Ecological Indicators 67 (2016) 657–672

Contents lists available at ScienceDirect

Ecological Indicators

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

Fatty acid profiling as bioindicator of chemical stress in marine organisms: A review

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ARTICLE INFO

Article history:
Received 9 November 2015
Received in revised form 21 March 2016
Accepted 22 March 2016
Available online 25 April 2016

Keywords:
Fatty acids
Bioindicators
Pesticides
Metals
Organic and inorganic pollutants
Marine organisms

ABSTRACT

The development of industrial, anthropogenic, and agricultural activities is the main factor leading to contaminants' increasing in marine ecosystems. Contaminants include the great variety of pesticides and heavy metal pollutants. One of the major environmental concerns about herbicides and heavy metals contamination is their bioaccumulation in the ecosystem's primary producers and its subsequent propagation through the trophic chain. Over the last decades, the use of biochemical markers considerably contributed to the evaluation of contamination hazards. The fatty acid composition proved to be a good bioindicator to assess contamination levels. This paper provides a review of current knowledge on the fatty acids response in marine species after exposure to the chemical stressors including organic and inorganic pollutants, mainly pesticides and heavy metals. This review underlines the consistent directional trends in changes of saturated fatty acids, monounsaturated fatty acids and polyunsaturated fatty acids, and summarizes the mechanisms of action leading to their alteration and possible consequences of these changes to marine species from different trophic levels.

1. Introduction

In the last decades, contaminants' discharges are one of the themes that concerned the scientific community and politicians and received special attention from media because of the threat and adverse effects that they may cause in aquatic ecosystems (McKnight et al., 2012). The development of industrial, anthropogenic, and agricultural activities are the main factors leading to their increase in aquatic ecosystems (Peixoto et al., 2006).

Marine ecosystems play the role of the ultimate storage for a great variety of organic and inorganic pollutants, which are constantly discharging due to the active anthropogenic activities (Kennish, 1996). There are five main pollutant sources of marine ecosystems: (1) landscape level causes; (2) industrial and domestic discharges; (3) inflows from rivers; (4) shipping and (5) precipitation from atmosphere. The great input to the sea pollution gives land-based sources – more than 80% (Kennish, 2000). Among them are intensive agriculture activities discharging the great variety of chemical stressors with organic and inorganic nature, contaminating the marine aquatic environment.

Contaminants include the different kind of pesticides and heavy metal pollutants. Pesticides represent a large group of toxic chemicals. Their use is reducing in most developed countries, although the world level of herbicides production is still up to 40% (Peixoto et al., 2006). One of the major environmental concerns about herbicide contamination is its bioaccumulation in the marine ecosystem's primary producers and its subsequent propagation through the trophic chain (Galhano et al., 2011).

Metal contaminants may not directly damage the organisms when entering the marine aquatic ecosystem; however, as pesticides, they can be accumulated into marine aquatic organisms through the different kind of processes and effects, such as bioaccumulation, bioconcentration, and the food chain process and ultimately endanger the health of humans by seafood consumption (Al-Malki and Moselhy, 2011).

The various anthropogenic pressures and behaviors that cause ecological stresses at these systems, affect not only the water quality, but also the biological communities of these ecosystems (Gonçalves et al., 2012, 2016; Neves et al., 2015). Thus, marine

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http://dx.doi.org/10.1016/j.ecolind.2016.03.044
1470-160X/

contamination directly affects marine aquatic biota. The review and meta-analysis of numerous studies about this issue proved that anthropogenic contamination of marine habitats is clearly reduces marine species richness and evenness (Johnston and Roberts, 2009).

Over the past decades, the bioindicator and biomarker approach has attracted considerable attention of scientists, mainly toxicologists, and the international regulatory agencies as a new and potentially powerful tool for detecting, documenting and evaluating exposure to and the effects of contamination hazards for wildlife (Huggett et al., 1992).

In 1980s the amount of research applying biomarkers and their use in environmental studies significantly increased. Outcomes showed regularities between biomarkers responses and chemical exposure or biological response in both population and community levels. There were defined key parameters estimating biomarkers applications on molecular, cellular and whole animal levels, including biochemical biomarkers as well. The latter were used for different purposes, in most cases for environmental monitoring with estimation of the pollution levels *in situ*, and to a lesser extent for predictions – conducting experiments in laboratory conditions (Jemec et al., 2009).

Nutrients, mainly lipids and proteins, are involved in many vital functions of aquatic individuals. Since some of them can only be obtained from food and therefore referred to as 'essential nutrients' (*e.g.*, essential fatty acids or EFA), they proved to be useful trophic markers (De Troch et al., 2012; Kelly and Scheibling, 2012). On the other hand, analysis of fatty acids composition are used as biochemical markers in order to indicate bacterial symbiosis, demonstrating as a valuable screening tool for detecting symbionts in species (*e.g.*, Zhukova and Eliseikina, 2012) and have been advocated as qualitative markers for tracing or confirming predator-prey relationships in the marine environment (Grahl-Nielsen et al., 2003; Iverson et al., 2004; Budge et al., 2006).

