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Ship-source pollution by polychlorinated biphenyls and brominated flame retardants

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ABSTRACT

Polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs) are groups of anthropogenic contaminants that have been routinely used in many applications for several decades. Prior to the discovery of their detrimental health effects and subsequent implementation of regulatory measures they were widely applied in shipbuilding. They are still found onboard active and inactive ships and pose a risk to human and environment. Therefore, it is important to continue to carry out preventive actions. Incorporating life-cycle thinking is necessary in order to minimise the environmental impact of persistent pollutant emissions by ships. Reducing the use of toxic or untested alternatives in shipbuilding in accordance with precautionary principle could contribute to sustainability of shipping.

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1. Introduction

In comparison to land and air traffic, shipping is more environmentally friendly and energy efficient transport mode. Nevertheless, the environmental impact of maritime sector is significant and a lot of effort is put into reducing it. [12] The most important global environmental effect of shipbuilding, shipping and vessel dismantling and recycling is emission of hazardous chemicals. Persistent organic pollutants (POPs), chemicals which are associated with a broad spectrum of adverse health effects are important group of the pollutants that can be emitted by ship throughout its entire lifespan. Two classes of POPs that were widely used in shipbuilding are polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs). They are stable, lipophilic chemicals of anthropogenic origin that persist for long periods of time in the environment. [17] They are globally circulated by atmospheric transport and watercourses and tend to bioaccumulate and biomagnify along the trophic chains. Due to their physico-chemical properties they are ubiquitously present contaminants, both in human beings and all environmental media, even in the most remote areas.

Recognizing their harmful effect on human health and environment PCBs and several BFRs are subject to regulation relating to usage in various sectors including shipping. Usage of new installation of materials which contain PCBs is prohibited for all ships by Hong Kong International Convention for the Safe and Environmentally Sound Recycling of Ships, 2009 (henceforth Hong Kong Convention) which will entry into force 24 months after ratification by 15 States, representing 40 per cent of world merchant shipping by gross tonnage, combined maximum annual ship recycling volume not less than 3 per cent of their combined tonnage. [18] Two groups of BFRs, polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) are listed as items for the inventory of hazardous materials.

Operational phase of the ship can extend to 30 or more years. [12] Therefore, many ships that contain PCBs or banned BFRs will be in use for a certain time. Furthermore, other types of halogenated flame retardants are used abundantly, although research data showing that associated health and environmental risks outweigh their putative fire safety benefits exist. [14] Additionally, large quantities of PCBs and BFRs exist in products that are intended to be used for a long time, which are transported by ships. This paper reviews and discusses sources of pollution by PCBs and BFRs *during* a *ship's life cycle,* their environmental fate and impacts and related regulations.

2. Polychlorinated biphenyls and brominated flame retardants

PCBs are a family of organochlorine compounds, differing in number and position of chlorine atoms in the molecule. [19] Out of 209 theoretically possible isomers and congeners, around 130 occur in commercial products or mixtures. Due to their non-flammability, chemical stability, high boiling point, and electrical insulating properties they have been used in a number of industrial and commercial closed and open-ended applications, including coolants and lubricants in transformers, fluids in capacitors and hydraulic transfer systems, plasticizers in paints, dyes, sealing liquids, plastics and rubber products, etc. Estimates have put the world-wide production of PCBs in excess of 900 000 tons and possibly near to 1.2 million tons in the period from 1930 until 1983. Although concerns about environmental fate and effects on living organisms have risen in the 60s, they were produced since 90s. [4] They have been banned globally by the Stockholm Convention, which entered into force in 2004. However, they are still released into the environment as a result of improper management of PCB-containing products or waste. High emissions continue in developing countries implicated as recipients of wastes due to lower environmental and social standards. PCBs have been demonstrated to cause a number of toxic responses in human and animals, which depend on many factors including composition and concentration of congeners. The large amount of research provides evidence of association between exposures to PCBs and harmful effects on the *immune, reproductive, neurological and endocrine system.* Based on animal and epidemiological studies PCBs are classified as probable human carcinogens. [7]

