anaerobic pathway of bacteria and Archaea leading to cobalamin, and the aerobic pathway of cyanobacteria resulting in pseudo-cobalamin (Raux et al., 1999). Cobalamin cannot be synthesized by most eukaryotes, including animals (Gräsbeck and Salonen, 1976). Overcoming potential limitations due to B<sub>12</sub> auxotrophy seems to be governed by a non-cobalamin methionine synthase in higher plants and certain algal taxa (Croft et al., 2006). Moreover, B<sub>1</sub> deficiency syndromes in fish (Marcquenski and Brown, 1997) and sea birds (Balk et al., 2009) may be coupled to B<sub>12</sub> shortage in resources. Overall, the metabolic pathways of B<sub>1</sub>, B<sub>9</sub>, B<sub>12</sub> and the AA methionine are interwoven, and also relevant on the ecological level by impacting nitrogen (N) and sulfur metabolism of eukaryotic phytoplankton (Bertrand and Allen, 2012). This makes it difficult to determine the vitamin that is the most limiting (**Table 1**).

## Main Producers

### Lipid soluble vitamins

The syntheses of the lipophilic vitamins A and E are tightly connected to the metabolic capacity of algae in aquatic (Huang et al., 2017) and of plants in terrestrial (Saini et al., 2015) ecosystems. In marine and freshwater, microalgae as well as makrophytes represent the dominant source (Cuvelier et al., 2003; Huang et al., 2017) (**Table 1**). Pro-vitamin A dominates in leaves and fruits, whereas seeds comprise the highest amounts of vitamin E, and leaves of vitamin K (Aseni-Fabado and Munné-Bosch, 2010). Fungi and yeast are major producer of ergosterol, the precursor of ergocalciferol (i.e., pro-vitamin D<sub>2</sub>), but UVB exposure is necessary for conversion, restricting the supply to aboveground habitats. Traditionally higher plants were thought to contain only negligible amounts of D<sub>3</sub> but recent work raises evidence for a broader distribution (Jäpelt and Jakobsen, 2013). Whether these contents are sufficient to subsidize decomposer food webs in lightless soil habitats remains to be explored.

### Water soluble vitamins

In aquatic systems, red and green algae are a good source of B vitamins, especially B<sub>1</sub>, and B<sub>9</sub> (Croft et al., 2006) (**Table 1**). In contrast, main B<sub>12</sub> producer seem to be ammonium oxidizing thaumarchaeota, primarily under cold conditions, i.e., at greater depth, during winter and in polar-regions (Doxey et al., 2015). Interestingly, most algae—especially those groups known to provide LC- $\omega$ 3PUFA to food webs—are only minor vitamin B suppliers, as many of them are auxotroph in respect to B<sub>1</sub> (20%), B<sub>7</sub> (5%) and especially B<sub>12</sub> (50%) (Provasoli and Carlucci, 1974; Croft et al., 2006). Although cyanobacteria are rich in B<sub>1</sub>, they are

an inefficient source of B<sub>12</sub> as they only contain the nutritionally inferior pseudo-cobalamin (Helliwell et al., 2016).

In terrestrial systems, higher plants are the major producers of B-vitamins (Roje, 2007), delivering these water-soluble vitamins via root exudation into the rhizosphere and additionally supporting their mycorrhiza symbionts (Grayston et al., 1996) (**Table 1**). The second important vitamin B sources are soil bacteria, with phosphate-solubilising taxa azotobacters and rhizobia as significant producers (Vranova et al., 2013). The cumulative vitamin production by bacteria in the rhizosphere enhances general bioavailability and complements root exudates (Baya et al., 1981), likely important for the associated fungi and fauna.

## Trophic Transfer and Biomarkers

Lipophilic vitamins synthesized by algae or vascular plants are generally transferred to heterotrophic consumers via predator-prey interactions. In contrast, syntrophic relationships with microbes seem to be important to overcome certain vitamin B limitations, as shown for marine algae co-cultured with bacteria (Paerl et al., 2015). Beneficial microbe-algae (Croft et al., 2005) and algae-algae interactions (Carlucci and Bowes, 1970; Baker et al., 1981) seem rather to be the rule than the exception. However, their role in overcoming B<sub>12</sub> limitation sustaining global primary production is debated (e.g., Droop, 2007). In nature, B<sub>12</sub> is acquired from soluble surroundings with specific transporters by B<sub>12</sub> auxotrophic algal cells (Bertrand and Allen, 2012), ensuring rapid uptake. For food webs of marine pelagic systems there is evidence that B<sub>1</sub> is not accumulated but rather diluted from phytoplankton to zooplankton to fish (Sylvander et al., 2013).

