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STUDY OF THE PRESENCE OF BIPHENYL POLYCHLORATES IN THE WATERS OF THE BENGALAS RIVER, NOVA FRIBURGO, RIO DE JANEIRO

Carla Mariah de Oliveira Fujimaki
Laboratório de Estudos em Farmacologia Experimental (LEFEx), Faculdade de Farmácia, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil

Cleverton Kleiton Freitas de Lima
Laboratório de Estudos em Farmacologia Experimental (LEFEx), Faculdade de Farmácia, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil

Ana Luísa Palhares Miranda
Laboratório de Estudos em Farmacologia Experimental (LEFEx), Faculdade de Farmácia, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil

Robson Roney Bernardo
Universidade Federal do Rio de Janeiro. Núcleo Multidisciplinar de Pesquisas, NUMPEX, Campus Prof. Geraldo Cidade, Duque de Caxias, RJ, Brasil

Abstract: Biphenyl polychlorinated (PCBs) belongs to a class of products persistent, bio accumulative and toxic synthetic organic chemicals. They are highly lipophilic pollutants and can accumulate in the food chain and adipose tissue. Although the use and production of PCBs have been severely banned in many countries, the legislation allows for the operation of equipment already installed, until it is fully replaced or replaced with a PCB-free product. The present study has the objective of verifying the presence of PCBs in the Bengalas River, in the Municipality of Nova Friburgo. Three collection points were analyzed monthly in the river from its source. The samples were collected monthly and lyophilized for a period of seven months. Subsequently, they were subjected to solid phase extraction (silica) with dichloromethane:hexane (1: 1: v/v) solvent. The samples were evaporated in a nitrogen atmosphere and analyzed by gas chromatography coupled to Mass Spectrometry (GC-MS), using tetrachloromethoxyylene as an internal standard. The analyses showed the presence of different types of PCBs and this result implies important deleterious effects on aquatic life as well as on those that use the waters of the river.
Keywords: Biphenyl-polychlorinated (PCBs), Bengalas River, water.

INTRODUCTION

The emergence of prominent industrial society and the need to mechanize agriculture led to the development of new synthetic chemicals such as pesticides and chlorinated hydrocarbons, which are considered to be persistent organic pollutants (POPs). Companies such as General Electric, Westinghouse, Monsanto, Ciba, and others have developed a series of polychlorinated hydrocarbons widely used in industrial applications that act as lubricants in electrical equipment such as capacitors and transformers (Faroon and Ruiz, 2015).

Bi-Phenylspolychlorinated (PCBs) belongs to a class of products persistent, bioaccumulative and toxic synthetic organic chemicals. They consist of two bonded benzene rings in which one or more hydrogen atoms are replaced by chlorine atoms (Lehmann et al. 2015). There are 209 congeners of PCBs classified according to the number and position of the chlorine atoms in the molecule, and affinity with aryl receptors, in this case structurally related to dioxins (Alcala and Phillips, 2017). PCBs as persistent organic pollutants are highly lipophilic and may accumulate in the food chain and in white adipose tissue (Faroon and Ruiz, 2015). These storage deposits function as reservoirs that are released into the blood, especially during periods of fasting or weight loss. The retention of these substances in adipose tissue may limit the ability to estimate the actual load of these chemicals from measurements on serum or urine levels (Gore *et al*., 2015). The toxicological response includes carcinogenicity, immunotoxicity, dermal toxicity and adverse effects on the reproductive, developmental and endocrine systems (Van den Berg et al. 1988). Due to the impact on public health and the environment, the use and production of PCBs were severely restricted or banned in many countries, as in Japan in 1972. In the same year, Sweden restricted its use and production; made in 1977, Norway in 1980, Finland in 1985 and Denmark in 1986 (WHO, 2003). In Brazil, the manufacture, sale, and use of PCBs occurred through the Ordinance through Interministerial Ordinance 19, dated January 2, 1981. However, it allows the operation of equipment already installed, until its complete replacement or exchange of dielectric fluid by exempt product of PCBs. On June 10, 1983, the Ministry of the Interior established

