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A Mini-Review on Polycyclic Aromatic Hydrocarbons (PAHs) in Some Smoked Fish

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ABSTRACT

The effects of sources that cause pollution in the environment in organisms can occur in different ways. The participation of polycyclic aromatic hydrocarbons (PAHs), one of the pollutants caused by organic materials, into aquatic ecosystems by washing from the atmosphere and soil causes accumulation in aquatic ecosystems and is easily transported to the upper trophic zones through the food chain. Consumption of these products with high nutritional value poses a threat to human health. The processing of these products, which are widely consumed as fresh, with different processes is another way to remain under the influence of PAH. As it is known, PAHs are formed as a result of pyrolysis and prosynthesis of organic materials that are not sufficiently burned. In this sense, smoked products that are not produced under suitable conditions may carry a risk for the formation of PAH. In this study, the factors that cause PAH formation in smoked products and the appropriate processing processes developed to eliminate these factors were compiled.

INTRODUCTION

Seafood attracts attention because they constitute healthy protein sources that have an important place in human nutrition, as well as because terrestrial resources cannot meet the needs of the increasing population. Although fresh consumption is common, salted, dried, canned, and smoked products produced with different processing techniques in the food industry are offered for consumption by extending their shelf life (Abraha et al., 2018). These processing techniques, which are developed with new technologies today, are basically based on the history of humanity. Salting, drying, and smoking is preservation methods that human beings have discovered in order to keep meat and fish products intact (Horner, 1997; Slámová et al., 2021). It provides an increase in flavor due to the aroma added to the meat, as well as the storage of the products applied by the smoking method. Various woods and fragrant plants are used to create different aromas. Industrial applications in fish smoking 19th century were started and continue to be developed with new technologies today.

One of the basic principles of smoking is to remove some of the water contained in the meat and to prevent microbial spoilage by passing the antibacterial substances in wood smoke to the meat. However, the composition of the smoke and the processing conditions affect the sensory quality of the product, its shelf life, and healthy product acquisition (Ceylan & Şengör, 2015; Jinadasa et al., 2020). Carcinogenic components of wood smoke, such as PAH, nitro-PAH or PAH derivatives such as oxygenated PAH, and to a lesser extent N-nitroso compounds and heterocyclic aromatic amines, which are formed as a result of insufficient combustion of organic materials, can cause potential health problems in smoked products (Öz, 2020). It has been reported that N-nitroso compounds are in lower concentrations in hot-smoked fish than in other foods

(Roper et al., 1981). It has been reported that the carboxylic acid content of N-nitrosothiazolidine is found at a concentration of 1 mg/kg (wet weight) in smoked poultry (Mondagere, 1986). Heterocyclic aromatic amines have been found in heavily smoked, dried mackerel at concentrations below 1 μg/kg (Kato et al., 1986).

It has been reported that wood smoke contains a large number of PAHs (Pirsaheb et al., 2018), and 61 of them which has different molecular mass weights are clearly identified in products, meanwhile 15 PAHs of them cause mutagenicity/genotoxicity in somatic cells in experimental animals by the Scientific Committee on Food (Stołyhwo & Sikorski, 2005; Mihalca et al., 2011; Mahugija & Njale, 2018).

PAHs are classified according to their chemical structures and molecular weights, and carcinogenic and mutagenic effects are seen in PAHs with high molecular weights (228-278 g/mol) which contain five–seven rings such as benzo(a)pyrene, dibenz(a,h)anthracene and indeno(1, 2, 3-c, d)pyrene (Palm et al., 2011). Among these, Benzo[a]Pyrene (BaP), with a molecular mass of 252 Dalton, has been accepted as a marker of carcinogenic PAHs in wood smoke, smoked products, and environmental samples due to its strong mutagenic and carcinogenic effect (SCF, 2002).

The most important uptake route of PAHs by human is foods prepared as grilling, smoking, frying, roasting at the highest temperature and less breathing and smoking (Silva et al., 2011). Due to the carcinogenic and mutagenic properties, PAHs are included priority pollutants lists by The United States Environmental Protection Agency (USEPA), European Union Scientific Committee for Food (EUSCF), and the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

Maximum BaP level for smoked seafood and other products is 5.0 μg/kg established by European Commission (Regulation (EC) No 2008/2005) (Wretling et al., 2010; Mihalca et al., 2011). After this decision, BaP concentrations were determined in commercially smoked products, and it was reported that BaP levels did not exceed the maximum acceptable limit in the meat and seafood examined (Duedahl-Olesen et al., 2006; Reinik et al., 2007). In one study, while the BaP concentration was 0.15 μg/kg, only one of the samples in the products exceeded the limit, due to intense smoke odors and darkening, while all products were considered to have rich BaP content (Jira et al., 2006).