In aquatic ecosystems, B<sub>12</sub> provision by endosymbionts is known for certain ciliates (Baker et al., 1981). More recently, Fiore et al. (2015) showed symbiotic interactions with Archaea and bacteria to be crucial for the Caribbean giant barrel sponge (*Xestospongia muta*) in obtaining B-vitamins and essential AA. So far, mutualistic relationships of sponges or corals are rather viewed in the light of carbon acquisition but should also be connected to the acquisition of essential biomolecules. In contrast to aquatic ecosystems, the importance of gut symbionts as suppliers of vitamins to their terrestrial vertebrate and invertebrate hosts has been recognized for a long time, especially for bacteria or ciliates as endosymbionts in social insects such as wood feeding termites or insects that suck on plant sap, which is poor in vitamins (Moran et al., 2003; McCutcheon et al., 2009). B<sub>2</sub> is provided by gut bacteria to earthworms (Sulik et al., 2012) or by the mutualistic *Wolbachia* bacteria to nematodes (Taylor et al., 2012). Moreover, the intestinal flora plays a major role in the provision with B<sub>7</sub>, as shown for humans (Magnúsdóttir et al., 2015). Overall, the provision with B vitamins by mutualistic prokaryotes in invertebrates and vertebrates as “hidden” trophic interactions complicates determination of their trophic transfer in food web studies.

## Amino Acids

### Biochemistry and Functionality

AA are the structural elements of enzymes, regulating key metabolic pathways important for health, survival and growth, e.g., neurological and immunological functions (Wu, 2010). Traditionally, AA are classified as non-essential (dispensable) and essential (indispensable). The former can be *de novo* synthesized by the consumer, whereas the latter must be provided with the diet. Nine AA have been assigned as essential in humans and other vertebrates, i.e., isoleucine, histidine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine (Young, 1994), yet requirements vary between taxonomic entities. In addition, arginine is essential for terrestrial carnivores (Morris, 1985). A third category is named conditionally indispensable or “functional” AA, which are semi-essential as synthesis rates in certain taxa are limiting (Wu, 2010). A relevant example is arginine in many mammals (Wu et al., 2013). The metabolic flexibility in consumers, such as compensatory mechanisms can affect AA limitation. Only recently, the upregulation of AA retention efficiency as a response to nitrogen deficiency was shown in copepods (Burian et al., 2018). In conclusion, we are still at the start of understanding which AA are essential in different animal groups, and what implication this dependency has for food web ecology.

### Main Producers

In aquatic food webs, phytoplankton, particularly protein-rich algae (above 50% dry weight - Bleakley and Hayes, 2017) are a main source for AA (Table 1). Aquatic macrophytes, in contrast, display a much lower protein (Rather and Nazir, 2015) and consequently AA content, due to more structural components (cellulose, hemicellulose, lignin). Terrestrial plants, their leaves, flowers and fruits provide AA to herbivores in terrestrial food webs (Takizawa et al., 2017). However, AA levels are typically low and supply often needs to be enriched via mutualistic interactions with gut microbiota in herbivores (Cantalapiedra-Hijar et al., 2016 for lambs). Microbial derived proteins further represent an important resource for essential AA in detritivore food webs as shown by Steffan et al. (2017) analyzing invertebrates (moths, beetles) and vertebrates (fish). Degradation of plant litter by bacteria and fungi provide AA for detritivores (Larsen et al., 2009). Protein is hydrolysed via extracellular enzymes, followed by adsorption of free AA from the soil solution (Czmicik et al., 2005). Particularly bacteria, which can acquire AA by both, *de novo* synthesis using inorganic nitrogen, and by direct incorporation of organic substrates, comprise diverse AA (McMahon and McCarthy, 2016). Moreover, AA can be derived from endo-symbiotic gut bacteria, e.g., in earthworms and enchytraeids (Larsen et al., 2016) or intracellular co-symbionts like *Buchnera* in nematodes and insects (Moran et al., 2003; McCutcheon et al., 2009).

### Trophic Transfer and Biomarkers

In contrast to terrestrial systems, protein limitation *per se* is rather unlikely in pelagic aquatic systems, but certain essential AA may become in short supply (review by Müller-Navarra,

2008). Moreover, trophic transfer of AA can be impaired by co-limiting resources such as sterols (Wacker and Martin-Creuzburg, 2012 for a rotifer). In addition, a meta-analysis of zooplankton across 29 oligotrophic lakes by Guisande et al. (2003) revealed taxa specific AA composition, likely indicating distinct food sources.

