Fate and Transport of Ibuprofen in the Natural Surface Water of the Pasig River, Philippines

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Abstract: Ibuprofen is one of the pharmaceutical drugs that can be obtained over the counter in the Philippines. It is widely used for easing inflammation and pain. The Pasig River situated in a highly industrialized and urbanized area in the Philippines was studied. This is in order to know if Ibuprofen can be detected in this natural aqueous milieu using in-situ passive probe (Polar Organic Chemical Integrative Sampler or POCIS). This river is facing a lot of challenges with regard to the sewage systems and waste water treatments.

This study shows the occurrence of the Ibuprofen in the important river of the capital of the country. Despite, different physico-chemical conditions of the Pasig River, Ibuprofen was still present. Compared to the concentrations found in the literatures, for a river, the concentration presented is high. Ibuprofen as an emerging pollutant can pose significant environmental concerns in terms its persistence and exposure of the microorganisms in this aquatic system. Concerns on human health can be raised as well as this river serves as an important source of water for daily use for those who does not have direct access to the local water service.

Keywords: Ibuprofen, POCIS, Pasik River, environmental risks, natural tropical aqueous system, emergent pollutant

1 Introduction

Ibuprofen is one of the essential medicines in the Philippines according to the National Formulary Committee of the National Drug Policy on Pharmaceutical Management. Acquiring is easy as this is an over the counter drug. It is an active ingredient used for: pain management (non-opioid analgesic), non-steroidal anti-inflammatory drug (non-selective COX inhibitor), antirheumatics (anti-inflammatory). Its efficiency may have been marked the medical efficiency, however, environmental concerns are growing. Ibuprofen is one of the emerging contaminants that can be detected in natural surface waters.

Pharmaceutical drugs are normally made for biological activity. Hence, there is an increasing the concerns on its adverse effects and toxicological potential [1]. Its low degradation rates in receiving water makes it susceptible to persist in the aquatic media [2].

This environmental concerns led to the rising interest of knowing the state of the water quality with respect to the fate and occurrence of the emerging organic contaminant such as Ibuprofen. The issue heightens when sources for water such as lakes, river, *etc.* are at stake. Philippines, a tropical country, is in the water "hotsposts" in Asia and the Pacific [3]. This is one of the countries that is facing the problem of water availability and use, threatened with poor water quality. The Pasig River located in the capital of the Philippines is facing this environmental distress. The area has a population of 11.63 million [3] with a growth rate of 2.02% [4]. It is a highly industrialized and urbanized setting where the river becomes an open receiver of all contaminants. This river serves as water source for those who have no direct access to water and recreational area (*e.g.* swimming area and fishing) to some people.

Detecting and tracing organic contaminants, however, is not easy. Very low concentration of the organic contaminants in the aqueous system makes detection and quantification challenging. Conventional grab water sampling cannot address this limit. In this study Polar Organic Chemical Integrative Samplers (POCIS) were used. The use of POCIS showed a lot of advantages with respect to this difficulty. POCIS can measure organic pollutants in trace level and ultra-trace level [5], [6]. POCIS is a tested tool, providing good assessments of the total weighted average concentrations of pharmaceutical drugs [7]. It is viable even the natural aqueous system in a tropical setting (*e.g.* high water temperature, presence of salinity, etc.) in terms of detection [8].

2 Materials and Methods

2.1 Site description and sampling approach

The Pasig River is an estuary in nature. It connects the biggest freshwater lake of the country, Laguna Lake, to Manila Bay (saline water). It is located in the capital of the Philippines, Manila. This area has a highly industrialized and urbanized setting. This river has four major tributaries (East to West: Napindan, Taguig-Pateros, Marikina, and San Juan Rivers) with forty-three minor tributaries.