Normative Instruction 001 SEMA / STC / CRC, which governs the storage, handling, and transportation of contaminated PCBs and /or waste (CONAMA,1994). The National Environmental Council (CONAMA/Brazil) considering that the deposit of such waste poses considerable risk and danger to the environment and public health, with resolution 19 authorizing the export of hazardous wastes containing PCBs, in whatever form they are presented (CONAMA, 1994).The present study has the objective of analyzing the presence of biphenyl - polychlorates in the waters of the Bengalas River, a mountainous region located in the interior of the state of Rio de Janeiro (Nova Friburgo), Brazil.

MATERIALS AND METHODS

SAMPLES

Bengalas River samples were collected from September 2016 to April 2017 in the city of Nova Friburgo (RJ) at three points on the river, named A (source, PT1), B (inside the city, PT2) and C (end of the city, PT3) between September 2016 and March 2017.

SAMPLES ANALYSIS

Then, they were taken to the NUMPEX Laboratory of the Federal University of Rio de Janeiro, Pólo Xerem, in Duque de Caxias, where they were lyophilized (Liobras Model L101) with operating temperature -55°C. The lyophilized samples were submitted to solid phase extraction (SPE) with cartridge in a silica-alumina (1:1 w/w) eluent with dichloromethane:hexane eluent (9:1 v/v), were collected and concentrated in an N_2 atmosphere for further chromatographic analysis in gaseous phase at Laboratory of Radioisotopes Eduardo Pena Franco for the detection of PCBs. The previously purified samples were dissolved in 1.0 ml dichloromethane, a 100 µl aliquot was taken and placed in a vial which was evaporated to dryness. Then 50 µl of isooctane and 50 µl of TCMX (tetrachloromethoxyylene, internal standard) at 200 ppb diluted in isooctane were added. The samples were injected into the Agilent 7890 Gas Chromatograph coupled to a Mass Spectrometer (GC-MS), Agilent 5975C MSD, equipped with a silica capillary column fused to 60 mx 0.25 µm x 0.25 µm film thickness (HP-FMS, Quadrex Corporation, Woodbridge, USA). Helium gas was used as a carrier at 17 psi pressure at a constant flow of 3.0 mL/min. The automatic injection was performed in splitless mode at 250°C and pressure of 25,051 psi, the mass spectrometer operated in electron impact mode and in the mode of selected ion monitoring (SIM mode-selected ion monitoring). The temperature programs were: 100°C for 2 minutes, increasing 15°C per minute to 205°C, increasing 2°C per minute to 290°C, held for 5 minutes and increasing from 10°C per minute to 300° C for 5 minutes, the race had a total of 71.5 minutes.

RESULTS AND DISCUSSION

The Bengalas river is the river that crosses the city of Nova Friburgo and has tributaries of Saint Anthony and Conego rivers and belongs to the basin of the Dois Rios river (Figure 1). Twelve municipalities are located wholly or partially in the Dois Rios river basin: Bom Jardim, Cantagalo, Carmo, Cordeiro, Dois Barras, Itauco, Macuco, Nova Friburgo, Santa Maria Magdalena, Sao Sebastiao do Alto, Trajano de Moraes and Sao Fidelis (Telles et al. 2016).