The AA composition of primary producers can be markedly different to their animal consumers or microbial degraders (Steffan et al., 2015; Takizawa et al., 2017), offering great potential to follow the transfer of specific AA along the trophic cascade. Two AA categories are distinguished as biomarker in food web ecology: The so called “source” AA exhibiting small  $^{15}\text{N}$ -discrimination but preserve the  $^{15}\text{N}/^{14}\text{N}$  ratio ( $\delta^{15}\text{N}$ ) of the food (McMahon and McCarthy, 2016), while the amino-N of “trophic” AA is routinely exchanged in the metabolic pool (O’Conell, 2017). Thus,  $^{15}\text{N}$  of “trophic” AA is enriched along the trophic cascade (McMahon et al., 2016) (see Table 3). However, it is important to note that the categorization in “source” and “trophic” AA is based on differences in cycling of the N moiety and not on changes within the carbon skeleton. The latter is distinguishing essential and non-essential AA, respectively. The respective parameters and calculations to assign trophic positions by the stable isotope signal of AA are summarized in Table 3.

The broadest biomarker application received the AA couple glutamic acid (Glu; trophic) and phenylalanine (Phe; source). The underlying assumption is that the isotopic fractionation is constant across binary links with the trophic discrimination factor ( $\text{TDF}_{\text{Glu-Phe}}$ ) being 7.6‰ (Chikaraishi et al., 2007) (Table 3).  $\text{TDF}_{\text{Glu-Phe}}$  was successfully applied to assign trophic positions of consumers in very different trophic relationships. These comprised arthropod functional groups in orchard food webs, ranging from sap-feeding herbivores over parasitoids and hyperparasitoids to predators (Steffan et al., 2013) as well as food chains with a broad phylogenetic spectrum, ranging from bacteria and fungi over insects to mammals (Steffan et al., 2015). However, recent work questions a single fixed value for  $\text{TDF}_{\text{Glu-Phe}}$  and reports variability from 0 to 10‰ depending on diet quality, consumer nitrogen excretion, and trophic level (Nielsen et al., 2015; McMahon and McCarthy, 2016; O’Conell, 2017; Pollierer et al., 2019).

Another premise in applying  $\delta^{15}\text{N}$  of AA in food web ecology is the absolute term “ $\beta$ ”, the difference in  $\delta^{15}\text{N}$  of AA in primary producers at the base of food webs (Table 3). For example, in primary producers,  $\delta^{15}\text{N}$  of AA in floral biomass seem to depend on the absence or presence of active photosynthesis (Takizawa et al., 2017). At the consumer level interspecific differences in prey organisms may also lead to AA imbalance and subsequently variation in AA  $\delta^{15}\text{N}$  (Ventura and Catalan, 2010 for different crustacean zooplankton) or increased AA losses by N excretion (Saavedra et al., 2015). The  $\beta_{\text{Glu/Phe}}$  (Table 3) was initially proposed to be  $-3.4\text{‰}$  for coastal marine and  $+8.4\text{‰}$  for terrestrial primary producers (Chikaraishi et al., 2010) but variation in “ $\beta$ ” occurs, and its combination with  $\delta^{13}\text{C}$  in bulk tissue is recommended to enhance resolution (Choi et al., 2017).



**TABLE 3** | “Trophic” and “source” amino acids, fractionation factors, and formula used in in food web studies (Modified after McMahon and McCarthy, 2016).

Parameter	Abbreviation	Amino acid/Calculations	Information value
Trophic amino acid	Trophic AA	Glutamic acid (Glu), aspartic acid (Asp), alanine (Ala), isoleucine (Ile), leucine (Leu), proline (Pro), valine (Val)	Trophic level ( $\Delta^{15}\text{N}$ increases)
Source amino acid	Source AA	Phenylalanine (Phe), methionine (Met), lysine (Lys), tyrosine (Tyr)	Baseline $^{15}\text{N}$ (minor fractionation for $^{15}\text{N}$ )
Trophic fractionation	$\Delta^{15}\text{N}$	$\Delta^{15}\text{N}_{\text{AA}} = (\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{diet}})$	Individual AA trophic fractionation (i.e., $^{15}\text{N}$ enrichment during trophic transfer)
Trophic discrimination factor	TDF	$\text{TDF}_{x-y} = \Delta^{15}\text{N}_x - \Delta^{15}\text{N}_y$	Enrichment between a consumer and its diet in respect to a trophic AA—x (e.g., Glu) and a source AA—y (e.g., Phe)
Trophic position	TP	$\text{TP}_{x/y} = 1 + \left[ \frac{\delta^{15}\text{N}_x - \delta^{15}\text{N}_y - \beta_{x/y}}{\text{TDF}_{x-y}} \right]$	Consumer trophic position derived from the $\delta^{15}\text{N}$ baseline of a source AA (y) and the numbers of trophic transfers of a trophic AA (x); $\beta$ - difference in $\delta^{15}\text{N}$ of these AA in the primary producers at the food web base