Fig. 1 The Pasig River and the sampling sites

Pasig River is 27 km long and around 80 m wide. Four sampling sites (Fig. 1) were selected, representing the river sections: downstream (Site 1, near the mouth of the Manila Bay), midstream (Site 2 near San Juan River and Site 3 near Marikina and Taguig-Pateros River), and upstream (Site 4, near the opening of the Laguna Lake). The distance of each site is approximately 7 km. Three sampling campaigns were conducted. This corresponds to three distinct seasonal events: Period 1- dry season with simultaneous dredging activity; Period 2- a transition period from dry to wet event, and Period 3 – a wet event with pronounced continuous rainfall. The POCIS samplers (n=2) were left immersed for 18 days in each site in each period. Field blank was provided per sampling campaign. Physical parameters (water temperature, dissolved oxygen, conductivity, and pH) were measured using YSI 6600 V2 data probe. Strict protocol and sampling procedures were followed from site reconnaissance to laboratory transport.

2.2 POCIS

Each POCIS was assembled following the pharmaceutical configurations. The stainless steel rings were cleaned using dichloremethane (DCM) bought from Fisher Scientific. The bolts and nuts were soaked in methanol (pure, 99% bought at Fisher Scientific) and then put into the ultrasonic shaker for 24 hours. This was done twice. The membranes, polyethersulfone (PES), with pore size 0.1µm were bought at the VWR International SAS. Each POCIS consists of 200 mg of OASIS HLB sorbent, bought at Waters SAS. The sorbent was placed in between the PES then fixed firmly by the steel frames. After deployment, POCIS were sent to the laboratory of NIVA in Oslo, Norway, for extraction and analysis.

2.3 Ibuprofen Concentration Calculation

Accumulation of the contaminant (Ibuprofen in this case) in the POCIS is described by the equation of [9]:

$$C_s = C_w \times \frac{k_u}{k_e} \times (1 - exp^{-k_e t})$$

Where:

C_s = Concentration of Ibuprofen in the sorbent as time, *t* (µg/g)
C_w = Total weighted average (TWA) concentration of Ibuprofen in the water (µg/L)
k_u = uptake rate constant (L/g/d)
k_e = desorption or elimination rate constant (L/d)
t = Time of exposure (d)

As elimination rate k_e can be considered negligible during the integrative phase of uptake, equations can be reduced as follows [10], [11]

$$\boldsymbol{C_s} = \frac{C_w R_s t}{M_s}$$

Where:

R_s = Sampling rate (L/d)
M_s = Mass of sorbent in the POCIS (g)

From these equations, the Concentration Factor (CF) can be derived resulting as follows:

$$CF = \frac{C_s}{C_w} = \frac{R_s t}{M_s}$$

Considering this formula, the computed CF is 31.32 L/g. The Sampling rate (R_s) used is based from [8]. This R_s was chosen because it is the nearest water condition that Pasig River has. Similar conditions include high water temperature, influence of salinity, and nature of the aqueous solution (*i.e.* tropical water). Blank is under limit of detection (<1ng/L). The RSD is 5.8%.

3 Results and Discussion

3.1 Ibuprofen concentration detected in the Pasig River

Results showed that Ibuprofen can be detected in the Pasig River (Fig. 2). Highest concentrations varies among period except in the area near the mouth of Laguna Lake (Site 4). Highest concentration was found in the Madaluyong area near the San Juan River (Site 2) during Period 1. Least concentrations during Periods 2 and 3 were found near the mouth of the Laguna Lake (Site 4) and near Marikina River (Site 3) in Period 1.