Fatty acids (FA) are necessary for the production and permeability of cell membrane, they are the main components of lipids and used as fuel in all metabolic systems at all trophic levels, having an important role on neural levels of biochemical and physiological response (Neves et al., 2015).

As FA are one of the most important molecules transferred across the plant-animal interface in aquatic food webs, they were claimed to be a good bio-indicator of ecosystem health (Maazouzi et al., 2008; Ramírez et al., 2013) and bio-indicators of stress (Sanchez-Muros et al., 2013; Gonçalves et al., 2016).

Polyunsaturated fatty acids (PUFA) include many important compounds, such as EFA. PUFA and EFA are often used interchangeably since many biological functions of EFAs are exerted by EFA – derived PUFAs. PUFA are almost exclusively synthesized by plants, with animals being able of converting PUFA by elongation or desaturation, and only a few could synthesize this type of fatty acids (Neves et al., 2015).

Highly unsaturated fatty acids (HUFA) (*e.g.* ARA, EPA and DHA) play a key role in the health and function of all animals at all trophic levels, including plankton invertebrates, fish and humans and cannot be synthesized *de novo*, or at least not in sufficient amounts (Saito and Aono, 2014; Gonçalves et al., 2012). Indeed, eicosapentaenoic acid ($20{:}5n-3$, EPA) is an excellent energy source and precursor of eicosanoids, docosahexaenoic acid ($22{:}6n-3$, DHA) is involved in the maintenance of membrane structures and functions, while $n-6$ arachidonic acid ($20{:}4n-6$, ARA) is identified as affecting the growth and survival of scallops larval and post-larval stages (Costa et al., 2015). The long-chain n-3 PUFA are originated from phytoplankton and accumulate in marine animals in higher trophic levels through the food web (Saito and Aono, 2014). Some groups of organisms feed with high amounts of HUFA present higher growth rate, which strength the importance of fatty acids as ecophysiological indicators (Neves et al., 2015). In addition, ARA and DHA are considered most important for infants (Saito and Aono, 2014). Furthermore, lipid components are very sensitive to stressors and environmental changes (Gonçalves et al., 2012, 2016).

2. Toxic effects of chemical stressors and their action to metabolism

2.1. Metals effects

Heavy metals are one of the most significant groups of pollutants generated by industrial activities. It is known to seriously impact coastal zones and their inhabitants, influencing both organisms and ecosystem processes. This class of pollutants directly affects aquatic organisms, altering metabolic pathways, consequently compromising the structural and physicochemical properties of the membrane, and damaging cells, tissues and organs. This effect, when occurring during long term, can lead to higher mortality among a population, and change community structure and diversity (Bae and Lim, 2012; Gabryelak et al., 2000).

For living organisms all metals can be divided into essential elements, for instance copper (Cu), zinc (Zn) and toxic elements, such as mercury (Hg), cadmium (Cd), chromium (Cr). Therefore, some heavy metals become toxic only at very high amounts, because they are biologically essential and are natural components of the aquatic ecosystem. However, the rest of heavy metals are toxic to living organisms even at remarkably low concentrations (Bae and Lim, 2012). For example, in fish muscle, contents of essential elements (*e.g.*, Zn, Cu, Ni) are higher than those of toxic elements (*e.g.*, Hg, Cd, Pb) (Bae and Lim, 2012).

As mentioned above, copper is an essential element, necessary to maintain healthy cellular functioning (Mayor et al., 2013), acting as enzyme cofactor and key participant in several metabolic pathways (Ritter et al., 2008).

However, this heavy metal quickly becomes toxic when its supply exceeds the demand. The toxicity of dissolved copper depends on the pH and temperature of water, thus it will increase in the coming years as seawater pH decreases and temperature increases (Mayor et al., 2013). An excess of this metal may lead to detrimental effects on photosynthesis, chlorophyll synthesis, fatty acid metabolism, carbohydrate synthesis (Ritter et al., 2008), as well as on cellular respiration, ATP production, pigment synthesis and inhibition in cell division (Sibi et al., 2014).

There are three main processes explaining the mode of action of cupric and cuprous (Cu (II), Cu (I)) ions, which at high amounts significantly affect organismal cells: (1) The affinity of Cu (II) with thiol-, imidazole-, and carboxyl-groups of amino acid leads to their interactions and therefore to protein inactivation; (2) Cu (I) can be obtained from interactions between Cu (II) and deoxidants, take part in Fenton's reaction as a catalyzing agent for formation of hydroxyl radicals, belonging to the group of reactive oxygen species (ROS); (3) Both ions of copper displace essential cations from specific binding sites. By affecting organisms, at the cellular level, copper ions interfere in the metabolism of FAs and proteins, and may inhibit respiration and nitrogen fixation processes in photosynthetic organisms (Maazouzi et al., 2008; Ritter et al., 2014).

Another essential element is zinc that plays a pivotal role in processes such as cell division, growth, metabolic mechanisms, and physiological dynamics concerning immunity maintenance. It can act alone or as an enzyme cofactor in the prevention of damage caused by highly ROS such as superoxide anions, hydrogen peroxide, hydroxyl radicals, and singlet oxygen. The mechanism of action still remains unclear, but it is believed that proteins and PUFAs are the main target for these radicals. Furthermore, this metal may