Generally, inter-trophic AA  $^{15}\text{N}$  discrimination seem to be similar among bacteria, fungi and animals (Steffan et al., 2015), whereas the  $\delta^{15}\text{C}$  of essential AA exhibited very different pattern between plants and bacteria or fungi (Larsen et al., 2009). This allows enhancing the resolution in the application of AA as trophic markers by using their isotopic C signal. Stable isotope fingerprinting of  $^{13}\text{C}/^{12}\text{C}$  in AA is particularly successful in habitats where primary producers display distinctly different  $^{13}\text{C}$  signals (Figure 2). This approach was used to identify plant, fungal or bacterial origin of AA (Larsen et al., 2009), feeding habits of the Atlantic blue crab (Fantle et al., 1999) as well as movement and foraging ecology of birds (McMahon et al., 2015b). Only recently, this approach was employed to quantify the trophic levels and the basal resources in soil detritivores (earthworms, Potapov et al., 2019) as well as predators (gamasid mites, spiders; Pollierer et al., 2019). Overall, there is sufficient evidence that the “trophic” and “source” concept is pertinent for many organisms, yet a quest for a single TDF or “ $\beta$ ” value may not hold across food webs and ecosystems. Factors such as AA limitation or excretion can lead to mismatches in biochemical stoichiometry, which calls for more physiological and environmental studies to improve the application of AA in trophic ecology.

## FORCES BEHIND ENVIRONMENTAL DISTRIBUTION

### Natural Environmental Conditions

There are vast differences in the comprehension of what drives the distribution of essential biochemicals in ecosystems with the least known about AA and for terrestrial systems. In aquatic habitats, strong negative correlations between total phosphorus and the lakes’ summer seston content of EPA and DHA—but not ALA—were reported (Müller-Navarra et al., 2004; Table 1). Those were connected to the relative abundances of algal groups (Müller-Navarra et al., 2004; Sushchik et al., 2014) and—via

trophic transfer—could even be detected in top predators, such as perch (Taipale et al., 2016b, 2018). The whole years’ distribution of PUFA is, however, more complex (Gladyshev et al., 2007). In addition, temperature and light can alter seston PUFA directly as shown for EPA in a clear water lake by Hartwich et al. (2012). Humic substances in dystrophic lakes may shield susceptible LC-PUFA from UV, but also exert direct toxic effects to consumers, such as daphnids (CasaNova et al., 2018 and references therein). Salinity gradients structuring estuaries can affect trophic dynamics of LC- $\omega$ 3PUFA, especially in larval fish (Litchi et al., 2017).

Vertical distributions of PUFA and sterols differ in particulate organic matter of aquatic ecosystems. Generally, LC-PUFA are depleted and sterols enriched during sinking, mainly because of the high susceptibility of LC-PUFA but high persistency of sterols against degradation (Wakeham and Canuel, 1986). Many profundal habitats depend on pelagic provision with PUFA, e.g., when algae blooms perish (Ahlgren et al., 1997), and consumers have adapted to this low availability. For example, benthic harpacticoid copepods have a more efficient conversion of C<sub>18</sub>-PUFA to the respective LC-PUFA than pelagic calanoid copepods (Nanton and Castell, 1998). Aquatic phanerogams contain only ALA and allocthonous carbon is devoid of nutritional LC-PUFA alongside protein (Brett et al., 2017).

