Occurrence of Ibuprofen in the Waters of the Bengal River in Nova Friburgo

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Abstract: The increasing use of pharmaceuticals throughout the world is generating a new environmental problem where they are found in low concentrations, but the long-term risks to various organisms, as well as human health, are not yet known. These drugs, as well as their metabolites, are introduced into aquatic environments through excretions or discharges and may cause the same exposure as POPs (Persistent Organic Pollutants) due to its continued entry into the environment. The aim of this work is to develop a sensitive analytical method for the detection of ibuprofen and its metabolites in the Bengalas river that crosses the city of Nova Friburgo in the state of Rio de Janeiro. Three collection points were analyzed monthly in the river from its source, as well as points of treated water throughout the city. The samples were collected monthly and lyophilized. Subsequently, they were subjected to a solid phase extraction (silica) with the solvent dichloromethane: hexane (1:1; v/v). The samples were evaporated over a nitrogen atmosphere and subjected to a LC-MS (Liquid Chromatography with Mass Spectrometry) with 5% acetic acid gradient: acetonitrile as the mobile phase. In the search for drugs, there were found ions and fragments of ibuprofen (m/z 206, 205, 177) that were sought and compared to with their standard. These indicators can result in deleterious effects on aquatic life in these bodies of water, as well as on those who use this water from the Bengalas river.

Key words: Ibuprofen, Bengalas river, pharmaceuticals.

1. Introduction

Pharmaceuticals, personal care products and illicit drugs have been considered as emerging environmental pollutants that persist in freshwater natural resources [1]. These organic pollutants enter the water systems from various sources such as human excretion (sewage), illicit disposal, landfill leakage, water drainage or industries [2]. Several studies report that these substances are present in low concentrations (ng/L, μg/L) and that the level of these compounds present in water can cause undesirable physiological effects, both in animals and humans, acting as endocrine disrupters [3].

The city of Nova Friburgo is in the mountainous region of the state of Rio de Janeiro and has a population of 150 thousand people. The municipality of Nova Friburgo is bathed by the Rio Grande, Rio Bengalas, Ribeirao de Sao Jose and Captain and Rio Macae basins. The main rivers that cut the center of the city are the Saint Anthony river, Rio Canon and the Bengalas river, that forms after the meeting of these rivers. The city presents some hospitals and public health posts in which there are several standardized medications that are used by the population of the region and one of them is the ibuprofen [4].

Pharmaceuticals are known as chemicals of environmental concern due to health risks associated with exposure of aquatic life to these compounds and possible risks to human health when they reach drinking water, therefore, water sources should be monitored regularly [5]. Several authors have reported the occurrence of pharmaceutical residues in waters in Europe, Asia and the USA [6], but there is limited information about their occurrence in Brazil water bodies.
Ibuprofen known as a non-steroidal anti-inflammatory drug has been widely used in the treatment of pain and inflammation in rheumatic disease and other disorders of skeletal muscle [7]. There is evidence that intrauterine exposure causes congenital malformation, such as cryptorchidism (absence of testis in the scrotal sac) and hypospadias (melting defect of the midline of the male ventral urethra) [8].

The objective of this study was to investigate the presence of ibuprofen in the Bengalas river, in the municipality of Nova Friburgo, state of Rio de Janeiro.

2. Material and Methods

2.1 Sample Collection

Samples of the waters of the Bengalas river were collected in the city of Nova Friburgo (RJ) at three points, named A (nascent; PT1 (Point 1)), B (inside the city; PT2) and C (final city; PT3), from October to December 2017. Afterwards, they were taken to the NUMPEX Laboratory of the Federal University of Rio de Janeiro, Campus Xerem, in Duque de Caxias. These were lyophilized (Liobras Model L101) with working temperature of -55 °C.

