



## ANIMAL SCIENCE

# PAHs impacts on aquatic organisms: contamination and risk assessment of seafood following an oil spill accident

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**Abstract:** Oil spills, intrinsically related to the petroleum production chain, represent a risk to the marine environment and a potential threat to humans through seafood consumption. We revised the NE Brazil oil spill and other accidents along the Brazilian coast, with a focus on seafood contamination, covering topics such as bioaccumulation, bioaccessibility, and risk analysis. Comprehensive knowledge of the impacts of spills helps in the interpretation of the dynamics of hydrocarbons released into the sea, contributing to actions to control their negative impacts. Currently, no legal limits have been established permanently in Brazil for PAHs in seafood edible tissues.

**Key words:** bioaccumulation, Brazilian seafood, human health, oil spill, PAH, toxicity.

## INTRODUCTION

The land-sea transition region encompasses various ecosystems, connecting rivers, estuaries, bays, and the coastal ocean (Bauer et al. 2013). Features such as high rates of primary and secondary productions, high abundance, and biodiversity of flora and fauna are examples of many marine ecosystem services used by humans to build their well-being. Consequently, it results in the attraction and settlement of over 38% of the World's population in the coastal zone (Unep 2014). Indeed, human activities are recognized as posing threats to the health of major Earth systems, including the ocean and its coastal zone, at local, regional, and/or global scales (Ekins et al. 2019).

Developments in the fossil fuel industry - in pace with modern society's demand for energy - have the potential to affect coastal ocean ecosystems and human health (Patin 1999). Most of the oil (and related refined products) directly

affecting coastal (and marine) ecosystems come from chronic inputs, and are related to the oil and gas exploration, production, transportation, refining, and use (NRC 2003). However, acute events of large oil spills also have negative environmental consequences, as observed in the case of the Deep-Water Horizon rig blowout (Ramseur 2010) or the Exxon Valdez in Alaska (Peterson et al. 2003), just to name a few examples. Social and economic impacts are also relevant aspects in the case of a coastal oil spill, including a drastic drop in revenues from tourism and fisheries marketing by local traditional communities and the contamination of seafood (Storelli et al. 2013, Wenzl & Zelinkova 2019).

In a scenario of the high environmental and socio-economic vulnerability of coastal locations and the human population affected by an oil spill, negative impacts can be aggravated due to the different social groups directly impacted by such accidents, the activities affected, and the

profile of the compounds present in the oil and their persistence and bioaccumulation in the marine environment (Fattal et al. 2010, Duran & Cravo-Laureau 2016).

Petroleum and its products are sources of PAHs that are characterized by a predominance of 2-3 rings and alkyl homologs in the naphthalene, phenanthrene, dibenzothiophene, and chrysene series (Tissot & Welt 1984, Wang et al. 2003). Another important origin of polyaromatic compounds includes the combustion of fossil fuels and biomass burning, which produces non-alkylated compounds with 4-6 rings known as pyrogenic PAHs (Wang et al. 1999). The distinct molecular distribution of PAHs is used as tool for assigning sources of petrogenic and/or pyrolytic compounds in the atmosphere, water, sediments, and biological tissues (Tsapakis & Stephanou 2005, Mirza et al. 2012, Asagbra et al. 2015, Sun et al. 2016). For example, bivalves collected near water discharge platforms show enhanced levels of naphthalenes, phenanthrenes, or dibenzothiophenes, all characteristic of petroleum (Neff et al. 2011). A similar bioaccumulation profile of petroleum-derived PAHs is also observed in Guanabara Bay, an oil-residue chronically impacted bay surrounded by the Rio de Janeiro metropolitan region (Francioni et al. 2005, Ramos et al. 2017).

The fisheries body-burden of contaminants in affected areas includes a myriad of organic compounds and inorganic elements (including radioactive) that are present in crude oils (Barescut et al. 2009, Jisr et al. 2020, Ilori & Chetty 2021). Herein, the focus will be on organic compounds, particularly those with a cyclic aromatic structure. In petroleum, the monocyclic aromatic hydrocarbons, namely benzene, toluene, ethylbenzene, and isomers of xylenes (the BTEX fraction) are abundant components but also highly volatile and cause short-term impacts (Neff et al. 2011). In contrast, compounds

with two up to six-fused benzene rings, known collectively as the polycyclic aromatic hydrocarbons (PAHs) (Anderson & Achten 2015, Stout et al. 2015), are of environmental relevance because they are ubiquitous and persistent in aquatic systems, bioaccumulate through the chain food and can act as agents of endocrine disruption, mutagenicity (IARC 2010, Bergman et al. 2013) and/or carcinogenicity (Hwang et al. 2012). In addition, the recognition of the adverse effects of PAHs on human health has resulted in the establishment by government agencies of threshold levels that guarantee the safety of seafood for human consumption, as will be detailed later.

Here, the impact of PAHs derived from the oil spill on fisheries and food safety in coastal systems is addressed. The main goal is to gather information on these subjects obtained following the recent major oil spills around the world, with a focus on the Brazilian scenario. The information available in the country on these subjects, following the mysterious oil spill (Lourenço et al. 2020) that hit the NE Brazilian coast from August 2019 through January 2020 (Soares et al. 2020) was compiled to help understand the dynamics of hydrocarbons released at sea and their potential environmental and socio-economic impacts on the coastal zone and local communities. The purpose of this review is to help guide emergency actions in the aftermath of the oil spill in Brazil, as well as to support the design of public programs and communication to fishermen and consumers about the environmental impacts of oil spills.

### **Oil spill accidents**

Brazil is a reference in oil exploration from marine sources and is also a route for transporting oil from neighbouring countries. In 2020, the average oil production in the country reached 2.94 million barrels per day, while

natural gas reached 127 million cubic meters per day (Petrobras 2020). This high oil production presents associated risks and demands from the petroleum industry, among other environmental requirements, an Individual Emergency Plan (PEI) to prevent accidents and control/mitigate the environmental impacts in the aftermath (Brasil 2019).

In Brazil, oil accidents have been reported in many parts of the country. Back in the 1970s, three accidents of great magnitude were reported: (i) the *Takimya Maru* vessel (1974) in the São Sebastião channel, in the state of São Paulo; (ii) the *Brazilian Marina* (1978) vessel in Rio de Janeiro, in Guanabara Bay (1975), and: (iii) in 2001, when the P36 oil exploration platform in the Campos Basin in Rio de Janeiro caught fire and sank, 1,300 m<sup>3</sup> of gas and 350 m<sup>3</sup> of oil were spilled (Cetesb 2012).

In 2000, Guanabara Bay in Rio de Janeiro was once again affected by an oil spill, the rupture of an oil pipeline leaked approximately 1,300 m<sup>3</sup> of marine fuel (Meniconi et al. 2001). In 2004, in the state of Paraná (South Brazil), the explosion of the Chilean *Vicuña* vessel caused the spilling of millions of liters of bunker oil in the Paranaguá Port, which affected four municipalities and caused the paralysis of fishing for two months (Noernberg et al. 2008). In 2011, another environmental contamination caused by the spill of 3,700 oil barrels, covered 182 km<sup>2</sup> of an area of Campos Bay (Matos et al. 2019). In Pará, in 2015, in the northern region of Brazil, a ship carrying around five thousand oxen sank and spilled about 135 m<sup>3</sup> of oil into the Pará river, in the city of Barcarena. Most of the animals that were to be transported drowned and the oil spilled into the river to such an extent that there was no longer any visual evidence of their presence (O'Briens 2016, Oceana 2020). Matos et al. (2019) reported several accidents with oil spills in the state of Maranhão (Northeast). In

another accident in the Northeast region, in 2015, the leakage of a pipeline connecting the PCM-5 and PCM-6 production vessels spilled 7,000 liters of oil into the sea, in the Bay of Sergipe-Alagoas (Brasil 2017). In 2016, in the Sergipe State, Petrobras was fined for the spill of 1.8 tons of oil, which spread over 30 km in 3 days (Brasil 2017). The causes of the accident are still unclear.

The Brazilian Institute for the Environment and Renewable Natural Resources (IBAMA) also reports several oil spill accidents. For instance, in February 2019, the rupture of a hose during the transfer of oil from the platform P-58 to the São Sebastião ship spilled oil on the coast of Espírito Santo state, SE of Brazil, that spread for 2.4 km; although the slick has been quickly dispersed, the environmental impact has not been measured yet (IBAMA 2019).

More recently, starting in August 2019 and extending for several months, the coastline of 11 states from the Northeast and the Southeast regions were hit by oil residues, causing social, human health, and environmental disruption (Pena et al. 2019). This accident, already considered the biggest environmental disaster in Brazil, impacted 3,600 km of coastline, more than 980 beaches, and more than 5,000 tons of oiled wastes were removed from the marine and land areas (Brasil 2019, Soares et al. 2020). The Brazilian National Health Surveillance Agency (ANVISA) characterizes the product dumped on the coasts of Pernambuco and Paraíba as crude oil, before spreading to the Southeast Region, into the states of Espírito Santo and Rio de Janeiro (Carmo & Teixeira 2020). Chemical analyses classified the oil as Venezuelan crude, but the accident's origin and causes are not yet known (Disner & Torres 2020). According to reports, almost two years after the accident, oil stains reappeared on some Brazilian beaches (northeast) (Brasil de Fato 2020, *Jornal da Band*

2021). The medium and long-term impacts of the oil spill remain unpredictable.

### PAHs toxicity

As previously mentioned, among the several hundreds of hydrocarbons found in petroleum, the major compounds of environmental concern – due to their negative impacts on the ecosystem and human health – are the aromatic ones, which may represent as much as 5% of crude oils (Hodson 2017). Whereas the petroleum abundant monocyclic aromatics hydrocarbons (BTEX) are relevant only in the short-term impacts after an oil spill, as they are quickly transported to the atmosphere, the polycyclic aromatic hydrocarbons (PAHs), with two to at least 6 fused rings, are persistent and bioaccumulative toxicants (Neff 2002).

The toxicities of several PAHs are well established and, in the case of human health, are usually associated with several types of cancers and degenerative diseases (Albers 2003, Hamidi et al. 2016). In wildlife, the negative effect of PAHs exposure includes, for example, reduction of marine plant diversity (Saifullah & Chaghtai 2005), hematopoietic disorders in oysters *Crassostrea gigas* (Donoghy et al. 2010), and reduced functionality of the innate and acquired immune systems in fish (Reynaud & Deschaux 2006), among others.

The recognition of the risk associated with PAHs exposure has led the United States Environmental Protection Agency (EPA) to rank in the early 1970s sixteen compounds as priority pollutants. These included only non-alkylated with 2 to 6 fused rings PAHs, which reflected the limited analytical capability of quantifying PAHs in environmental samples, rather than the recognition of their intrinsic toxicities (Anderson & Achten 2015). The list is now known to be limited in properly addressing the environmental fate and effect of PAHs in aquatic systems, and

over forty individual PAHs, including parental and alkylated compounds, are included in such evaluations (Stout et al. 2015, Boehm et al. 2018). The presence of oxygenated and nitrated-derivatives PAHs is also a matter of concern in recent years (Cousin & Cachot 2014, Wincent et al. 2015).

Paradoxically, that most of the information regarding negative biological effects is available for parental rather than alkylated PAHs (Fallahtafti et al. 2012). For instance, both the US-EPA and the International Agency for Research on Cancer (IARC 2010) include only parental compounds in the list of PAHs that may pose a carcinogenic risk to humans (Table I). Humans are exposed to PAHs through inhalation, dermatological contact, or consumption of contaminated food. The PAHs represent high risks to human health due to their lipophilic characteristic (Hamidi et al. 2016). These lipophilic compounds are easily bioaccumulated in organisms and biomagnified through the marine food chain, reflecting seafood contamination, including seaweed (Figure 1) (Fogaça et al. 2018, Nisha et al. 2019). To control the health risk due to consumption of contaminated seafood, the ‘limit of concern’ (LOC) is usually considered. The LOC represents the maximum concentration of carcinogenic PAHs allowed in the seafood in a risk assessment protocol, which also considers other aspects, like consumption habits, time of exposure, and population age (e.g., Wenzl & Zelinkova 2019).

One approach to defining the LOC of PAHs in seafood is the consideration of toxic equivalencies (TEQ) of individual PAHs (only 4 to 6 ring-PAHs) to benzo(a)pyrene, as adopted by NOAA/USA after the Gulf of Mexico Deep-Water Horizon oil spill in 2010 (Ylitalo et al. 2012). This was the same approach adopted by the Brazilian Health Regulatory Agency (ANVISA) after the mysterious oil spill in NE Brazil by launching a Technical Note (27/2019/SEI/GGALI/

**Table I. PAH classification.**









Compound	Classification		Molecular weight g/mol	Number of rings	Carcinogenicity
	IARC <sup>a</sup>	USEPA <sup>b</sup>			
Naphthalene	2B	C	128.1	2	Weak
Acenaphthylene	3	Not available	152.1	3	Weak
Acenaphthene	3	Not available	154.2	3	Weak
Fluorene	3	D	166.2	3	Weak
Phenanthrene	3	D	178.2	3	High
Anthracene	3	D	178.2	3	Weak
Fluoranthene	3	D	202.3	4	Weak
Pyrene	3	D	202.3	4	High
Benz(a)anthracene	3	B2	228.3	4	Moderate
Chrysene	2B	B2	228.3	4	High
Benzo(b)fluoranthene	2B	B2	252.3	5	Moderate
Benzo(k)fluoranthene	2B	B2	252.3	5	Moderate
Benz(a)pyrene	1	B2	252.3	5	High
Dibenzo (ah)anthracene	2A	B2	278.4	5	Moderate
Benzo(g,h,i)perylene	3	D	276.3	6	Moderate
Indeno(1,2,3-c,d)pyrene	2B	B2	276.3	6	High

<sup>a</sup> 1 - carcinogenic to humans; 2A - probably carcinogenic to humans; 2B - possible carcinogenic to humans; 3 - unclassifiable as carcinogenic in humans; 4 - probably not carcinogenic to humans (IARC 2002; IARC 2009). <sup>b</sup> A - human carcinogens; B - probable human carcinogens; B2 - probable human carcinogens based on sufficient carcinogenicity evidence in animals; C - possible human carcinogens; D - not classifiable yet; E - evidence of non-carcinogenicity for humans (USEPA 1986).

DIRE2/ANVISA). In this note, it was considered the consumption of 180 g of fish per day and 60 g of crustaceans and molluscs per day, five-year of exposure, and the benzo(a)pyrene (BaP) equivalent, which means the weighted sum for 8 PAHs (benzo(a)anthracene, chrysene, benzo(a)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indene(1,2,3-cd)pyrene and benzo(g,h,i)perylene). The calculated LOC in BaP-toxic equivalents was 6 µg/kg (or ng/g) for fish and 18 µg/kg (or ng/g) for crustaceans and molluscs.

Another example to establish LOC for PAHs is the legislation adopted in the European

community for regular consumption of fisheries that might be chronically contaminated, which defines the maximum concentration (i.e., the LOC) of 5.0 µg/kg for benzo(a)pyrene or 30.0 µg/kg for the sum of benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene and chrysene (Regulation EC n.835/2011). It is noteworthy that this regulation is an update of an earlier version (Regulation EC n. 1881/2006), excluding threshold values for edible fishes and crustaceans based on the assumption that these animals can metabolize PAHs and thus have a low tendency to accumulate them in muscle tissues.

Type of seafood	Trophic level/Contact with PAH	Bioaccumulation	PAH effects	PAH bioaccessibility
Fishes 	Carnivore/Omnivorous Low contact	Low 	Liver tissue necropsy, changes in gills, growth reduction, behavioral changes	Low 
Crustaceans 	Carnivore/herbivore/detractor Middle contact		Branchial lesions	
Mollusks 	Filters High contact		Not available	
Seaweed 	Filters High contact		High	

**Figure 1.** Oil spill impacts in different types of aquatic organisms based on where they live, feed, and breed and how mobile they are.

**Effect of PAH bioaccumulation reported in Brazilian aquatic organisms**

Several researchers have focused on identifying and quantifying the environment PAHs to evaluate their effects on aquatic organisms and the ecological disturbances in marine wildlife (Maranho et al. 2006, Froehner et al. 2011, Craveiro et al. 2021). PAH can bioaccumulate in different animal groups through biomagnification, even over long distances, being transported by sea currents and wind actions, reaching vulnerable ecosystems (Szewczyk 2006). Due to its persistence in the environment, studies show that even months and years after an oil spill at sea, it is still possible to find PAH residues in animal tissues, water, and sediment (Silva et al. 2009, Souza-Bastos & Freire 2011). In a short time, there was a reduction in the richness, diversity, and uniformity of the seaweed *Jania capillacea* due to its oil coating, on Paiva beach (Pernambuco state, North-eastern Brazil), however, after two months its characteristics

soon returned to the original state (Craveiro et al. 2021).

The impact of the oil spill causes different levels of PAH bioaccumulation in filtering and high trophic level aquatic organisms (Figure 1) (Euzebio et al. 2019, Instituto Terra-Mar 2019). Filtering organisms, such as molluscs, can absorb high levels of contaminants in their tissues (Wilson et al. 1992, Araújo et al. 2016, Shi et al. 2016). Fish and crustaceans have shown a low capacity to bioaccumulate PAH (Graham et al. 2015, Lourenço et al. 2018).

Since the feeding habits influence PAH bioaccumulation, carnivorous fish shall accumulate higher levels of these compounds. However, Soares-Gomes et al. (2010) did not observe a significant difference in the PAH concentrations among the carnivore sea bass (*Centropomus parallelus*), the detritivore benthic mullet (*Mugil liza*), and the detractor crustacean mangrove crab (*Ucides cordatus*). Although the authors observed those barnacle organisms

were the most sensitive to the presence of oil in the water, due to their low efficiency in metabolizing such compounds. Elasmobranch, fish, invertebrate, and mammal species are especially vulnerable to exposure to oil spills, as they are species restricted to a depth of less than 100 m (Magris & Giarrizzo 2020).

Several species exposed to oil have shown physiological abnormalities associated with high concentrations of these compounds in their tissues. Researchers have found that the PAH presence in the environment causes necropsy in fish liver tissues; histological changes in branchial cells, with negative consequences for gas exchange and osmoregulation; growth reduction, among other impacts (Silva et al. 2009, Short 2017). The tetra *Astyanax* spp. showed gill alterations, liver inflammation, and histopathological injuries when exposed to water contaminated by the oil spill in the Pantanal Arroio Saldanha, in Parana state (Silva et al. 2009). The marine catfish (*Genidens genidens*) collected from Guanabara Bay, Rio de Janeiro State, showed blood alterations, genotoxic and physiological damage (Freire et al. 2020). Mangrove crabs, used as bioindicators of environmental health in a port and mangrove region in Brazil Northeastern, showed branchial lesions when collected near the port region, associated with the poor water quality and presence of PAHs (Carvalho Neta et al. 2019).

The PAH presence in the marine environment is not necessarily the result only of oil spills, it is also associated with intense urban-industrial activity (Froehner et al. 2011), which intensifies the impacts of contamination on aquatic organisms.

These effects are correlated with highly contaminated areas where aquatic organisms live. Mussels (*Perna perna*) collected in an area with intense urban-industrial activity showed high PAH concentration in their tissues

compared to those further away from the urban area (Santiago et al. 2016). Camargo et al. (2017) have shown that the presence of PAHs was a cause of alteration in the structure of the benthic macrofauna in Guanabara and Laranjeira bays (Rio de Janeiro and Paraná state, respectively).

The presence of PAH in the marine environment will not always be reflected in acute adverse effects on aquatic organisms, especially those that metabolize and excrete such compounds (Bandowe et al. 2014, Lourenço et al. 2018). For instance, Lourenço et al. (2018) evaluated the presence of PAH and trace elements in *Coranx crysos* and *Tylosurus acus* tissues and demonstrated that their presence characterizes the production of water from oil and gas platforms in the Campos Basin (Rio de Janeiro state) as minimally polluted.

Another effect observed in aquatic organisms exposed to PAH is related to the behaviour of these species. Tambaqui fish (*Colossoma macropomum*) showed changes such as reduction in swimming activity and predatory behaviour, associated with the lamellar and gill fusion, when exposed to insoluble crude oil fractions from an Oil Company located on the Urucu River, in the state of Amazonas (Kochhann et al. 2015). The presence of oil in the water affected the fish breathing and the water-air interface (Magris & Giarrizzo 2020).

### **PAH consumption and health risk**

The impact of the oil spill has irremediable effects on many aquatic species (Baršienė et al. 2008, Bado-Nilles et al. 2009, Chen & Denison 2011, Yüewen & Adzigbl 2018). In addition, the presence of oil slicks or their fractions makes these organisms vulnerable, affecting the entire food web, including humans, since the consumption of oil-contaminated seafood represents a risk to human health.

The 2 to 6 ring PAHs are a concern for short and medium-term food safety (Yender et al. 2002). Although the toxicity potential of PAHs is recognized, to assess whether there is a risk in consuming seafood in oil-contaminated areas, a level of concern must be established (Gohlke et al. 2011). The Food and Drug Administration (FDA) provides guidelines for the types and amount of seafood that consumers can eat, after the Gulf of Mexico oil spill (Graham et al. 2015). Even in the USA, scientists are concerned about allowable intake doses combined with food consumption data or consumption scenarios (Scholl et al. 2012) to determine the risk associated. This is because some ethnic groups have a higher consumption of seafood per kg of body weight. In this case, these thresholds, as well as the risk assessment of seafood intake in general, are questionable (Marques et al. 2011).

The PAH intake of seafood was estimated to be 15.3 ng / kg body weight per day for Koreans. Furthermore, high molecular weight and carcinogenic PAH profile have been observed in bivalves molluscs, although these food products only account for 29% of total PAHs consumption (Moon et al. 2010).

The PAH concentrations of 0.04 to 1.17 ng/kg body weight per day found in *Sardina pilchardus* and *Solea solea* collected at Catania by Ferrante et al. (2018), did not represent a risk to human consumption, as such concentrations are below the defined maximum limit by European Food Safety Authority (EFSA). Although low molecular weight PAHs are not classified as carcinogens, their chronic ingestion can cause negative impacts on human health (Rotkin-Ellman et al. 2012).

It seems that the concern about the concentration of PAHs in aquatic organisms for human health is due to the culture of consumption of such proteins. For the adult population of Kuwait, the estimated mean

daily consumption of seafood was 66.4 g/day, lower than that set by the US EPA (142.2 g/day) (Alomirah et al. 2009). These authors observed that even the high presence of low molecular weight (LMW) PAH in fish consumed by the Kuwait population does not pose a health risk. The high concentration of naphthalene and phenanthrene in fish also poses no risk to the Canadian population, even with an average daily intake of PAH from seafood was 1.097 ng/day for men and 1.051 ng/day for women (Ohiozebau et al. 2017).

Recently, in Brazil, Massone et al. (2021) observed levels of some PAHs with carcinogenic potential in sardine muscles (*Sardinella brasiliensis*). The authors state that the presence of B(a)P, whose concentration was higher than 6 µg/kg in 4% of their samples, does not represent a risk to the consumption of this fish. However, it is important to continue monitoring Brazilian fish to ensure food safety.

The PAH profile in fish muscles is generally characterized by low molecular weight compounds, most likely due to the difficulty of organisms to bioaccumulate high molecular weight PAH (Ni & Guo 2013, Akhbarizadeh et al. 2019). The concentration of PAH in fish muscles also varies according to their trophic level, due to the interaction between PAH and the lipid content of different species (Recabarren-Villalón et al. 2021). Furthermore, intrinsic (sexual maturation stage, age, body weight) and extrinsic factors (food web position, lifestyle, food availability) contribute to the differences in the concentration of these compounds (Mahugija & Njale 2018, Habibullah-Al-Mamun et al. 2019).

Most studies on the concern about the consumption of contaminated fish, such as Oliveira et al. (2020), highlight the concentration and profile of PAH in fish muscles. These authors observed that the Portuguese population is



more vulnerable to the carcinogenicity of PAHs when they feed on whitemouth *Argyrosomus regius* from captivity, due to the high presence of high molecular weight (HMW) PAHs in their samples.

To enhance the taste and improve the appearance, fish are often consumed after undergoing some culinary processing. However, its nutritional content can change according to the addition of spices and/or thermal processing. Thus boiling, cooking, grilling, and roasting, among others, can reduce the concentration of contaminants in food matrices, making them safer (Mi et al. 2017, Girard et al. 2018).

Depending on the culinary treatment, PAHs may also tend to aggregate to lipid particles in the gastrointestinal tract, due to their lipophilic characteristics, making them more bioaccessible during the digestive process (Harris et al. 2013). The EC Regulation number 1881/2006 and subsequent amendments (EC Regulation No. 835/2011 and 1327/2014) set the maximum allowable concentration of B(a)P for non-smoked fish (2 µg/kg wet weight), for crustaceans and cephalopod molluscs not smoked (5 µg/kg wet weight) and for not smoked bivalve molluscs (10 µg/kg wet weight) (Ferrante et al. 2018).

The PAH dietary daily intake (DDI) in smoked fish for Nigerians was estimated to *Clarias gariepinus* (0.039 mg/day), *Tilapia zilli* (0.052 mg/day), *Ethmalosa fimbriata* (0.038 mg/day) and *Scomber scombrus* (0.195 mg/day). A DDI value for the total carcinogenic PAHs (ΣCPAHs) was highest for *E. fimbriata*, indicating a greater risk of consumption of this species compared to the others (Tongo et al. 2017). It is evident, therefore, that cooking techniques using burning can make PAH bioavailable to the human body through seafood consumption.

In countries whose fish consumption represents the main source of animal protein, the risk analysis for human health is extremely

important to ensure food safety. The average consumption of fish in the world is 20.5 kg/per capita, however, in Brazil, such consumption depends on the region. In the Amazonian region, for example, they consume about 50 kg/per capita/year of seafood, about five times higher than the Brazilian average and almost three times higher than the world consumption (Gervásio 2019, FAO 2020).

Although the vast majority of studies indicate that there is no risk in consuming seafood with some levels of PAH, it is important to continue monitoring these compounds. Fish consumption contributes 13.1% and 8.1% of LMW and HMW PAH, respectively, being the third category of foods that provide the most contaminants for humans through their daily consumption (Yu et al. 2015).

Yu et al. (2012) observed that consumption in large quantities of clam *Macra chinensis* e snail *Bellamya* poses a risk to human health due to the high potency equivalent concentrations and PAH values could pose a carcinogenic risk.

The presence of PAH in the edible tissues of octopus *Octopus vulgaris*, *Octopus maya*, and *Eledone cirrhosa* do not represent a health risk, with overall LMW PAH concentrations being 86–92% of the total (Oliveira et al. 2018). The concentration of non-carcinogenic PAH can also reveal a picture of risk to human health and aquatic organisms (Nasher et al. 2016) because it represents a chronic exposure of consumers and bioaccumulation of these compounds in the environment.

Fish consumption is generally encouraged due to the benefits associated with its lipid composition, omega-3 and omega-6, and other nutrients; on the other hand, depending on the fishing/farming location, these organisms may be more vulnerable to contaminants, and consuming them may pose a health risk (Oliveira et al. 2020, Ju et al. 2022). Thus, the

risk assessment for the consumption of fish associated with sites of intense anthropogenic activity and accidents with oil spills must continue.

In addition, there are new tools to assess the bioavailable amount of contaminants in seafood. Bioaccessibility refers to the portion of the food that is released after digestion in the gastrointestinal tract (Saura-Calixto et al. 2007), reaching the systemic circulation and becoming bioavailable. Quantifying the bioaccessibility of these compounds would make risk analysis more realistic (Afonso et al. 2015). Bioaccessibility reduced the PAHs concentration in marine and freshwater fish muscles. This shows that the level of concern about the consumption of contaminated seafood is overestimated. Besides, the LMW PAHs are more bioaccessible for the gastrointestinal tract than those HMW PAHs, because of the hydrophobic characteristics (Wang et al. 2010).

Recently, studies have shown that bioaccessibility has reduced the level of daily intake of PAHs in samples of mussels (Fogaça et al. 2018) and oysters (Hong et al. 2016). Unfortunately, in Brazil, there are still no studies on the PAH bioaccessibility in seafood. And the results of the PAH bioaccumulation analyses in samples collected after the oil spill in NE Brazil are still in the processing and publication phase. Therefore, there will be only one scenario of the impact of the accident in the coming years.

## CONCLUSIONS

In the year that Ocean Decade begins, it is necessary a greater scientific and civil demand from the government authorities in assigning plausible punishments to those responsible for the causes of oil spills. In addition, the literature lacks further scientific research on the chronic effects of exposure to spots by aquatic

organisms, especially those targeted by fishing and aquaculture, whether or not the product is validated for human consumption.

## Acknowledgments

This work was supported by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Grant 26/2019, Program Capes Entre-Mares 0009/2020).

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#### How to cite

MELO PTS, TORRES JPM, RAMOS LRV, FOGAÇA FHS, MASSONE CG & CARREIRA RS. 2022. PAHs impacts on aquatic organisms: contamination and risk assessment of seafood following an oil spill accident. *An Acad Bras Cienc* 94: e20211215. DOI 10.1590/0001-376520220211215.

*Manuscript received on August 31, 2021;  
accepted for publication on February 1, 2022*

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### Author contributions

Authors contributed to the article as follows: Melo PTSM was responsible for the investigation and writing. Carreira RS, Massone CG, and Torres JPM were responsible for the supervision, writing, and manuscript preparation. Fogaça FHS and Ramos LRV were responsible for the elaboration of the figures and tables and general support in the elaboration and writing of the manuscript. All authors approved the article.