Among more than 175 different chemical flame retardants, *substances* applied to consumer goods to inhibit or suppress the combustion process, the brominated flame retardants have a highest market share due to high performance efficiency and low cost. BFRs *consist of different groups of* compounds, whose only common feature is that they contain bromine. [3] They are commonly used in electronics and electrical equipment, wire and cable compounds, insulation foams, seating and furniture in transport vehicles and public buildings. Because they are not chemically bound to products in which they are used, they can leach out during normal use or as products age. Since BFRs were detected in environmental samples at the end of the 70s, a number of research studies addressed their input, presence and fate in the environment and the effects on human health. They have been detected in human blood, adipose tissue and breast milk. Research data indicated that BFRs interfere with the hormone system, *exhibit toxic* effects on immune, neurological and reproductive system, fetal/child development and they have been shown to cause cancer. [5] Therefore, several conventional BFRs (BFRs launched onto the market in the past) have been banned or voluntarily phased out by manufacturers. However, the overall production of BFRs increases due to replacement by so called new BFRs (NBFRs) in spite to the fact that there is a limited body of knowledge regarding their chemical properties, exposure pathways, environmental fate and impacts. [9]

3. Ship as a source of pollution by polychlorinated biphenyls and brominated flame retardants

During construction, service life and disposal ships have a significant impact on environment [12]. The potential impact of pollutant emissions from shipbuilding can be very considerable. The main environmental issues are emissions during metal working activities, surface treatment operations, ship maintenance and repair activities. During operational phase accidental oil spills and solid and hazardous waste discharges are major issues of concern. Ship dismantling and recycling activities have a significant environmental and social impact since large quantities of hazardous gases, fluids and solids are generated and released into the air, water and soil.

Shipyard activities were significant source for the release of PCBs. Despite the fact that PCBs production is generally banned, the use restricted, the discharge prohibited and the disposal regulated in some countries 30 or 20 years ago, PCBs are still present in the receiving environment. Since PCBs are poorly soluble in water and tend to accumulate in sediments, surrounding areas can be seriously contaminated. Furthermore, PCBs level in contaminated marine sediments can remain elevated long after emissions by land-based sources have virtually ceased. [16] For example, PCBs concentrations were measured in shallow coastal marine sediments in Cantabria, Spain. Sampling locations were affected by the industry and shipping traffic. High levels of PCBs were detected in samples collected at locations near shipyards. [2]

Harbour and ship channel maintenance dredging and sediment disposal also pose a risk of contamination by PCBs due to their chemical stability. The sediment quality could be severely impaired particularly in the vicinity of industrial centres. [11] A study performed in the Houston Ship Channel showed that PCBs concentrations in sediments were relatively high 20 years after they were banned. Research data have indicated that PCBs monitoring should be continued to assess the temporal trends in concentration and homolog patterns. Namely, information about the content and assemblage is necessary to avoid underestimation or overestimation of associated risks since different congeners illicit different toxic responses.

