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POLYCYCLIC AROMATIC HYDROCARBONS IN SEAFOOD FROM THE MEDITERRANEAN SEA

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are formed as a result of insufficient combustion of organic compounds and cause pollution in the environment. While its natural resources are volcanic activities, forest fires, organic matter decomposition, its anthropogenic resources are fossil fuels and petroleum derivatives. Aquatic ecosystems constitute the final discharge points of PAHs that mix with the atmosphere and soil. The transmission of PAHs accumulated in aquatic organisms to the upper trophic zones through the food chain is transmitted to humans by the consumption of seafood. It is known that there are more than a hundred PAH compounds in the environment, but 16 of them are considered as priority pollutants due to their carcinogenic effects. The Mediterranean is highly vulnerable to these pollutants as it is a sea that is heavily influenced by industrial and agricultural activities and has a limited connection with the ocean. It has been determined that the bioaccumulation of 16 carcinogenic PAH species in some consumable fish and invertebrate species in the Mediterranean poses a potential threat and the importance of risk assessments for human health has been emphasized. In this study, the general characteristics, sources, participation in aquatic ecosystems, accumulation and toxic effects of PAHs and their accumulation in consumable species living in the Mediterranean are presented.

K E Y W O R D S: Polycyclic aromatic hydrocarbons, pollution, Sea food, Mediterranean Sea.

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Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds consisting of two or more fused aromatic rings. Compounds of these organic compounds ranging from bicyclic naphthalene and naphthalene derivatives to complex ring structures containing 10 rings constitute various types of PAHs. In other words, they are classified according to the number of aromatic rings and the configuration of the rings. PAHs containing six or fewer aromatic rings are generally known as "small" PAHs, while those containing more than six aromatic rings are called "large" PAHs. Depending on the configuration of the rings, those containing only a fused six-membered benzene ring are classified as Variable PAHs, and those containing both six-membered benzene and five-membered carbon rings are classified as Non-variable PAHs. This distinction in the configuration of the rings determines the properties of PAHs (Abdel-Shafy and Mansour, 2016).

In their purest form, PAHs are low volatility solids at room temperature and vary in appearance from colorless to white or pale yellow-green. They are relatively insoluble in water and most of them can be photo oxidized and reduced to simpler substances (Abdel-Shafy and Mansour, 2016; Ferrante et al., 2018).

Occurrence and Sources of PAHs

The formation of PAHs takes place in two stages: pyrolysis and prosynthesis. Large PAH molecules are formed by the condensation (prosynthesis) of free radicals formed as a result of the decomposition (prolysis) of small organic compounds under high temperatures (Di Bella et al., 2020). The temperature has an important role in the structure and diversity of PAHs. Small PAHs occur more often than large PAHs. The reason for this is the addition of sequential rings in the formation of large PAHs, kinetic limitations in production, and the low formation of certain structures with more isomers (Abdel-Shafy and Mansour, 2016).

PAHs that enter the environment as a result of natural or anthropogenic activities such as volcanic activities, forest fires, and oil spills are the most important environmental pollutants. They are formed as a result of insufficient combustion of fossil fuels such as wood, coal, oil, gas, and materials containing carbon (such as biomass formed by dead plants and animals) (Perugini et al., 2007a). They are found in the exhaust gas, cigarette smoke, tobacco products, and smoked and charcoal-cooked foods. According to their source, PAHs are classified as pyrogenic PAHs (sourced from fossil fuels), petrogenic PAHs (derived from crude oil), and biological PAHs (biodegraded or synthesized by some plants and bacteria) (Abdel-Shafy and Mansour, 2016).

16 of the PAHs were listed by the United States Environmental Protection Agency (US EPA) as priority pollutants in the 1970s. These priority PAHs include naphthalene, acenaphethylene, acenaphthene, fluorene, anthracene, phenanthrene, floranthene, pyrene, chrysanthemum, benz[a]anthracene, benzo[b]florentine, benzo[k]floranthene, benzo[a]pyrene (B[a]pyrene (B[a]pyrene). a]P), indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, and dibenz[a,h]anthracene. Among these priority PAHs, B[a]P, PAH is known to be a human carcinogen and is widely used in studies (Di Bella et al., 2020).

Participation, Uptake and Accumulation of PAHs in Aquatic Ecosystems

The effect of PAHs on environmental health is based on the industrial revolution that started with the discovery of fossil fuels. Increasing urbanization and industrialization in parallel with the increase in human population have increased the release of PAHs to the environment and the rate of exposure of living creatures to these substances. The persistence of this situation has led to significant health problems. Aquatic ecosystems form the final discharge areas of PAHs that participate in the environment (Ferrante et al., 2015; 2017). It is known that PAHs added to the environment at increasing concentrations accumulate in aquatic organisms and are transmitted to the upper trophic chains (Perugini et al., 2007b). The fact that these

basic nutritional sources (Copat et al., 2012; Conti et al., 2015; Nwaichi and Ntorgbo, 2016), which are rich in protein, minerals, vitamins, and unsaturated fatty acids, are under the influence of PAHs, cause them to be transported to humans through consumption (Conte et al., 2015; Copat et al., 2013, 2014; Domingo, 2016).

PAHs that participate in aquatic ecosystems remain suspended in the water column for a while and then precipitate in the sediment and accumulate there. It has been reported that this process occurs quite rapidly for PAHs (Ferrante et al., 2015). It has been emphasized that vertebrate and invertebrate animals, plants, and microorganisms living in the water column and sediment can accumulate even very low ambient concentrations of PAHs at high concentrations (Ferrante et al., 2015).