Among PAHs with high molecular weight, it is necessary to determine their maximum levels in drinking water and food, taking into account the carcinogenic potential of those other than BaP.

Factors Affecting the Formation of PAH in Smoking and Solution Suggestions

Smoke Formation Temperature and Filtration

Factors causing PAH formation in smoked products were determined and studies were carried out to develop appropriate methods. The most important factor affecting the formation of PAH is the smoke formation temperature (Ceylan & Şengör, 2015; Jinadasa et al., 2020). When the smoke generation temperature was optimized between 400 and 600 °C, the fish had less PAH formation than when it was outside this range (Hokkanen et al., 2018). It has been reported that BaP formation does not occur in products produced by keeping the temperature of wood pyrolysis below 425°C and the oxidation temperature of pyrolysis volatile products below 375°C using a two-stage smoke generator. In the study, it was stated that as a result of reducing the temperature of wood chips or sawdust pile to 300-400°C and using filters, the PAH content in the smoke could be reduced by about 10 times (Tilgner & Miler, 1963).

Resins

Resin, any natural or synthetic organic compound consisting of a noncrystalline or viscous liquid substance from wind, fire, lightning, or other cause. Most natural resins are exuded from trees, especially pines and firs. Resin formation occurs as a result of injury to the bark. Plants secrete resins for their protective benefits in response to injury. The resin protects the plant from insects and pathogens. Natural or synthetically produced resins are used in many areas in the industry and are also used as chelators due to their ion exchange capacity.

In the smoking industries, the types of wood used to add flavor and aroma to meat vary. Resins on trees used in smoking have also been reported to increase the PAH content in the smoked product. It has been reported that smoke flavors produced commercially for use in the meat and fish industries contain only trace amounts of PAH as a result of the removal of the resinous parts (White et al., 1971; Miler & Sikorski, 1990).

Canned Oils

Although it is known that a significant portion of the PAHs in smoked foods come from wood smoke, the PAH contamination in canned smoked fish is also caused by the vegetable oils used in the can. Some oils are known to contain high amounts of PAHs, at the level of 50 μg/kg. It is stated that the source of PAH in oils may be direct drying processes of oilseeds or the olive mass remaining after

pressing (Stołyhwo & Sikorski, 2005). It has been reported that grape seed oil contains BaP at concentrations of about 20 μg/kg (Moret et al., 2000). It has been reported that the content of BaP in cans of smoked sardines is five times higher in canned oil than in fish (Lawrence & Weber, 1984). To reduce contamination of oils with PAHs, it is recommended to add about 20% activated carbon to the bleaching earth in the refining process.

Traditional Ovens

Studies have reported that in cold and hot-smoked fish, PAH content can vary from raw material to approximately 0.05-60 μg/kg concentration of BaP depending on the fish species, smoking method and smoking parameters, smoke composition, and exposure (Petrun & Rubenchik, 1966; Tilgner & Daun, 1969; Wierzchowski & Gajewska, 1972; Lawrence & Weber, 1984; Nistor, 1985; Duedahl-Olesen et al., 2015; Jinadasa et al., 2020). It has been determined that the BaP content is generally lower, approximately 0.1 μg/kg BaP in smoke-smoked fish produced under modern, fully automatic controlled conditions compared to conventional ovens.

While the BaP content of commercially hot and cold smoked fish was found at a concentration of 4.2-60 μg/kg, BaP content was found to be 1.7 μg/kg in anchovy smoked in an electrostatic device with smoke produced at 25-300°C (Petrun & Rubenchik, 1966). With recent applications, BaP has not been detected in commercially smoked sardines, silver carp, squid, or tuna (Kannappan et al., 2000).

In a study conducted with a large number of smoked marine fish, the total PAH concentration was found to be 46.5 μg/kg in swordfish and 124 μg/kg in herring. BaP, which was not detected in a few fish species, was determined as 0.7 μg/kg in salmon (Storelli et al., 2003).

The average BaP content was determined as 5.12 and 8.43 μg/kg, respectively, in lean and fatty hot-smoked trout fillets by heating the fish to an internal temperature of 82°C for 30 minutes (Zabik et al., 1996). BaP concentration was found to be approximately 12 μg/kg wet weight in fatty sardines smoked for 6 hours at 45-70°C using smoke produced in a conventional oven at 400-600°C. BaP content was determined as only 1.6 μg/kg in fish that were smoked at 45°C for 3.5 hours in filtered smoke produced at a temperature of 300-400°C, followed by drying in the sun for 4-5 hours (Changrasekhar & Kaveriappa, 1985).