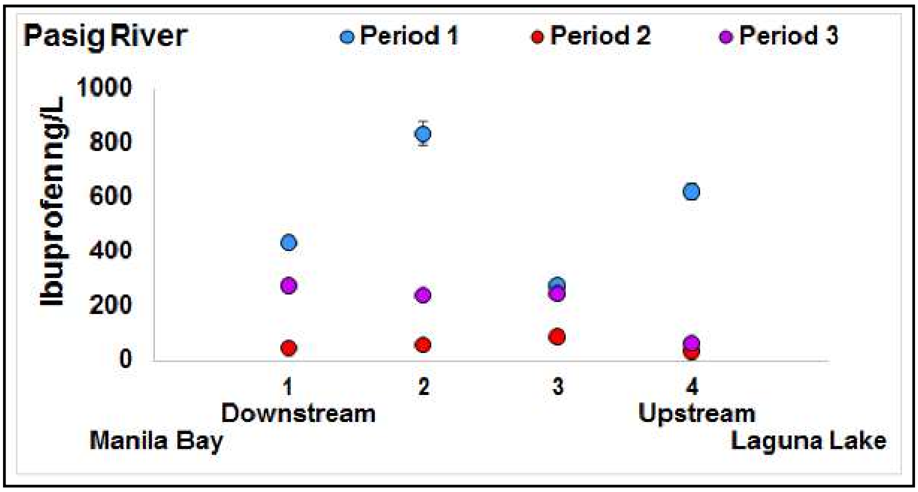

Fig. 2 Ibuprofen concentration in the Pasig River

The concentration of Ibuprofen is found least during Period 2, where the average tropical water temperature is the lowest (26 ± 0.78 °C). Concentration ranges from 30 ± 2 to 85 ± 5 ng/L. Although Periods 1 and 3 have the same average tropical water temperature (31 ± 2 °C), Ibuprofen concentration varies. Period 1 has the highest concentration with a range of 276 ± 15 to 838 ± 50 ng/L. Period 3, however, is lower as the concentration ranges from 60 ± 3 to 276 ± 15 ng/L.

Fig. 3 presents the physico-chemical background of the water of the Pasig River during the sampling campaigns. Study showed that the solubility of Ibuprofen varies according to the temperature of the aqueous solution. At higher temperature, higher rate of solubility was observed [12], [13]. Thus, higher concentration can be detected; following the concept of adsorption to POCIS. The data follows this concept (Ibuprofen concentration: 31°C>26°C), however, it can be observed that in Period 1 and 3, having the same water temperature, concentration varied (Period 1>Period 3).

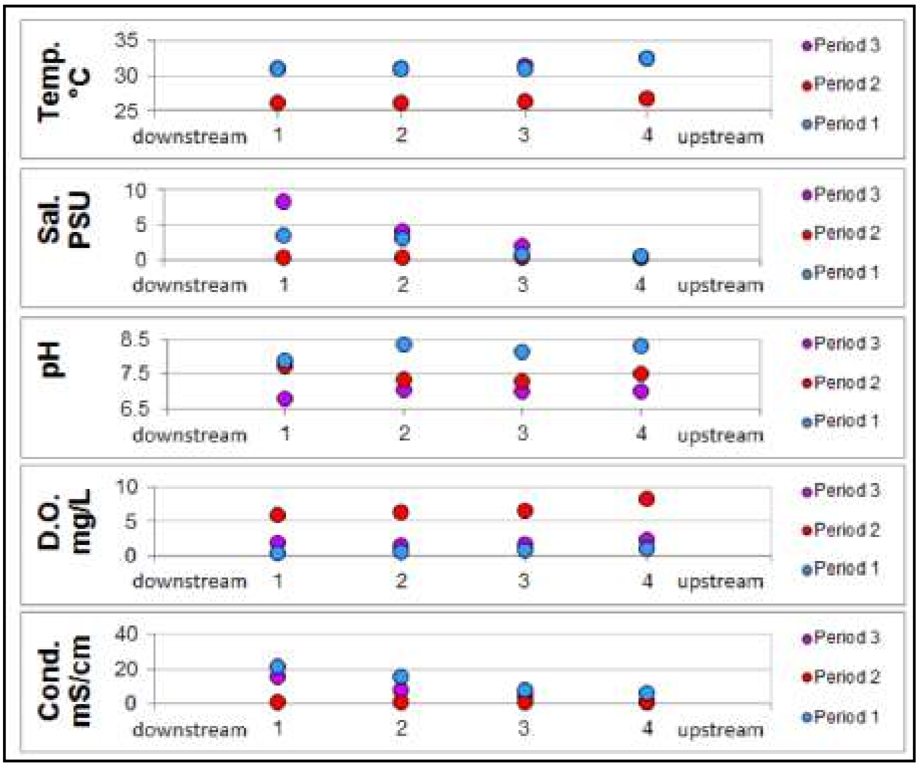

Fig. 3 Physico-chemical parameters

Conductivity, on the average, followed the trend of the water temperature as Period 1 (13 $\pm$ 0.46 mS/cm) is the highest, followed by Period 3 (7.23 $\pm$0.76 mS /cm) and Period 2 (0.83 $\pm$ 0.01 mS /cm) as the least. Water conductivity gives an idea of the ionic content of the aqueous solution [14].