Although the city of Nova Friburgo does not contain industries that justify the presence of PCBs in the waters of the Bengalas River, these pollutants can be generated from the industries of the state of Rio de Janeiro and can be transported by clouds along with other particles of pollutants that are suspended in the air, and when they find colder atmospheric layers, like those of the mountainous

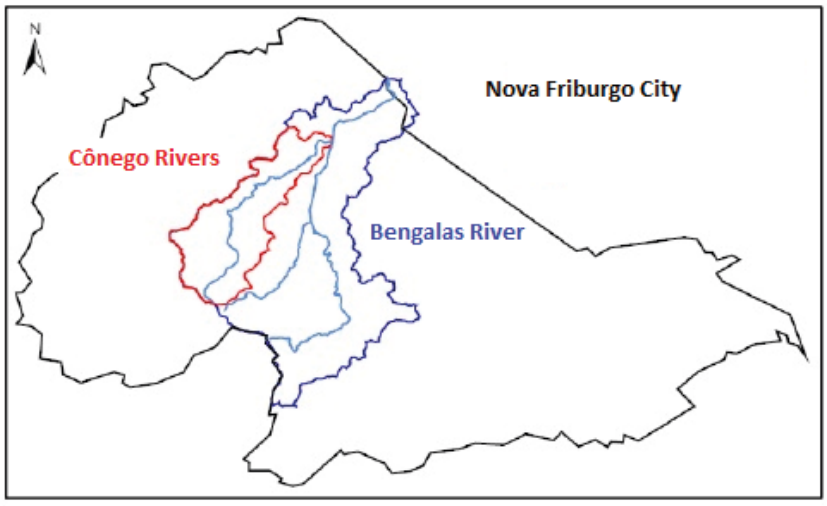

Figure 1. Dois river basin map

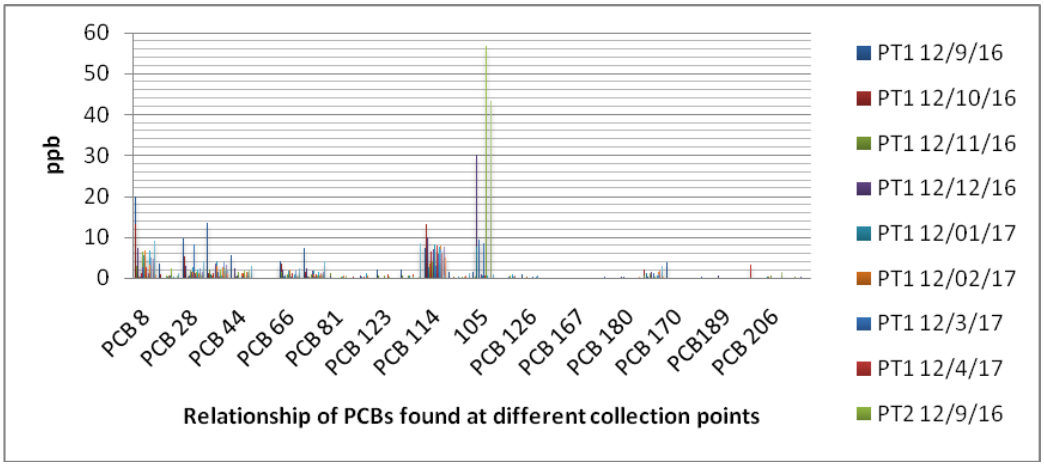

Figure 2. Number of PCBs along with the collection points on the Bengalas River.