2.2 Sample Preparation

The lyophilized residue was taken to the Radioisotope Laboratory Eduardo Pena Franco of the Federal University of Rio de Janeiro for the removal of interferents from the matrix, as well as the concentration and isolation of the analytes, solid phase extraction was performed using silica gel G60, 70-230 mesh (2 g) and solvent dichloromethane: hexane (1:1; v/v; 4 mL). The resulting elute was slowly evaporated under nitrogen, yielding a solid residue which was resuspended in 1 mL of dichloromethane, then a 2 μL aliquot transferred to a 100 mL volumetric flask, and dichloromethane was added until the volume of 100 mL. From this solution, a 2 μL aliquot was withdrawn, transferred to a 100 mL volumetric flask and the volume completed. At the end of the serial dilution, a 60 μL aliquot was placed in the insert and vial for analysis.

2.3 LC-MS (Liquid Chromatography with Mass Spectrometry): Detection of Ibuprofen

Identification and quantification analysis of ibuprofen by mass-coupled high-performance liquid chromatography, Agilent 1200 series LC coupled to MS/MS quadrupole QTRAP 3200 (Applied Biosystems). The chromatographic column used was 50 × 2.1 mm C18 100A (SilaChrom). The total run time was 40 minutes, with gradients being 95% H2O and 5% ACN (Acetonitrile) from 0 to 25 min, 10% H2O and 90% ACN from 25 to 37 min, 95% H2O and 5% ACN from 37 to 40 min, with an injection volume of 10 μL and scanning at Q1 from 100 to 420 Da, positive mode.

3. 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 (Fig. 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 [4].

Three points were established for the collection and analysis of ibuprofen from incoming waters that are part of the Bengalas river. The location coordinates were obtained with the aid of a compass, at PT1: 22°20’40” S, 42°33’28” W; PT2: 22°17’49” S, 42°32’23” W and PT3: 22°16’3″ S, 42°31’56” W.

Anti-inflammatory ibuprofen has been extensively used in recent years, and although the elimination of this substance in wastewater treatment processes is greater than 90%, the concentrations of ibuprofen and its metabolites that may be found in water may still be measurable receptors [9].
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The total and maximum concentration of ibuprofen were verified at PT3 with approximately 20 ppb, describing the inability of wastewater treatment plants to remove complex pharmaceuticals as they were constructed with the main objective of removing carbon, nitrogen, phosphorus compounds and easily or moderately biodegradable microorganisms [10]. Fig. 2 shows the concentrations of ibuprofen in samples A, B, C, D, E and F.

Preliminary analyzes of the water collected along the Bengalas river showed the presence of ibuprofen and its metabolites, both phase I and phase II, according to Fig. 3. The mass spectrum reveals several ionic fragments, including the fraction of the metabolite derivative mono hydroxylated (m/z 221, Fig. 4), derived from ibuprofen phase I metabolism and the ion m/z 205, for ibuprofen molecule, as described by Brozinski, J. M., et al. [9].

The m/z 161, 177 fragments correspond to derivate ions of m/z 205 and 221 respectively, according to the analysis performed by Brozinski, J. M., et al. [9] (Fig. 5). The ion m/z 124 corresponds to the ionic fragment referring to the precursor 312, derived from the taurine conjugated metabolite of ibuprofen [11].
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Fig. 3 Fragments of ibuprofen and their metabolites.

Fig. 4 Metabolite derivative mono hydroxylated according to Brozinski, J. M., et al. [9].

Fig. 5 Fragments correspond to the m/z 161, 177.
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According to studies by Zwiener, C. F. F. H. and Frimmel, F. H. [12], the m/z 121 and 177 fragments may correspond to the oxidation products of ibuprofen (Fig. 6).

4. Conclusion

The method was developed to study the presence of ibuprofen and its metabolites in aqueous samples, rivers and their tributaries and effluents, using the lyophilization process, solid phase extraction followed by LC-MS/MS analysis. Preliminary results showed that the concentrations of the pharmaceuticals and their metabolites can have a great impact on the ecosystem, as well as public health, considering that these substances can reach the river basins and even in low concentrations, can promote harmful health effects.

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