Pronounced differences also exist in the distribution of B<sub>12</sub> in aquatic ecosystems with Archaea preferentially producing B<sub>12</sub> in cold areas and times of the year (Doxey et al., 2015). Primary production can be B<sub>12</sub> limited in high-nutrient low-chlorophyll areas (Koch et al., 2011 for Gulf of Alaska), and the competition for B<sub>12</sub> between eukaryotic algae and heterotrophic bacteria impact total phytoplankton quantity, species composition and succession (Koch et al., 2012). The vitamins B<sub>1</sub>, B<sub>7</sub>, and B<sub>12</sub> seem to co-act in controlling algal succession and blooms in the ocean (Sañudo-Wilhelmy et al., 2006, Gobler et al., 2007). Occurrence of harmful algae blooms in marine systems may be favored by high vitamin B presence, as especially toxin-producing chryso- and dinophytes are vitamin B auxotrophs (75% B<sub>1</sub>, 37% B<sub>7</sub>, and 100% B<sub>12</sub>; Tang et al., 2010). In freshwater systems, algal

blooms dominated by cyanobacteria reduce resource quality at the food web base. Cyanobacteria lack LC- $\omega$ 3PUFA and sterols, their pseudo-cobalamin is no source of B<sub>12</sub> for most herbivores, and, moreover, they potentially contain toxins.

## $\omega$ 3PUFA—Aquatic vs. Terrestrial Food Webs and Interlinks

In contrast to aquatic systems with a predominant supply of LC- $\omega$ 3PUFA (EPA, DHA) by micro-algae, higher plants as major primary producers in terrestrial ecosystems provide only C<sub>18</sub>- $\omega$ 3PUFA (ALA; **Figure 3**). This questions the main origin of LC- $\omega$ 3PUFAs in terrestrial food webs. The potential of aquatic derived LC- $\omega$ 3PUFA to subsidize terrestrial ecosystems was first estimated by Gladyshev et al. (2009). Trophic transfer to land can occur when terrestrial predators (bears, herons, eagles; **Figure 3**) directly feed on aquatic animals (molluscs, crustaceans, fish). The same applies when terrestrial predators (swallows; Twining et al., 2016) feed on terrestrial stages of prey with both, aquatic and terrestrial life stages (e.g., after insects' emergence; Borisova et al., 2016). In addition, the wax and wane of flooding events (Junk et al., 1989), with algal production in temporary shallow water habitats of riparian areas, is a crucial source of LC- $\omega$ 3PUFA. In sum, aquatic systems are currently considered a major origin of LC- $\omega$ 3PUFA for residential terrestrial animals, including humans (Gladyshev et al., 2013; Hixson et al., 2015; Colombo et al., 2017) (**Figure 3**).

However, this hypothesis is controversial. For example, the highest DHA contents were not found in water birds, such as waterfowls feeding in aquatic habitats, but instead, in terrestrial feeders such as Passeriformes species (Gladyshev et al., 2016). Correspondingly, Fontaneto et al. (2011) suggested terrestrial insects, which besides ARA and ALA also comprise EPA, as a better source for LC-PUFA than aquatic insects due to their higher abundance and accessibility to terrestrial consumers. Moreover, the contribution of  $\omega$ 3PUFA derived from photosynthetic microalgae in biological soil crusts (**Table 2**) to food webs in nutrient poor and dry desert, dune and tundra habitats remains to be explored.

A so far neglected source of LC- $\omega$ 3PUFA in terrestrial ecosystems is the soil fauna (**Figure 3**). Across a wide taxonomic range of soil invertebrates the capability to synthesize LC- $\omega$ 3PUFA *de novo* was shown. The entire set of desaturases and elongases to produce LC- $\omega$ 3PUFA occurs in the nematode *Caenorhabditis elegans* (Watts and Browse, 2002). Recent molecular studies proved the presence of  $\omega$ 3FA desaturase enzymes in several other free-living soil nematode taxa (Menzel et al., 2019) as well as in terrestrial oligochaetes and insects (Kabeya et al., 2018). EPA synthesis was further indicated for soil Collembola (Menzel et al., 2018) and earthworms (Petersen and Holmstrup, 2000).

Proportions of EPA in total fatty acids reported are 3.5% for free-living soil nematodes (Kühn et al., 2018) and up to 17.4% for yeast feed Collembola (Chamberlain and Black, 2005). In particular, earthworms (their body, gut and burrow lining) are a rich source for LC- $\omega$ 3PUFA, with EPA being 7.5 times higher than in bulk soil (Sampedro et al., 2006). This