In terms of salinity, for Period 1 only half of the Pasig River stretch reached the saline water (mouth of the Manila Bay until the intersection near San Juan River). Pasig River has no influence of salinity during Period 2. Period 3, highest level of salinity, was brackish, salinity reached Site 3 while the site near the Laguna Lake remained in the freshwater level. High salinity can induce slight increase in Ibuprofen adsorption [15]. [16], however, showed that the increase in salinity has an indirect effect on Ibuprofen. According to this study, high salinity induced potential release of increase of microbial population. This can be a plausible condition (limiting the adsorption rate) on why Period 3 has higher detected Ibuprofen concentration than Period 1.

For pH, in between Period 1 and 3, Period 1 being alkaline/basic while Period 3 is acidic. From here, it can be observed that Ibuprofen sorption favors acidic environment. This is the hydrophobic repulsion (main contribution of adsorption) decreases as pH increases [17], [18].

Opposite tendency was observed for the average dissolved oxygen (DO) as Period 2 as the highest in acceptable level of more than 5mg/L (6.7 $\pm$ 0.13 mg/L), followed by Period 3 which is in hypoxia (1.8 $\pm$ 0.15 mg/L). Period 1 is the least, experiencing close to the level of anoxia (0.72 $\pm$ 0.33 mg/L). DO presents an overview of the aquatic life in the natural aqueous solution [19]. Low DO level can induce production of microorganisms feeding in the aqueous system. Hypoxia favors phytoplankton blooms, while, anoxia can cause environmental stresses due to bacterial formation. A study showed that if Ibuprofen is at low level, the presence of a diatom *Navicula sp.* could hinder the degradation of this pharmaceutical drug [20]. Thus, prolonging its stress on the aquatic system.

It is also interesting to look at the sources and supply of this pharmaceutical drug, yet as this river is an open reservoir, with uncontrolled waste dumping and water treatment plants and proper sewerage system lacking, uncertainty is high. Nonetheless, it is still interesting to give accounts of the fate and occurrence of this pharmaceutical drug in a natural aqueous systems if environmental risks is of concern.

3.2 Ibuprofen concentration and mass transport in the Pasig River

Based from the literature (Table 1), the concentration of Ibuprofen in the Pasig River is relatively high if the natural aqueous systems (*i.e.* rivers and estuaries) will be looked into. The Pasig River's Ibuprofen concentration is close to the maximum values found in the UK estuaries. However, the Pasig River has higher minimum level (26 ng/L compared to <8 ng/L of UK estuaries). Also the range of concentration in the Pasig River is almost the same as what can be detected in the waste water treatment plants (WWTPs). Hence, it is important to note that the Ibuprofen concentration found in the Pasig River is in an alarming state.

Table 1. Environmental occurrence of Ibuprofen in the Aqueous Systems

Location/Aqueous System and Ibuprofen Concentration	Reference
Italy: Tap water 0.03 to 0.02 ng/L	[5]
Johannesburg: Goudkoppies WWTP: Influent: 40 ng/L; Effluent: 13 ng/L Northern WWTP: Influent: 112 ng/L; Effluent:25 ng/L	[7]
Italy: River: 0.67 ng/L; Tap water: 0.20 ng/L	[21]
San Francisco Bay water- max.: 37.9 ng/L	[22]
Mackinaw River Illinois, USA: Influent: 18 600- 26 200 ng/L; Lagoon: 1 840-13 900 ng/L; Effluent: 146-5 030 ng/L; Upstream: 1.77-4.65 ng/L; Downstream: 43.6-1 210 ng/L Mackinaw River: na-4.75 ng/L	[23]
Charleston Harbor, South California: WTP1: Influent: 14 317 ng/L; Effluent: 928 ng/L WTP2: Influent: 24 033 ng/L ; Effluent: 2 600 ng/L Surface water: 8 ng/L	[24]
NE, Spain Drinking Water Treatment Plant (DWTP), Raw water Conventional Treatment: Diox+sand filtered: 71-216 ng/L; Ozonated: 28-58 ng/L; GAC filtered: <LOD Advance Treatment: Ultrafiltration: 79-202 ng/L; Reverse Osmosis: <LOD; Remineralization: <LOD	[25]
South Wales, UK: River Taff: Usptream: 5-48 ng/L; Downstream: 12-62 ng/L WWTP Cilfynydd: influent: 968-2 986 ng/L; effluent: 131-424 ng/L River Ely: upstream: <0.3-56 ng/L; downstream: 4-74 ng/L WWTP Colsech: influent: 948-6 328 ng/L; effluent: 65-491 ng/L	[26]
Lower Tyne Catchment, UK, Howdown WTW: Raw: 7 741-33 746 ng/L; Pre-UV: 8 771-15 778 ng/L; Final: 1 979-4 239 ng/L	[27]
UK Estuaries: Mersey: <8 – 368 ng/L; Tyne: <8 – 698 ng/L; Thames: <8 – 928 ng/L	[28]