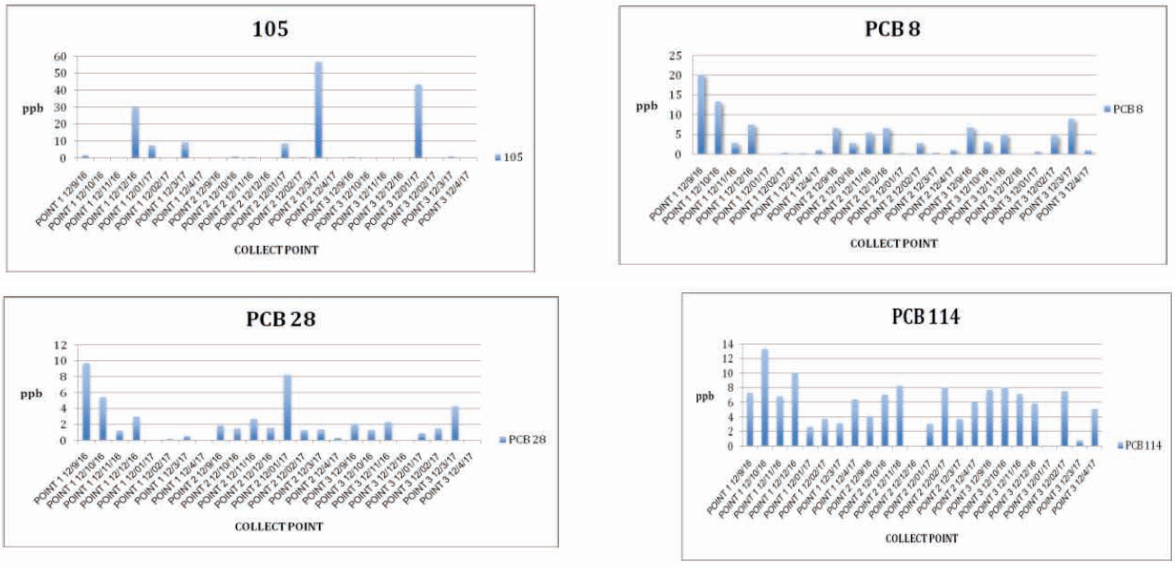

Figure 3. Main PCBs found in the waters of points 1, 2 and 3, Bengalas River, Nova Friburgo.

region of Nova Friburgo, condense in a geological phenomenon called grasshopper effect (Fernández-González et al. 2014) , contaminating the different ecosystems. Figure 2 showed the different PCBs found along the Bengalas River at collection points 1, 2, and 3, whose concentrations range from approximately 0.1 to 55.0 ppb.

Although PCBs exhibit lipophilic characteristics and low solubility in water, these substances may be associated with suspended solids that eventually undergo deposition in the form of surface sediments and is considered the main reservoir of PCBs in the aquatic environment (Baquar et al. 2017). Figure 3 shows the PCBs found in the highest concentrations, at collection points 1, 2, and 3. We can verify that the highest concentrations of PCBs are found in point 1, source: Estrada da Torre, s/n, Cascatinha (22°20'40"S 42°33'28"W), with the exception of PCB105, and these concentrations may be related to the grasshopper effect, a geochemical process where PCBs can be transported from warmer regions to regions such as the mountainous region of Nova Friburgo (Fernández-González et al. 2014).

The most common congeners of PCBs found in the Bengalas River are number 8 (102 ngL^{-1}), 28 (51 ngL^{-1}), 105 (162 ngL^{-1}), and 114 (136 ngL^{-1}). Its spatial conformation indicates a genotoxic potential and the classification regarding planarity or co-planarity is observed. The planar conformation presents ortho (2,2') chlorine atoms in the PCB molecule, while in the coplanar conformation there are no chlorine atoms at this position. The coplanar conformation is considered the most toxic having a similar action as that of tetrachlorodibenzodioxine (TCDD), which is considered as toxicological reference standard while the others act with a mechanism of induction type phenobarbital or with a mixed type mechanism (Penteado and Vaz 2001). In Figure 4 we can see that congeners 105 and 114 are potentially more toxic and that they presented on average a higher concentration of these.

We can verify the presence of PCBs at points 2, Jardel Hottz Street (22°17'49"S 42°32›23»W) and 3, Av. Hans Gaiser, 26, RJ 116 (22°16'3"S 42°31'56"W). Since PCBs were used as electrical insulating liquids, and because the city has old electrical structures, these concentrations are likely to come from discards of products that still contain these substances. Although banned at the Stockholm Convention on Persistent Organic Pollutants (2001), PCBs are still used in a number of developing countries because of their availability, low price and adaptability (Mahmood *et al.* 2014). PCBs are organic pollutants of wide environmental scope, with characteristics of bioaccumulation and acting in the food chain where they can act in several organs like endocrine, reproductive, and immunological causing several complications in these systems (Letcher *et al.*, 2010). Due to its hydrophobic characteristics, its deposition may occur in the form of surface sediments, thus being a reservoir of PCBs in this medium (Wei *et al.* 2008). Another worrying issue is the structural relationship between dioxins and PCBs (Figure 4) and dioxins cause an increase in the incidence of cancer in different parts of the body (Assunção and Pesqueiro, 1999).

