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Research article

Monitoring pharmaceuticals and personal care products in water and fish from the Gulf of Urabá, Colombia

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ABSTRACT

Gulf of Urabá is considered a tourist zone of Antioquia Department attracts a large number of visitors to explore the aquatic ecosystem and beaches thus offering a large economic benefit. However, this region has been affected by various anthropogenic effects thus generating an environmental problematic that affect aquatic ecosystem. Over the years, several research has been evaluated pollutant such as pesticides, metals and physicochemical parameters, even our laboratory had found several toxic metals in fish from this same area.

The presence of emerging pollutant in matrices such as seawater and fish from Gulf of Urabá have not been reported, and to the best of our knowledge, this is the first study. This work presents important aspects relating to sampling, monitoring and surveillance of seawater and several fish species caught in the area in order to determinate the content of emerging pollutant (triclosan, ibuprofen, diclofenac) using UPLC-QqQ/MS. In general, all three pharmaceuticals in different sampling sites were detected and total concentrations ranged from 0.10 to 1.54 μg/L in surface water. However, emerging pollutants content in fish muscle was not detected. In addition, a high variability in triclosan, ibuprofen and diclofenac concentrations according to the season of sampling was found. Regarding to seasonal variations, most emerging pollutant in the surface water had variation in levels both dry and wet season. Better removal was presented in the dry season, due to stronger irradiation and greater activity of microorganisms.

1. Introduction

Over the years, a large number of publications have reported the worldwide occurrence of pharmaceuticals and personal care products (PPCPs), an important group of emerging contaminants that have been widely detected in various environments such as food (Dasenaki and Thomaidis, 2015); fish (Ramirez et al., 2007); soil (Chen et al., 2011); sediment (Liu and Wong, 2013); and various water bodies, mainly wastewater effluents (Gracia-Lor et al., 2012; Vidal-Dorsch et al., 2012), rivers (Yao et al., 2018) and seawater (Borecka et al., 2015) (Lolić et al., 2015). PPCPs are a diverse group of chemicals that include human and veterinary drugs, food supplements and other chemicals used in cosmetics, fragrances and sun-screen agents (Ellis, 2006).

These compounds enter the aquatic environment either directly via through wash-off from skin and bathing suits of recreational users, or indirectly through effluents of wastewater treatment plants (WWTPs) (Buchberger, 2011). Usually, several pharmaceutical products are commonly discarded into toilets or sinks when they are expired in households (Zhang et al., 2008). Meanwhile, some pharmaceuticals are not completely metabolized when ingested by humans and animals, so the native forms and their metabolites are excreted with urine and are introduced into the sewage system (Zhang et al., 2008). Further, wastewater from the pharmaceutical industry and hospitals contributes to the total loads of pharmaceuticals in municipal wastewater (Santos et al., 2013). In addition to the municipal wastewater, which is the main source of PPCP release into fresh or marine water environments, other pathways exist such as runoff, rural wastewater and household wastewater from small communities (Anderson et al., 2013).

The continuous loading of these pollutants into aquatic bodies causes some of these compounds to behave as pseudo-persistent organic pollutants, despite their short environmental half-life. Ngubane et al. studied the occurrence of naproxen, diclofenac and ibuprofen in the Umgeni river mouth and the sea water at the coastal zone where the Umgeni river enters the Indian ocean (Ngubane et al., 2019). The authors detected up to 0.16 μg/L and 0.17 μg/L of naproxen and ibuprofen, respectively. Also, they found that the occurrence of pharmaceuticals in the studied samples

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could be linked to the direct disposal of these upstream in the Umgeni River, while WWTPs disposing treated effluent with pharmaceutical residues into water bodies that feed into the Umgeni River could contribute to the load of pollutants in the study area (Ngubane et al., 2019). Similarly, naproxen, diclofenac and ibuprofen were detected in estuaries, which suggests that these pollutants are carried by surface water into the receiving oceans (Stewart et al., 2014).