The potential for contamination by PCBs is also present during the vessel navigation activities. Namely, many active ships were built prior to banning the production and restricting the use of PCBs. Hence, PCBs can be present in many materials and items onboard ships such as cable insulation, rubber and felt gaskets, thermal insulation material including fibreglass, felt, foam, and cork, voltage regulators, switches, reclosers, bushings, and electromagnets, electronic equipment, switchboards, and consoles, adhesives and tapes, oil-based paint, caulking, rubber isolation mounts, foundation mounts, pipe hangers, plastics, oil used in electrical equipment and motors, anchor windlasses, hydraulic systems, transformers, capacitors, and electronic equipment with capacitors and transformers inside, fluorescent light ballasts. [20] Thus, crew members can be inadvertently exposed during vessel operation and maintenance by inhalation, through skin following dermal contact with contaminated surfaces and through ingestion following oral contact with contaminated fingers. [15] Hence, in order to estimate occupational risk, exposure levels along with non-cancer hazard quotients and cancer risks were estimated for maintenance and engineering and nonmaintenance crew members on U.S. Navy older active and inactive ships and submarines. Air and breathing zone samples were PCBs free, contrary to the previously published data that showed their presence in inhalation vent gaskets and insulation. Therefore, due to uncertainty concerning the presence of airborne PCBs onboard it was nevertheless recommended to wear personal protective equipment during ventilation duct cleaning operations. PCBs were detected in surface wipe samples taken onboard in levels that could pose a health hazard to crews. To the best of our knowledge such studies have not been performed for BFRs. However, there is a possibility that enclosed spaces accommodating machinery or equipments with incorporated BFRs in order to meet the fire safety requirements exhibit elevated BFRs levels. Ships could be the relevant exposure environment for flame retardant chemicals for crew members, similarly to airplanes, another micro-environment with high flame retardant content due to strict fire safety regulations. BFRs concentrations in air aboard aircraft were measured in order to assess occupational exposure of flight crew. [1] Studies have showed that detected levels of BFR in airplane dust were elevated orders of magnitude relative to residential and office environments. In our opinion, performing similar study onboard ship could contribute to our knowledge regarding seafearers´ occupational hazards and possibly improve safety at work.

In addition to operation and maintenance activities another possible way of PCBs and BFRs exposure are accidents like fires, ship collisions or cargo damage such one that occurred onboard ship caring industrial waste. [6] Namely, during the voyage from the Thai port of Bangkok to Europe the ship with 19 containers of transformers for disposal encountered heavy seas. One transformer broke loose and about 400 L of oil containing Aroclor 1254 (a mixture of PCB congeners that was produced commercially by Monsanto) leaked. Unfortunately, during a recovery operation in the cargo hold crew members did not wear protective clothes. Consequently, they were exposed to PCBs by inhalation and skin penetration to a great extent in a short period of time. Additionally, since they slept on deck to avoid high temperatures in cabins, they were exposed to PCBs evaporating from opened cargo hold. Exposure associated symptoms observed in crew members were the temporary acne-form skin eruptions and liver function disorders. Since global transport of industrial waste by ships is linked to the possible accidents resulting with harm to human health and environment, education on pollutant nature and impacts and importance of precautionary measures is extremely important.

Fires on board ship are serious risk for surrounding environment regarding POPs contamination and may result with human exposure. During fire involving PCBs-filled electrical equipment a large amount of oily black soot is produced leading to PCBs exposure of crew by inhalation, ingestion, or skin contact during emergency response or cleanup activities. Additionally, when transformer fires occur, generated soot contains polychlorinated dibenzofurans, very toxic compounds which are known teratogens, mutagens, and suspected human carcinogens thus increasing the associated hazard. [10] Similarly to PCBs, uncontrolled combustion of BFRs can lead to the production of dibenzofurans, brominated dioxins and mixed bromo–chloro versions of these compounds, very toxic chemicals. Firefighters exposed to these compounds have elevated rates of four types of cancer that are potentially related to their exposure. [14]

Sunken wrecks pose a serious global threat to marine environment. [13] Following a short term release of fuel and/or other hazardous substances, a chronic leakage can occur. Therefore, data on contaminant composition and levels in the water and sediments around wrecks are important in order to assess the degree of danger to the surrounding fauna and flora. If the sediments at the site of the wreck facilitate their absorption, an elevated level of PCBs can be detected thus strengthening the negative effects of other organic pollutants. [4] Intentional sinking in order to create artificial reefs is one of the options for managing obsolete and decommissioned vessels. To ensure this is done safely, removal of materials that substances with potential adverse impact is recommended. [20] As materials of concern oil and fuel, azbestos, PCBs, paint, solids, debris and floatables are specified. All liquid PCBs materials should be removed. Regarding solid PCBs materials it is necessary to determine the amount of PCBs that could be released in order to decide on removing them ship before sinking. For materials remaining onboard a human health risk assessment and an ecological risk assessment should be performed. A human health exposure assessment involves recreational scuba divers, fishermen and people who consume seafood from the reef. An ecological risk assessment addresses potential effects to survival, growth, and reproduction for representative marine organisms that will live and feed on the new reef and organisms higher up the food chain. In addition to PCBs, risk assessment procedure should include BFRs, since they are also compounds of environmental concerns.