PAHs are taken up directly through the gills and skin, which interact directly with the environment, and indirectly through the digestion of contaminated drinking water and food (Perugini et al., 2007a, b; Conti et al., 2012). In general, toxic substances are transferred to metabolically active tissues to be detoxified by binding to the carrier proteins in the circulatory system when they are taken into the body, and the part that is not excreted above a certain concentration is stored in non-metabolic tissues. Like some organochlorine compounds, PAHs with lipophilic character tend to accumulate in fatty tissues (Di Bella et al., 2020). Therefore, oily fish (bluefish, some salmon, catfish, and carp) have higher concentrations of PAHs than lean fish (some sea bass, sunfish) (US EPA, 2007). Muscle tissue is the main edible part for humans and removes the internal organs, fat, and sometimes the skin before consumption can reduce the pollutant effect, while it is not possible to remove the pollutants accumulated in the muscle tissue. It should not be overlooked that the concentration of pollutants in the non-edible tissues here is in parallel with the pollutant load carried to the muscle tissue.

PAH Effect in the Mediterranean

The concentration of the environment is important in the uptake and accumulation of PAHs, and the geomorphological features of the region affect this situation. The Mediterranean Sea, which is an intercontinental inland sea and is under the influence of industrialization and agricultural activities throughout the entire basin, is highly vulnerable to organic and inorganic pollutants compared to the oceans (Conte et al., 2016; Conti et al., 2012; Domingo et al., 2008; Shen et al., 2017). Maritime accidents caused by commercial tankers in the Mediterranean, which have large ports as well as industry, agriculture, and urban discharge, have an important role in increasing the ambient concentration of PAHs (Balcıoğlu et al., 2014; Tornero and Hanke, 2016). The Mediterranean, which is heavily under the influence of anthropogenic activities, is also under the influence of PAHs due to its submarine volcanic emission feature. Although PAHs can degrade under the influence of light, they cause permanent pollution in the environment due to their low solubility in water and their physicochemical properties (Winquist et al., 2013; Cristaldi et al., 2017). The Mediterranean, which has a limited connection with the open seas, is very sensitive to the accumulation of these pollutants. Therefore, in order to ensure reliable seafood consumption, risk analyzes should be made with precision and the sustainability of these controls should be ensured (Ferrante et al., 2015).

In the western Mediterranean, 11 types of PAHs have been found in atmospheric aerosols, rivers, seawater, and sediment. Atmospheric precipitation and the Rhone River were stated to be the main sources of PAH inclusion in the Western Mediterranean. It has been reported that 50% of PAHs accumulate at depths of 0-200 m. It is known that the participation of PAHs also varies seasonally. It is also supported by other studies that the PAH concentration in the winter season doubles compared to the spring season. Seasonal discrimination has been associated with the frequency of use of PAH sources and the intensity of biological activity (Lipiatou et al., 1997).

The accumulation of 16 PAH species classified as priority pollutants by the US EPA has been proven in fish (*Sardina pilchardus, Solea solea*) and crustacean (*Donax trunculus*) species located in different trophic zones of the food chain in the

Mediterranean. Risk analysis evaluations based on the consumption amount of these seafood products show that they will be transported to humans. In one study, it was stated that the accumulation was higher in the crustacean species than in fish. It has been reported that the concentration in seafood products will have a low risk of chronic systemic effects in humans due to consumption, and the risk of cancer may be a health concern, especially for mollusk consumption, depending on the frequency and amount of consumption (Ferrante et al., 2015). It is supported by studies that PAHs can be accumulated at high concentrations in invertebrate species such as filter feeding bivalves. It has been stated that mussels can be evaluated as biomonitoring organisms (Mzoughi and Chouba, 2012).

Studies emphasize that the Mediterranean is heavily influenced by PAHs as a result of intense industrial and agricultural practices as well as urban discharges, the distribution of PAHs in the water column and sediment is high, and the participation varies seasonally depending on the intensity of resource use. It has been determined that edible seafood living in regions with intense anthropogenic PAH participation in the Mediterranean are more affected than those living in areas away from pollution. It has been concluded that PAHs can be transmitted to humans depending on the consumption of these seafood products. 16 PAHs identified by the International Agency for Research on Cancer (IARC) have been classified as possible human carcinogens. It has been reported that this group of PAHs can cause mutagenic effects in humans and other animal species (IARC, 2010; Balcioglu et al., 2014; Vecchio et al., 2015; Zanghì et al., 2017; Moraleda-Cibrià n et al., 2015).

2. CONCLUSION

Polycyclic aromatic hydrocarbons (PAHs) are produced from the pyrolysis and incomplete combustion of organic matter. They are classified as genotoxic and carcinogenic to humans. The inclusion of PAHs in aquatic ecosystems under the influence of natural or anthropogenic sources causes accumulation and toxic effects in aquatic organisms. Seafood is one of the main sources of protein for humans. They are healthy food sources due to their easily digestible feature as well as the richness of unsaturated fatty acids, vitamins, and minerals. Seafood is also considered to be a good bioindicator of environmental contamination due to its ability to accumulate pollutants directly from the environment and indirectly through the food chain (Di Bella et al., 2020).

The risks caused by organic or inorganic pollutants transferred to the human body due to seafood consumption raise concerns in terms of the safety of these food sources recommended for consumption all over the world. For this reason, environmental monitoring studies and risk assessments should be carried out regularly. In order to avoid the possible pollutant effect in the consumption of seafood with rich nutritional content, especially fish, it is recommended that the fishing of these products be carried out in areas away from the effect of pollution. Most importantly, it is recommended to provide the necessary conditions to minimize the effect of anthropogenic factors that cause environmental pollution.

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