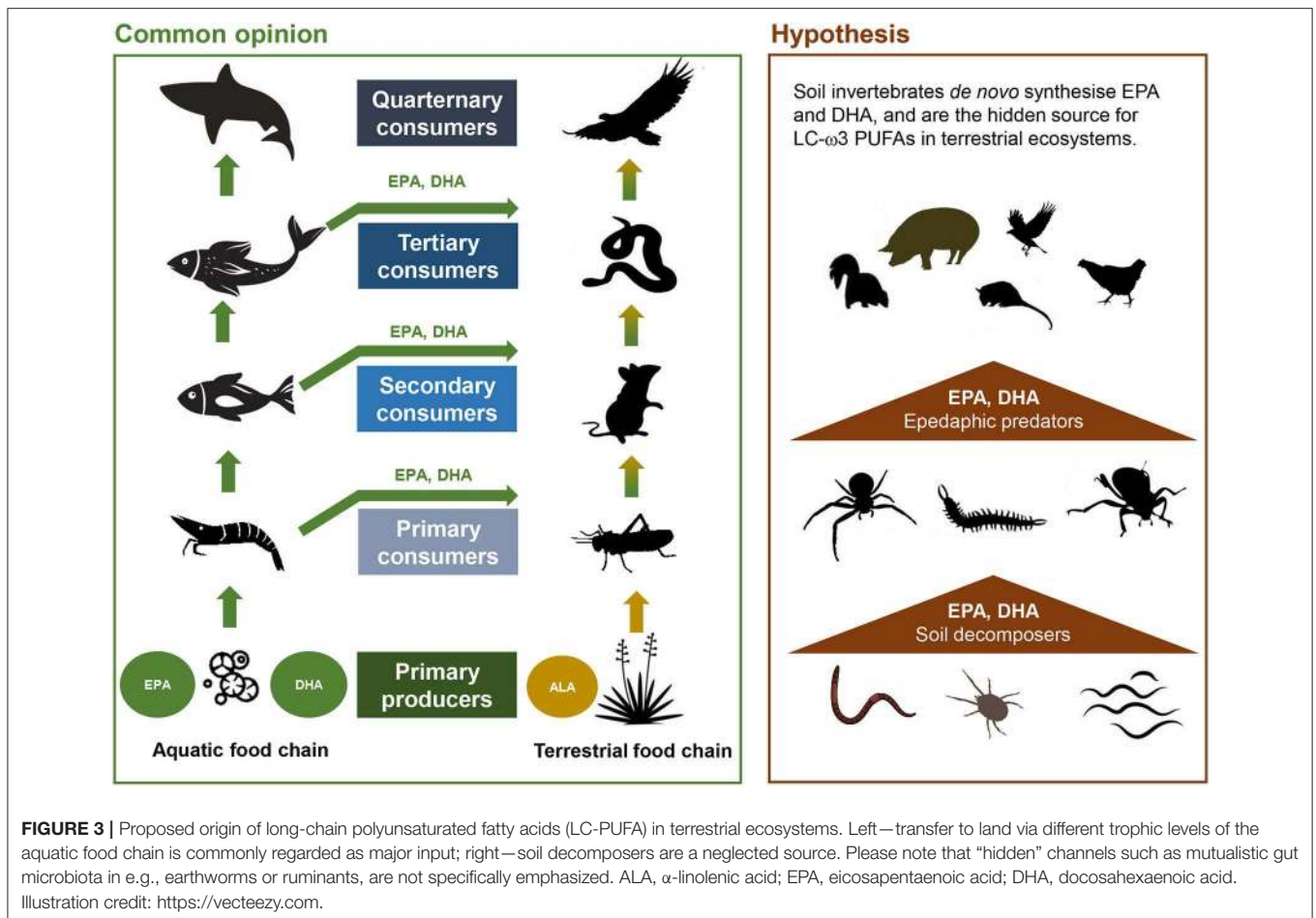
represents a considerable source irrespective of whether LC- $\omega$ 3PUFA are acquired by the animal itself or from gut microbiota. Comparable to aquatic food webs, EPA seems to be selectively retained in soil decomposer food chains as suggested by the occurrence in top predator such as centipedes and spiders (Pollierer et al., 2010; Ferlian et al., 2012). In sum, there is sufficient evidence that belowground biota build central deposits for essential LC- $\omega$ 3PUFA, which can fuel higher trophic levels above ground (**Figure 3**).