After a ship has reached the end of service, a method for disposing has to be selected. Recycling is considered as the best option for ships withdrawn from operation. [18]. However, it is also considered as one of the most hazardous occupations due to substantial health and safety hazards, especially since vast majority of industry activities is concentrated in Asia's developing countries. Currently, ship dismantling activities receive a great attention due to the detrimental impacts of emitted POPs on the environment. Contrary to the observed steady decline in environmental levels of PCBs in developed regions like USA and Europe, the level of PCBs is increasing in the countries such Bangladesh, India and Pakistan where ship dismantling has concentrated for the last 3 decades due to lower costs and less stringent environmental requirements. The quantity of PCBs present in a typical merchant ship varies between 250 and 800 kg, principally in the paint and on the scrap metal. [8] Therefore, ship–breaking significantly contributes to PCBs emission along electronic waste recycling units and open solid waste dumping grounds. Associated occupational health problems of workers involved in the dismantling could be substantial, particularly since many of them do not use protective equipment due to lack of awareness of the presence and effects of POPs. Furthermore, for people living in the areas near ship demolition plants direct inhalation could constitute a significant proportion of the total exposure. Therefore, it is important to monitor PCBs levels and to assess the health risks, especially in industrial regions where a number of pollution sources exists.

An exposure of workers during dismantling of flame-retarded products and population living in recycling communities has been *associated* with a number of adverse health effects such as abnormal thyroid hormone concentrations, inconsistent neurodevelopmental outcomes in children, reproductive abnormalities in boys, male reproductive disorders, decreased fecundity in women. [3] Although since the late 1990s there has been extensive research on brominated flame retardants, little toxicity information is available for many BFRs and NBFRs. There is a lack of knowledge regarding many relevant factors such as data on low-dose and chronic exposures, intergenerational health effects, simultaneous exposure to multiple chemicals with similar mechanisms. An assessment of combined exposure is especially relevant for ship dismantling since groups of pollutants that have a common toxic mode of action can be emitted.

Two classes of flame retardants that are covered by the Hong Kong Convention, PBBs and PBDEs, have received much regulatory attention worldwide [5]. PBBs are no longer produced or used in Europe and United States. The manufacture of PBBs was banned in the United States in 1976 after poisonings in Michigan. The use of three types of commercial PBDEs products, pentaBDE, octaBDE, and decaBDE is restricted in the European Union. In the United States their production ceased after the voluntary phase out. In order to reduce environmental and human health risks associated with ship dismantling those two classes of BFRs should be treated as prohibited PCBs. Furthermore, recent research found that many novel BFRs and banned BFRs exhibit similar properties. [9]. Therefore, addition of currently unregulated BFRs to the list of items for the inventory of hazardous materials could contribute to reducing adverse impacts of ship recycling.

4. Conclusions

Despite the bans and phasing out of PCBs and some BFRs, human exposure to shipping-related emissions will continue for many years due to the slow turnover of the fleets, the fact that many products containing them are still in use and their environmental persistence. Therefore, it is important to continue research regarding *occupational* exposures and *raise awareness on the preventive measures.*

An experience with PCBs and BFRs emphasises the need for *strengthening implementation* of life cycle approach to ships. Because environmental pollution knows no boundaries, global cooperation between shipbuilding, shipping and ship dismantling industry is necessary in order to *improve sustainability of the maritime sector.* Applying precautionary policies on emerging contaminants in shipbuilding have the potential to improve eco-efficiency of maritime transport.

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