Environmental apprehension can be higher if mass transport will be considered. For example, the Pasig River Rehabilitation Commission reported that the water flow of the Pasig River can range from 12 m^3/sec to 275 m^3/sec [29]. This then can mean that an estimate of 0.32 to 230 mg/second or 27 to 19 911 grams per day of Ibuprofen can be received by this important highly urbanized river.

3.3 Implications of the persistence of Ibuprofen in the natural aqueous system

Knowing the persistence of this pharmaceutical drug on the natural aqueous systems is essential. If the environmental factors such as sunlight, suspended solids and microorganisms will be considered, persistence ($t_{1/2}$) of Ibuprofen in raw water (*i.e.* samples from rivers) is about 64 days and around 20 days for lake water [30]. Under a stirred condition added with NaCl, the half-life ($t_{1/2}$) of Ibuprofen is 59 days [8]. Knowing the half-life, in this case, enables determining the duration of the pharmacologic activity of Ibuprofen in the natural tropical aqueous system. Recent researches showed that exposing the organism to Ibuprofen poses threats. In the study of [31], sea urchin (*Psammechinus miliaris*) was exposed to Ibuprofen. Results showed that the concentration detected in the sea urchin affects sperm motility and fertilization. Exposure of a tropical freshwater Zebrafish (*Danio rerio*) to Ibuprofen influenced the hatch rate, motion, locomotion, and gene expression [32].

The study of [20], showed interesting results on assessing the toxicity of Ibuprofen on a diatom (*Navicula sp.*). It was observed that Ibuprofen at low level (0.1 to 1 mg/L) can stimulate algal growth. At higher concentration (>1 mg/L), however, Ibuprofen can threaten the algal growth due to photosynthesis inhibition. Thus, the presence of Ibuprofen can affect activities of the microorganisms in the natural aqueous systems. Moreover, it is found out that Ibuprofen is subject to photochemical transformation through decarboxylation then radical formation and eventually oxidation [33]. Transformation is comparable to aromatic ketones raising more concerns on ecotoxic risk [34]. Another physico-chemical condition like high DO can enhance pharmaceutical biotransformation [35]. Thus, affecting the fate of this pharmaceutical drug.

4 Conclusion

The fate and occurrence of one of the common over the counter drugs in the Philippines, known as Ibuprofen, was detected in the Pasig River. Different physico-chemical conditions were encountered during the three sampling campaigns. Period 1 has the highest concentration of Ibuprofen. This period can be described having the highest physico-chemical condition but with the lowest DO level. The lowest concentration of Ibuprofen was found during Period 2. Unlike, Period 1, the physico-chemical parameters were lowest during this period but the DO level was the highest. Period 3 has higher Ibuprofen concentration than Period 2. Its water temperature is almost the same in Period 1 with the highest level of salinity.

Ibuprofen case in the Pasig River is in alarming state this is as: (*1*) it can be detected in even in different physico-chemical conditions of the Pasig River; (*2*) the concentration level is not negligible as it can be compared to the concentration found in wastewater treatment plants; (*3*) its persistence exposes microorganisms; and (*4*) it poses possible environmental risks to the aquatic system and concerns on human health. Hence, further monitoring and assessments of Ibuprofen in this natural tropical aqueous system.

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