Fatty and Lean Fish

PAHs are known to have high lipid affinity. It has been reported that the PAH concentration due to smoking is higher in fatty fish than in lean fish (Akpan et al., 1994; Başak et al., 2010). It was stated that the PAH concentration determined at the end of smoking in fish species with different total lipid levels (salmon and rainbow trout) had a positive correlation with the total lipid levels of the fish.

Exposure Time

Repeating the smoking process may increase PAH formation depending on the exposure time (Jinadasa et al., 2020). In an application with Atlantic bonito, it has been reported that a tar layer of approximately 3% by weight was formed on the surface of the fish as a result of overnight drying after repeated smoking cycles at 80-120°C for several hours. It has been also determined that the BaP content under the formed tar layer is 20-40 times higher than the deeper meat layer (Kikugawa et al., 1986).

Storage

Information on the persistence and distribution of smoke components, including PAHs, in different parts of smoked products during storage, is limited. The diffusion rate of smoke components in fish is controlled by the character of the surface as well as the properties of the meat and the accumulated compounds. Most of the smoke phenols accumulate in the skin and in the layer approximately 6 mm deep of the product, especially in adipose tissue. However, in some products, especially lean fish, up to 60% of the total phenol mass can penetrate deeper layers (Kurko & Mezenova, 1985).

According to Simko (1991), the concentration and distribution of BaP in smoked fish may change during storage due to the varying rate of diffusion and degradation depending on the characteristics of the product and environmental factors. Under the influence of light, PAHs are sensitive to photodegradation and oxidation. It is known that the half-life of PAHs varies from a few hours to a few days depending on the type of PAH. While the BaP concentration in the surface tissue of the fish was 10.6 μg/kg after smoking, it was found to be 0.0 μg/kg in the internal tissues, and it was reported to be 1.3 in the outer tissues and 0.1 in the internal tissues at the end of the 7-day storage period (Simko, 1991). In the same study, it was also determined that the BaP concentration, which was initially determined as 0.6 μg/kg, decreased to approximately 0.1 μg/kg after four days, as a result of aeration in daylight at 18°C.

PAHs in Smoked Food Sources Other Than Seafood

BaP contents were determined as a result of smoking in different products are approximately 0.01-1.11 μg/kg in lightly smoked ham, 0.18-2.08 μg/kg in cooked sausages, and 0.14-56.04 μg/kg in black smoked ham (Potthast, 1978).

Although some smoked fish products may contain high concentrations of PAH, it has been reported that the consumption of smoked meat and fish generally does not contribute to the human uptake of these compounds. According to the Scientific Committee on Food (SCF, 2002), the concentration of BaP from smoked fish accounts for only a small part of the total dietary intake in several European countries.

Fats, grains, and vegetables accounted for 90% of total BaP intake in the United Kingdom, while fats, cereals, sweets, and sugar accounted for 97% of total BaP intake in the Netherlands. However, in local communities where traditionally smoked fish forms a large part of the diet, BaP intake from these sources may be significantly higher.

In conclusion, smoked fish forms an important part of the human diet due to its desirable sensory properties, high nutritional value, and lipids rich in n-3 fatty acid levels. Wood smoke used for smoking fish can contain a wide variety of PAHs, including the most carcinogenic, depending mainly on the temperature of production. With the filtered smoke coming from external generators, smoking in modern smokehouses under suitable conditions allows the production of products away from carcinogenic PAHs. The BaP levels in hot-smoked fish are not above the limit set by different national and European regulations. However, heavily smoked products with smoke from conventional furnaces may contain about 50 mg/kg wet weight concentration of BaP. For this reason, it is very important to eliminate the factors that cause PAH formation in production by using modern application processes in terms of providing healthy products.

BaPs constitute the most carcinogenic group of PAHs, and BaP levels are examined in terms of food safety in smoked products (EFSA, 2008). According to the European Commission and the Turkish Food Codex, the acceptable level of BaP in smoked seafood has been reported to be 2.0 μg/kg (CR(EU), 2011; TFC, 2014).

CONCLUSION

Smoking was a process used to prevent meat from spoiling during the periods when coolers were not invented and wars continued. Today, it is applied to add aroma and flavor to meat as well as its antibacterial properties. Fish is one of the main sources of protein for humans and has a high nutritional content. Although it is mostly consumed fresh, a group of consumers prefer smoked fish. Researchers have encountered PAH contents in fish smoked in conventional ovens and have developed new methods to minimize their toxic effects. Research findings have reached the conclusion that fish produced with developing technology and new methods and kept under appropriate storage conditions are not harmful for consumption.

Compliance With Ethical Standards

Authors' Contribution

Both authors have contributed equally to the paper.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

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