CONCLUSIONS

Despite the studies, there are still many uncertainties regarding the effects of PCBs on both humans and other living organisms; making it impossible to analyze their effects on ecosystems. We can verify the presence of PCBs along the Bengalas River. The Bengalas River caters and divides the city of Nova Friburgo. It is still possible to find high concentrations of these compounds in the

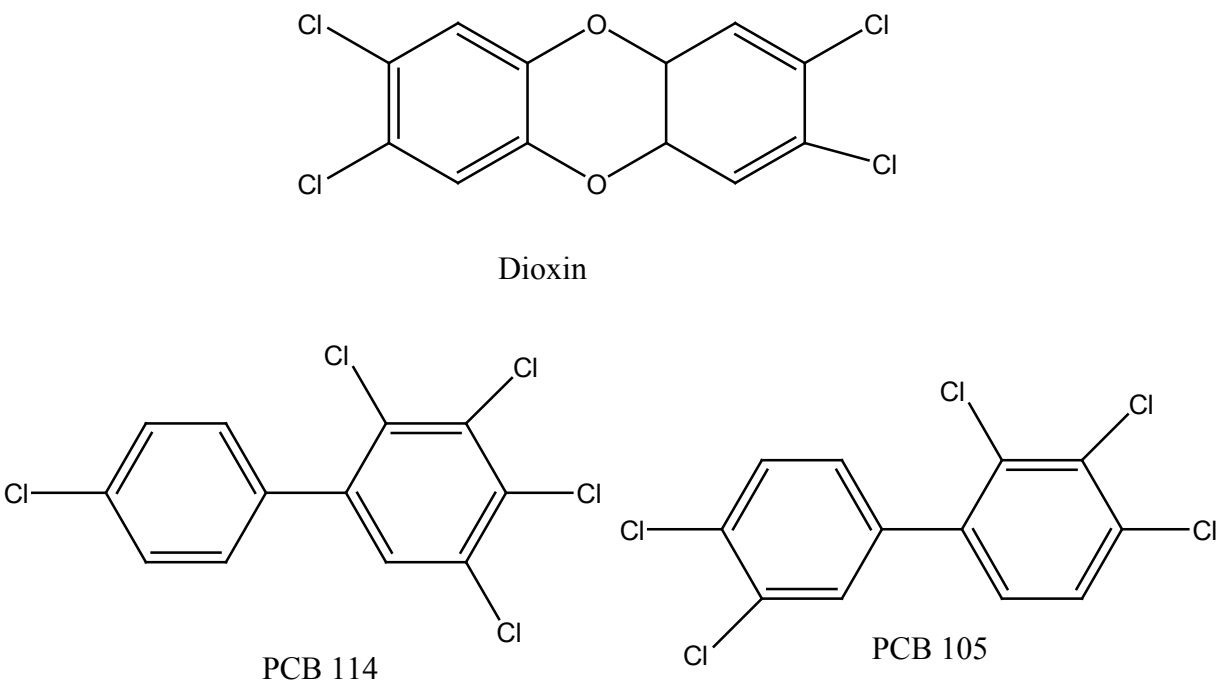

Figure 4. Relationship between dioxin structures and PCBs 105 and 114.

environment, permeating the trophic chain of the ecosystems in which they are found and consequently contaminating human beings. As these substances are known as important interferers of the endocrine system, future studies should be carried out to verify if the concentrations found can interfere in the different organic systems.

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