## Anthropogenic Impact

Since humans have settled, they preferentially modulated riparian areas, which have a central role in LC- $\omega$ 3PUFA production and export to land, thereby altering the ecological availability of these nutritional valuable biomolecules. A more recent anthropogenic impact is global climate change, i.e., elevated atmospheric CO<sub>2</sub> and temperature. Temperature changes act predominantly on PUFA, due to their central role in maintaining membrane fluidity in poikilothermic species (Hazel, 1995). The proposed food web impacts of increased temperature focus on a general decline of LC- $\omega$ 3PUFA in aquatic primary producers (e.g., Hixson and Arts, 2016). However, extrapolating temperature effects observed for algal cultures to a potential worldwide reduction in sestonic LC- $\omega$ 3PUFA may be misleading. As algal group composition mainly drives  $\omega$ 3PUFA content, all factors altering community structure, including nutrient regimes and their interactions (Suikkanen et al., 2013) need to be considered, not solely temperature. A recent statistical model predicts a 12% decline of EPA in top predator fish at increasing ocean surface temperatures off Australia, in an area also prone to alterations in nutrient regime (Pethybridge et al., 2015). Moreover, trophic transfer can be impacted by the mismatch in timing rather than by the biochemical composition of the prey (e.g., Seldon et al., 2018). In any case, melting of polar ice with increasing temperatures will affect the occurrence of ice-algae as reliable source of EPA for zooplankton productivity in the Arctic (Leu et al., 2011) and Antarctic (Kohlbach et al., 2017).

In terrestrial plants, the decline of the LC- $\omega$ 3PUFA precursor ALA with increasing temperature can reach 50% in soybeans (Byfield and Upchurch, 2007) and 77% in rapeseed (Namazkar et al., 2016). On one hand, this is due to low expression of  $\omega$ 3FA desaturase genes, on the other hand it is induced by general temperature stress that reduces the overall fat and seed biomass. Higher growing temperatures also lower vitamin contents in fruits and vegetables, as shown for vitamin C in kiwi (Richardson et al., 2004) or broccoli (Kumar et al., 2016). With elevated temperature, alterations in PUFA pattern and vitamin contents are expected in herbivores (Adler et al., 2013 for cow milk) accompanied by changes of plant community structure from C3 to less nutritious C4 (Warne et al., 2010). Finally, temperature increase can provoke proteomic responses of microorganisms affecting biosynthesis of essential nutrients in decomposer food chains (Mosier et al., 2015).

The ecological influences of elevated atmospheric CO<sub>2</sub> on essential biomolecules in aquatic ecosystems are not uniform, as CO<sub>2</sub> can be a potential limiting resource for primary producer but also a stressor by lowering the pH. Ocean acidification



can induce phytoplankton community shifts, which negatively influences trophic transfer of essential compounds (e.g., Rosoll et al., 2012). However, larval fish exhibited more whole-body fat at higher  $\text{CO}_2$ , including essential FAs (Díaz-Gill et al., 2015). Studies combining effects of warming and acidification found minor or no changes in the essential AA content in marine diatoms (Bermúdez et al., 2015) but an increase in EPA in primary producer and mesozooplankton consumer (Wang et al., 2017). By using AA-specific  $\delta^{13}\text{C}$  measured in long living deep-sea corals, McMahon et al. (2015a) could detect a shift toward non  $\text{N}_2$ -fixing cyanobacteria during warmer times, i.e., in the Medieval Climate Anomaly and the Industrial Era.

In terrestrial ecosystems, elevated  $\text{CO}_2$  *per se* and in combination with temperature increase, reduced ALA and vitamin C contents in fruits, oils and seeds of plants (Kahn et al., 2013; Namazkar et al., 2016). Increased droughts can up-regulate the metabolic pathways for thiamin ( $\text{B}_1$ ) reported for *Zea mays* (Rapala-Kozik et al., 2008), a response to enhance stress tolerance of the plant. Moreover, changes in land use affect the interactions between plants and the soil microbiome, altering vitamin exudation by roots as well as the production by rhizosphere bacteria. For example, herbicides reduced the production of B vitamins in the soil bacterium *Azotobacter*

(Murcia et al., 1997). Overall, such changes in the rhizosphere as a hot spot for diverse microbial communities and, thus, metabolic pathways and substrates, have considerable impact on the occurrence and availability of essential biomolecules for higher trophic levels.

## EVOLUTIONARY ASPECTS

Essential biomolecule physiology recently achieved attention as a trait within evolutionary concepts (reviewed by Ellers et al., 2012). For example, the loss of *de novo* synthesis of vitamin C in many mammals is connected to ample access by frugivory, leading to “relaxed selection” *sensu* Lahti et al. (2009). Under “environmental compensation” lost traits can be functionally compensated by others, e.g., in the case of vitamin D dietary provision is substituted by light. According to the “Black Queen Hypothesis,” genes and related traits can be lost as the metabolites are provided as common goods by other members of a consortium (Morris et al., 2012).