As is known, emerging pollutants can cause several adverse effects to the wildlife and aquatic ecosystems exposed to them and, consequently, are a risk to humans. PPCPs can be act as endocrine disruptors and cause feminization of fish, with some studies showing effects on the reproduction and fertility of fish (Hoeger et al., 2005). A salmonid species native to German rivers was investigated in order to evaluate the effect of diclofenac, one of the most prevalent pharmaceuticals in surface water. In this case, the results showed that water-borne diclofenac at levels of 5–50 μg/L affects kidney, gill and immune parameters in the fish (Hoeger et al., 2005). Ibuprofen can be accumulated in fish and alter cellular reactions in the liver, kidney and gills as well as disruption of the endocrine system by alteration of aromatase activity which then influences the balance of sex hormones (Paíga et al., 2015). On the other hand, triclosan commonly used as antifungal and antibacterial, causes adverse effects on aquatic ecosystems. Also, is weak endocrine disruptor that to bind with low affinity to both the androgen receptor and the estrogen receptor where cause both agonistic and antagonistic responses (Witorsch, 2014).

In general terms, the toxicity of PPCPs depend on the exposed organism, duration of exposure and contaminant concentration at which exposure occurs. Lately, a particular interest has arisen in the potential of these emergent pollutants to accumulate in tissues of aquatic organisms, such as crustaceans, molluscs and fish, as a consequence of their chronic exposure in aquatic ecosystems (Bringolf et al., 2010). Likewise, some authors have developed a multi-residue screening method of fish tissue for pharmaceuticals from multiple therapeutic classes, including a total of 25 compounds, using LC - MS/MS. The method was subsequently used to screen for target analytes in fish from an effluent-dominated stream, and diphenhydramine, diltiazem, carbamazepine, and norfluoxetine were detected in 11 environmental samples at concentrations ranging from 0.11 ng/g to 5.14 ng/g (Ramirez et al., 2007). Brozinski et al. studied the presence of 17 different pharmaceuticals and six different phase I metabolites in the bile of two wild fish species, bream (*Abramis brama*) and roach (*Rutilus rutilus*) caught from a lake that receives treated municipal wastewater via a small river (Brozinski et al., 2013). The study shows that pharmaceuticals originating from wastewater treatment plant effluents can be traced to the bile of wild bream and roach living in a lake where diclofenac, naproxen, and ibuprofen are present as pollutants. Diclofenac was found in five of the bream and roach samples, while ibuprofen was detected in three bream and two roach samples. Concentrations of diclofenac, naproxen, and ibuprofen were observed in bile (Brozinski et al., 2013).

Despite these efforts and the availability of relevant data from around the world, there is little information available on Latin America, especially Colombia, although some studies have been done. The presence of these contaminants in Colombia's reservoirs, specifically for PPCPs used in human applications and households were studied by Gracia-Lor et al. (2012). PPCPs were frequently detected, with the highest concentrations corresponding to methylparaben, in 51 reservoir water samples supplied with water from rivers or tributaries which receive urban and agricultural wastewater discharges. In addition, Botero-Coy et al. investigated the occurrence of 20 pharmaceuticals in wastewater from Colombia (Botero-Coy et al., 2018). In this case, raw wastewater samples from the hospital of Tumaco (Nariño), as well as from the city of Florencia (Caquetá) and influent and effluent wastewater samples collected in Bogotá and Medellin were analyzed. The highest concentrations (up to 50 μg/L) corresponded to acetaminophen, but several antibiotics, such as azithromycin, ciprofloxacin and norfloxacin, and antihypertensive drugs, such as losartan and valsartan, were commonly present in influent wastewater at levels above 1 μg/L (Botero-Coy et al., 2018). Concern over the presence of these contaminants is well founded, because these water resources not only flow through regions rich in biodiversity (the Pacific and Amazonian regions), but surface waters are also often used as a source for human consumption (Aristizabal-Ciro et al., 2017).

The Gulf of Urabá, located in the at northwest of the Department of Antioquia is a Colombian region which is a semienclosed body of water that extends from Punta Arenas on the eastern coast to Cape Tiburon in the west, with an area of 4.291 km^2 (Ortiz et al., 2003). Due to its biodiversity, this zone is well endowed with marine ecosystems and environments, and also has diverse fishery resources and banana crops, that form the main basis of the economy and food for the population (Ortiz et al., 2003; Taborda Marín et al., 2008). On the shores of the Gulf of Urabá there are several municipalities without sewage treatment plants. The main municipality of the Gulf of Urabá is Turbo, in which there is a tourist and commercial port, and the nearby sea is highly pollution. In the Gulf of Urabá there are several hotels that accommodate a large number of tourists. