University of California, Santa Cruz

Environmental Contaminants and Chemical Toxicants in Seafood and Consumer Risks

Senior essay submitted in the satisfaction of the senior exit requirements for the degree of:

Bachelor of Science in Chemistry

By: **Kyle Boog**

December 2017

Faculty Sponsor: Scott Oliver

Table of Contents

Abstract

Consumption of seafood can contribute to a healthy and balanced diet, but this food group can also contain potentially high/moderate levels of a number of environmental contaminants that can pose a risk to human health. Environmental contaminants refer to harmful chemicals present in soil, air, and water. They come from either human sources such as manufacturing or from natural sources such as algal blooms. The environmental contaminants that are discussed in this paper are brominated flame retardants (BFRs), perfluorinated compounds (PFCs) and polychlorinated biphenyls (PCBs) which all come from human sources. These contaminants get absorbed by the seafood and get transferred into our body when they are consumed. Other chemicals that are present in seafood are trace metals. Trace metals are metals that are present in living tissues in animals that function as catalysts in enzyme systems. There are also chemical toxicants that are in seafood caused by processing. These processing techniques induce the formation of contaminants in the form of nitrosamines or they add the contaminants such as when seafood is being sanitized through ozonation. All of the contaminants and toxicants pose risks when consumed in large quantities such as reproductive effects or other acute/chronic effects. Thus far there is potential to control these health effects. There are reference doses that the Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) have as a guide for safe food consumption.

Introduction to Environmental Contaminants

Environmental contaminants refer to harmful chemicals present in soil, air, and water. Since seafood has access to all three of these things, they are at risk. Environmental contaminants are a topic of growing interest in the scientific community since the consumption of seafood is a major route for human exposure. These contaminants include various types of pollutants such as brominated flame retardants (BFRs), perfluorinated compounds (PFCs) and polychlorinated biphenyls (PCBs).

Brominated Flame Retardants (BFRs)

Brominated flame retardants (BFRs) are mixtures of man-made chemicals that are intentionally added to a wide variety of commercial products, such as plastics, textiles, and electronics/electrical equipment.[1] BFR-treated products, either in use or as waste could release small amounts of chemicals to the environment, being able to contaminate air, soil and water. These pollutants could be exposed to humans through their diets. Diet has been estimated to be the main path of BFR entrance since seafood has high BFR content. The chemical structure of the BFR depend on the type of BFR compound and degree of bromination. **Figure 1** shows the chemical structure of different BFRs.

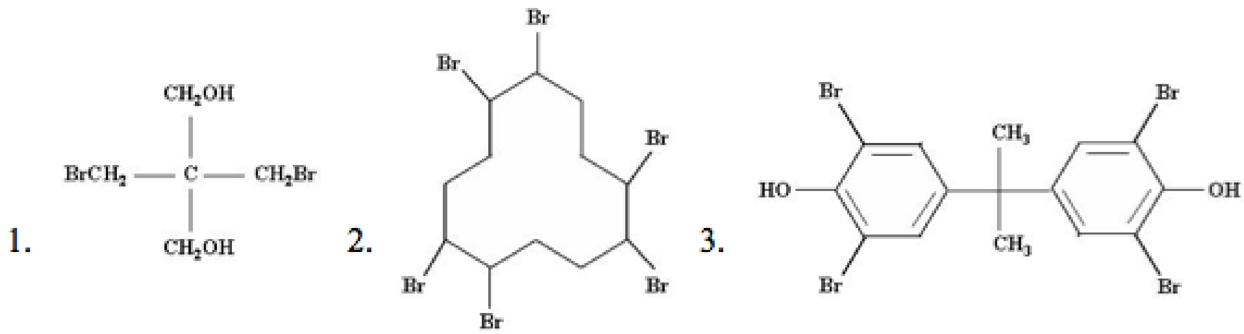


Figure 1: Chemical structures of different BFRs. 1. Aliphatic ex: dibromoneopentyl glycol (DBNPG) 2. Cycloaliphatic ex: hexabromocyclododecane (HBCD) 3. Aromatic ex: tetrabromobisphenol A (TBBPA)[2]

Based on their structure, BFRs can be divided and sorted into three different classes, which include aliphatic, cycloaliphatic and aromatic. The bromine moiety of the organic compound increases lipid solubility and reduces water solubility.[2] The bromine substituent and its potential organohalide metabolites increase the inherent toxicity of the compound as well, which makes many BFRs toxic. **Figure 2** shows a schematic representing the environmental behavior of BFRs. Almost all the BFRs used are the more substituted or higher brominated compounds.

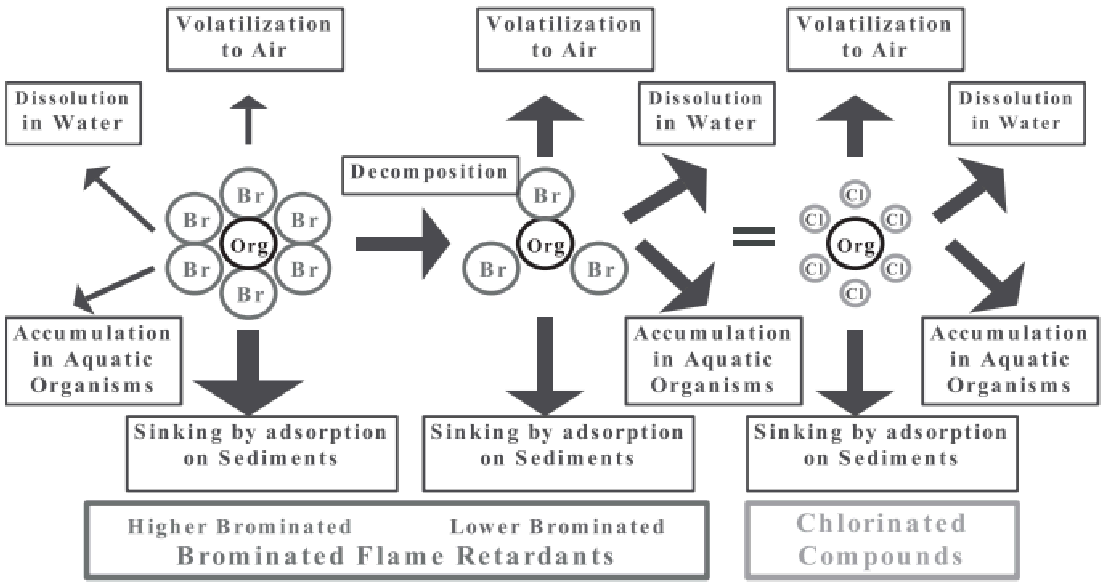


Figure 2: Schematic representation of environmental behavior of brominated flame retardants[3]

The more substituted or higher brominated compounds are less mobile in the environment since they have low volatility, water solubility, bioaccumulation, and strong adsorption on sediments. This is because the electron-withdrawing ability and physical size and shape, of the bromine substituent impacts the chemical reactivity of the compound. The majority of the higher brominated compounds end up in sediments. In contrast, the lower brominated compounds, including environmental decomposition products of BFRs, are more volatile, water soluble and bioaccumulative so they end up in marine organisms and in humans. The environmental behavior of the lower brominated compounds is very similar to the polychlorinated biphenyls (PCBs).

Perfluorinated Compounds (PFCs)

Perfluorinated compounds (PFCs) include a large group of anthropogenic fluorinated organic substances characterized by a fully fluorinated carbon backbone, typically 4-14 in length, and a charged functional moiety.[4] Their unique physicochemical properties such as oil and water repellence, resistance to thermal, chemical or biological degradation and extremely low surface tension make them suitable materials for many industrial applications. They are used in the formulation of stain repellents, coatings, textiles, paints, waxes polishes, electronics, fire-fighting foams, surfactants, emulsifiers, additives, food packaging and other products. Toxic and epidemiologic effects of PFCs have been extensively reviewed and the adverse outcomes have shown a moderate acute toxicity. The most commonly studied PFC substances are the perflouorinated sulfonates and the perfluorinated carboxylates; perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), which can be shown in **Figure 3**.

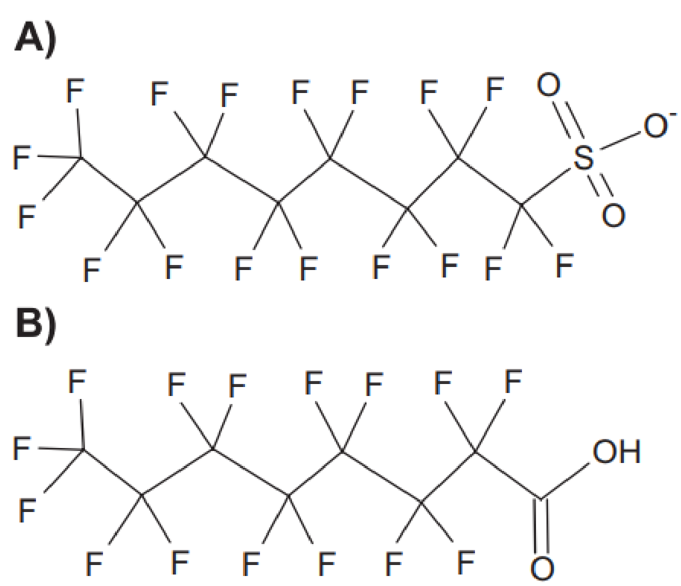


Figure 3: Chemical structure of typical perfluorinated substances. (A) Perfluorooctane sulfonate (PFOS) and (B) perfluorooctanoate (PFOA)[5]

PFOS and PFOA are considered reference substances and have been the most frequently quantified in food and drinking water. Fish and seafood are considered the major contributors to the exposure to PFOS and the long chain PFCs.

Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) include more than 200 different compounds that were used in various formulations as liquid insulators in electrical equipment.[6] PCB-containing oils leaked from electrical equipment directly into food substances, such as rice oil in Japan and Taiwan. The initial concerns were direct overt toxicity and reproductive effects, and acceptable daily intakes were defined as 100-fold and 10-fold below the no-effect levels in animal and humans, respectively.[6] The PCB mixtures that are consumed in seafood are likely to be different from the original mixtures due to the rapid degradation of some of the compounds in the environment and in the aquatic organisms. The chemical formula is $C_{12}H_{10-n}Cl_n$, where n is the number of chlorines that ranges from 1 to 10. The general chemical structure can be shown in **Figure 4**.

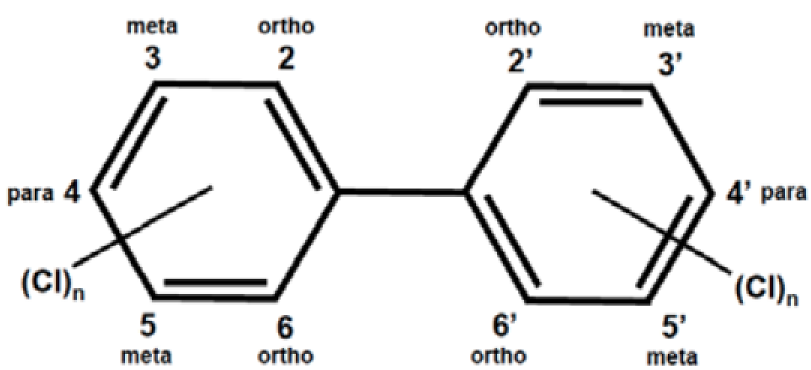


Figure 4: The general chemical structure of PCBs[7]

The chemical configuration of PCBs consists of a biphenyl structure of two connected benzene rings, where some or all of the hydrogen atoms are substituted by chlorine atoms. The toxicity of a specific PCB depends on both the number of chlorine atoms and the chlorination pattern, which can lead to the structure of toxic compounds.

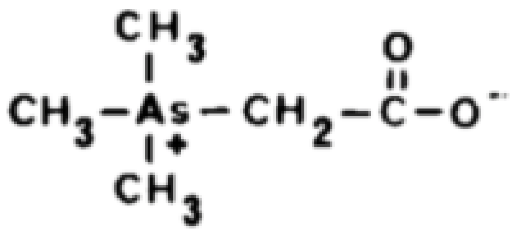
Chemical Toxicants and Potential Health Effects

1. Trace Metals

Different metals can be classified as having major, modest, minor, or no potential for toxicity.[6] The metals with major potential for toxicity include antimony, arsenic, cadmium, chromium, lead, mercury, and nickel. Contaminants with a modest potential for toxicity include copper, iron, manganese, selenium, and zinc. Contaminants with minor or no toxicity are aluminum, silver, strontium, thallium and tin. The metals discussed here are arsenic, cadmium, lead, mercury, and selenium.

a. Arsenic

Arsenic has a long history as a potent poison of humans and other animals. It is used in the manufacture of pesticides, herbicides, and other agricultural products and is a by-product of mining and smelting operations. When ingested, inorganic arsenic may cause acute or chronic toxicity and is of primary concern. Its toxicity is dependent on its oxidation state and route of exposure. The predominant forms of arsenic that exist in aquatic animals are in the organic form of either arsenobetaine or arsenocholine as shown in **Figure 5**.

1. 

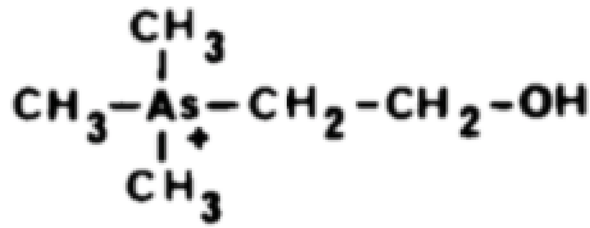
2. 

Figure 5: Chemical structures of organic forms of arsenic: 1. Arsenobetaine 2. Arsenocholine[7]

These forms have been dubbed "fish arsenic" and there are no toxic effects from their ingestion that have been reported in animals. Both organic arsenic in seafood and inorganic arsenic in water have shown to be absorbed by the gastrointestinal tract.

b. Cadmium

Cadmium is unique among toxic metals because it is a relatively recent contaminant of the aquatic environment. Its sources are solid waste dumping and cadmium-containing sewage sludge, the use of phosphatic fertilizers, electroplating and galvanizing manufacture, and mining wastewater. Invertebrates, both crustacean and bivalves, tend to cumulate metallic cadmium in large amounts by binding to various high-molecular-weight metallothioneine ligands. Because hepatopancreas may be considered a delicacy or marketed as "brown crab meat," the potential for ingesting large amounts of cadmium when eating lobsters or crabs is increased.

c. Lead

Lead has the longest history of environmental contamination and toxicity to humans. Sources of lead can be found in the environment and the metal is available is ubiquitous, being commonly found in food, water and air. Environmental lead is a product of storage battery, ammunition, solder, pigment, pipe, brass, and real lead manufacture. Oral ingestion of inorganic lead is the primary entry into humans. Lead damages the brain and leads to mental retardation in children. It can also cross the placental barrier and is a good correlation between maternal and fetal blood lead values so therefore fetus and newborn babies are at primary risk from contaminated seafood.

d. Mercury

Mercury exists in elemental form, as monovalent or divalent salts, and methylated where the methylated form is most toxic to humans. Methylmercury is formed in the environment from the divalent salts by anaerobic bacteria. It is easily absorbed after ingestion and it has a half-life in humans of 60-120 days and a half-life in fish of up to 2 years where elimination usually occurs in the urine and feces .[6] The metal is known to cause chromosomal alterations resulting in cellular damage, with the kidney and brain as target organs.

e. Selenium

Selenium is a metal that functions both as an essential nutrient as well as a poison at slightly higher levels. Selenium levels in water from seleniferous areas are often quite high due to contamination from fossil fuel combustions and paint, alloy, photoelectric battery, and rectifier manufacture. Selenium exists in a number of oxidation states and they may bond with other metals or organic substances such as amino acids. It is responsible for toxic hepatitis with eventual fibrosis in chronic exposures.

2. *Organic Compounds*

2, 3, 7, 8-Tetrachlorodibenzo-*p*-dioxin (TCDD), one type of organic compound, is a byproduct of industrial or combustion processes and is called a "dioxin," which refers to the polyhalogenated dibenzo-*p*-dioxins and furans.[8] The general population is exposed to dioxins through foods that contain animal fat such as seafood. Its effects have been linked to severe dermatitis and fetal toxicity. The general chemical structure of TCDD is shown in **Figure 6** where the location and number of chlorine substituent varies.

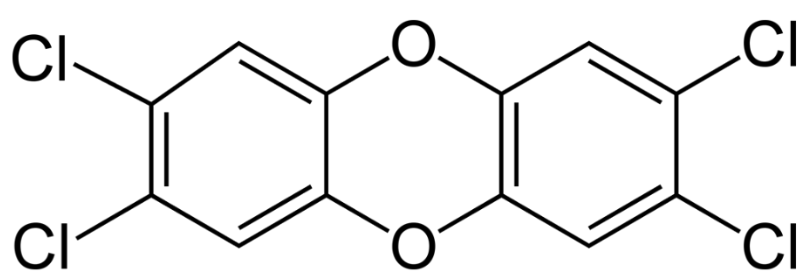


Figure 6: The general chemical structure of TCDD[8]

Since 1977, many independent studies have all found TCDD to be carcinogenic. The studies concluded that the TCDD caused tumors at numerous tissue sites and by different routes of exposure. Due to the chronic low-level exposure TCDD accumulates in human tissue at a high rate.

Dichlorodiphenyl trichloroethane (DDT), another type of organic compound, is a chlorinated hydrocarbon pesticide. In the 1950s, DDT was being manufactured and used on a massive scale in agriculture and in public health. The pollution of the lakes and eventually the seas by the pesticides were caused by the dissolving of the substances present in the atmosphere from the burning waste, in soils and landfills by rainfall and by the sewage distribution.[9] The compounds have low water solubility so it is easy for the fish and seafood to absorb and retain the compounds in the fatty tissues. At high doses, DTT is neurotoxic in animals and humans and there is some evidence that it can affect the reproductive system at occupational exposure levels. **Figure 7** shows the distribution of the organochlorine chemicals in the environment and their accumulation in seafood.

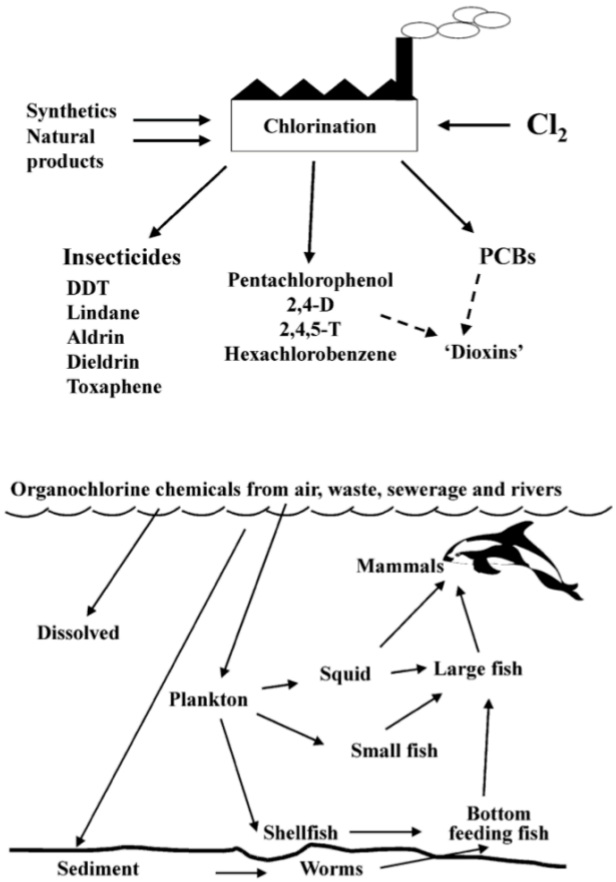


Figure 7. Production and distribution of persistent organochlorine chemicals in the environment and their accumulation in the marine food chain to edible shellfish, fish and mammals[10]

The distribution and uptake of organochlorine compounds from aquatic environments by marine life is dynamic, complex and subject to seasonal variations and local conditions. **Figure 7** shows that deepwater fish can also have significant levels of contamination due to the organochlorine chemicals being absorbed into the sediments and into the worms and eventually into the fish.

3. *Contaminants as a Result of Processing*

Nitrosamines

Nitrosamines, a contaminant as a result of processing, are a group of potent carcinogens, which have been detected in various fish products and can induce tumors in various animal species.[11] Humans are exposed to them through diet, other environmental sources and from endogenous synthesis within the body. They can be formed in smoked fish products as well as in the human stomach due to the presence of secondary amines and nitrite. The general chemical structure of TCDD can be shown in **Figure 8.**

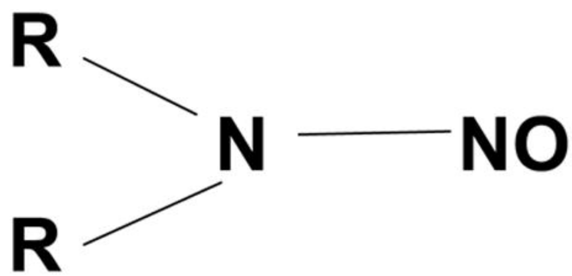


Figure 8: The general chemical structure of Nitrosamines[12]

Nitrosamines are formed by the reaction of nitrogen oxide with, mainly, secondary amines present in the fish. They are metabolically converted via oxidative enzymes into a number of metabolites, some of which bind to the DNA molecule to form adducts associated with activating point mutations which are found in numerous human cancers.

Residues of Ozonation

Ozone, another contaminant as a result of processing, has been shown to deactivate a large number of organisms which include bacteria and parasites.[13] It has been used in the food processing industry, both as gaseous ozone and dissolved in water to reduce bacteria on a wide range of food products and contact surfaces. The main objective is to reduce the bacteriological index that occur in the storage systems, so the bacteria does not grow on the meat or seafood. There is also concern that when ozone comes in contact with seafood, the ozone will become a component of the food and change the character. **Figure 9** shows halibut being washed with ozonized water so it reduces the bacteria.

Figure 9: Halibut fillets washing with ozonized water[13]

The ozonized water for dipping and washing fish or fish fillets shows an effective reduction of microbiological flora, while there is no physical effect on the fish. The FDA has raised questions about the safely of the process because of the likelihood of the reaction byproducts of the resulting oxidation such as the bromate ion if the water contains bromide ions and dichloroacetaldehyde if the water contains chlorine as a secondary disinfectant. The fish could potentially absorb the ozone and when injected could affect the health of others.

Consumer Risks

Classic Acute and Chronic Toxic Effects

The classic acute and chronic toxic effects are based on the types and levels of chemical contaminants in the seafood. For example, people with chronic lower level exposure to mercury can experience nonspecific health effects such as fatigue, difficulty concentrating, hair thinning, muscle and joint pain, sleep disturbance, and gastrointestinal upset.[14] Some classical signs and symptoms of higher level mercury exposure include numbness and tingling around the mouth, hands and feet, difficulty walking, slurred speech, coma, convulsions, and death.[15] Some other examples of chronic effects from chemical toxicants consist of how cadmium affects kidney functions and how lead impairs cognitive development in early childhood.

Reproductive Effects

The reproductive effects are different for each of the different contaminants and toxicants exposed in the seafood. One of the reproductive effects for PCB-contaminated seafood is that there is a relative risk of conception failure that rose in men but not in women. However, it can shorten the menstrual cycle length in woman. Another example is that outbreaks of methylmercury in Japan had suggested that the prenatal period was the most sensitive period in the life cycle to methylmercury.[15] Infants with severe brain damage were born to mothers minimally affected by methylmercury. There are also developmental effects that come with the reproductive effects. For example, children of mothers who had eaten high amounts of PCB-contaminated seafood during the six years preceding pregnancy and who continued to do so during pregnancy experienced significant decreases in birth weight and head circumference.[16] The babies now infants, exhibited weaker reflexes and greater motor immaturity.

Potential for Control

The health risks associated with seafood are identifiable and controllable by measures aimed at geographically restricted or species-specific problems. The risks that are associated with environmental contamination will require a major commitment on the part of both government and industry to change the methods of waste disposal in the society. Once the waste disposal in the society is changed, the human source contribution will be less which ultimately leads to less environmental contaminants. The Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) have reference doses for specific trace metals such as mercury.[17] These reference doses help control how much of the trace metals are being consumed. The reference doses are used as a guide for safe food consumption so one does not exceed reference dose.

Conclusion

Consumption of seafood can contribute to a healthy and balanced diet, but this food group can also contain potentially high/moderate levels of a number of environmental contaminants that can pose a risk to human health. All of the contaminants and toxicants pose risks when consumed in large quantities such as reproductive effects or other acute/chronic effects. To potentially control these effects, it is necessary to follow the reference doses as a guide for safe food consumption. Also, government and industry need to work together so the waste disposal in the society can change. Once the waste disposal in the society is changed, the human source contribution will be less which ultimately leads to less environmental contaminants.

References

1. Trabalón, Laura, et al. “Human Exposure to Brominated Flame Retardants through the Consumption of Fish and Shellfish in Tarragona County (Catalonia, Spain).” *Food and Chemical Toxicology*, vol. 104, **2017**, pp. 48–56.
2. Segev, Osnat, et al. “Environmental Impact of Flame Retardants (Persistence and Biodegradability).” *International Journal of Environmental Research and Public Health*, vol. 6, no. 2, May **2009**, pp. 478–491.
3. Watanabe, I. “Environmental Release and Behavior of Brominated Flame Retardants. *“Environment International*,” vol. 29, no. 6, **2003**, pp. 665–682.
4. Rainieri, Sandra, et al. “Toxic Effects of Perfluorinated Compounds at Human Cellular Level and on a Model Vertebrate.” *Food and Chemical Toxicology*, vol. 104, **2017**, pp. 14–25.
5. Fromme, Hermann, et al. “Perfluorinated Compounds - Exposure Assessment for the General Population in Western Countries.” *International Journal of Hygiene and Environmental Health*, vol. 212, no. 3, **2009**, pp. 239–270.
6. Ahmed, Farid E. “Occurrence of Chemical Contaminants in Seafood and Variability of Contaminant Levels.” *Seafood Safety*, National Academy Press, **1991**, pp. 111–171.
7. Christakopoulos, Alexandros, et al. “Cellular Metabolism of Arsenocholine.” *Journal of Applied Toxicology*, vol. 8, no. 2, **1988**, pp. 119–127.
8. Horwat, Merily, et al. “Biofilms at Work: Bio-, Phyto- and Rhizoremediation Approaches for Soils Contaminated with Polychlorinated Biphenyls.” *AIMS Bioengineering*, vol. 2, no. 4, **2015**, pp. 324–334.

9. Fisher, Art, et al. *DDT and DDE: Sources of Exposure and How to Avoid Them*. Nevada Cooperative Extension, **2003**.

10. "2,3,7,8-Tetrachlorodibenzo-p-Dioxin." *Encyclopedic Reference of Immunotoxicology*, pp. 632–632.

11. Smith, A.g., and S.d. Gangolli. "Organochlorine Chemicals in Seafood: Occurrence and Health Concerns." *Food and Chemical Toxicology*, vol. 40, no. 6, **2002**, pp. 767–779.

12. Schuller, Hildegard M. "Nitrosamines as Nicotinic Receptor Ligands." *Life Sciences*, vol. 80, no. 24-25, **2007**, pp. 2274–2280.

13. Gonçalves, Alex Augusto. "Ozone: An Emerging Technology for the Seafood Industry." *Brazilian Archives of Biology and Technology*, vol. 52, no. 6, **2009**, pp. 1527–1539.

14. Ahmed, Farid E. "Chemical Health Risk Assessment–Critique of Existing Practices and Suggestions for Improvement." *Seafood Safety*, National Academy Press, **1991**, pp. 172–267.

15. Silbernagel, Susan M., et al. "Recognizing and Preventing Overexposure to Methylmercury from Fish and Seafood Consumption: Information for Physicians." *Journal of Toxicology*, vol. 2011, **2011**, pp. 1–7.

16. Tanner, Caroline M. "Polychlorinated Biphenyls, Organochlorines & PD Risk: A Case Control Study in Alaska." Jan. **2010**

17. Merian, E. "Toxicity of Heavy Metals in the Environment." *Chemosphere*, vol. 9, no. 2, **1980**