Whether these evolutionary concepts will explain the environmental distribution in nutritional valuable molecules on a food web level warrants further investigation. With comparative genomics, Mee and Wang (2012) showed that AA *de novo*

synthesis of Eukarya is restricted to 4.1 AA (humans 11 AA), whereas Archaea on average *de novo* synthesize 8.3 and bacteria 7.9 out of 20 AA, respectively. Corresponding to the constitutive costs proposed by Lahti et al. (2009), most organisms do not synthesize those AA, which require many biochemical steps, thus are metabolically more costly to produce. Moreover, intra- and extracellular production of AA and vitamins differ between free-living bacteria and biofilms in marine benthos (Johnson et al., 2016), suggesting provision of essential biomolecules by the consortium in line with the “Black Queen Hypothesis.” Essential extracellular metabolites such as AA and vitamins may even be a valuable “currency” in microbial cross-feeding (Seth and Taga, 2014) and for microbial grazers at the base of aquatic and terrestrial decomposer food webs.

The dynamics of  $\omega$ 3- and  $\omega$ 6PUFA in food webs, however, do not fit those evolutionary trait considerations of dependencies through adaptive gene loss. In a phylogenetic study across 54 invertebrate taxa, including Acari, Crustacea, Insecta, and Nematoda, no indication of a link between the dietary availability of LA and its *de novo* synthesis was detected, rather LA synthesis was facilitated by the bi-functionality of desaturase enzymes (Malcicka et al., 2018). Generally, fewer steps are involved in the synthesis of LC-PUFA than for many other essential biomolecules. LC-PUFA are prone to peroxidation if not protected by antioxidants like vitamin E, with peroxidation products being harmful (Finkel and Holbrook, 2000). This suggests that, in contrast to other nutritional biomolecules, the response to oxidative stress may be the trait here, and the costs are related to features mitigating the damaging effects of LC-PUFA peroxidation (Monaghan et al., 2009). Nevertheless, holding genes such as the Fads2 desaturase to *de novo* synthesize DHA, is considered important for recurrent freshwater colonization and radiation in fishes (Ishikawa et al., 2019).

Overall, synthesis of specific nutritional biomolecules can be lost by species or whole systematic groups if it is more efficient to obtain those from the environment. This converts them into essential dietary compounds, yet constraints appear to differ according to biochemical susceptibility and synthesis pathways.

## CONCLUSION

Essential biomolecules play an important role in trophic interactions across taxa in aquatic and terrestrial ecosystems. Their availability at the base of the food web matters for the mode of trophic transfer, affecting food web structure as well as response to environmental changes. For example, algae

and higher plants as primary carbon fixers do not provide all essential biomolecules, and e.g., Archaea are the main producer of B<sub>12</sub>. As its’ biochemical functioning is tightly connected to other essential biomolecules (B vitamins and methionine), mutual to symbiotic trophic interactions are characteristic for provision. In contrast, LC- $\omega$ 3PUFA and AA are mainly transferred via predator-prey interactions and their minor metabolic alterations predetermine them for dietary tracing. Particularly in combination with compound-specific stable isotope analyses they provide quantitative estimates of resource flows. Terrestrial and aquatic food webs differ considerably in the amount and distribution of essential biomolecules, e.g., in FAs, and interlinks are important, especially from water to land.

However, our knowledge on the function of essential biomolecules in food webs is far from complete. Future food web research questions to be addressed are: (1) How are food web assemblages in different biomes adapted to the local sources of essential nutritional compounds? (2) Are there considerable exchanges/fluxes in essential compounds between terrestrial herbivore and detritivore food chains? (3) How do food chain loops, such as the microbial loop, contribute to the dynamics of essential biomolecules, besides known trophic-upgrading within PUFA? (4) How does the availability of essential biomolecules affect the organization of biotic consortia, e.g., aquatic biofilms or rhizosphere microbiomes? (5) What is the impact of hidden sources, e.g., gut microbiota, on the reconstruction of food webs using essential biomolecules as trophic markers? (6) What is the general role of essential biomolecules in food web dynamics at higher trophic levels compared to the frequently investigated plant-herbivore interface? Finally, as the capability for *de novo* synthesis can act as trait in evolution, a new research field opens up, connected to questions on how essential biomolecules can impact adaptations and radiation of species, including the diverse trophic interactions—from mutualism to parasitism.

## AUTHOR CONTRIBUTIONS

LR and DM-N contributed equally to the conception and writing of the work as well as to its content and interpretation.

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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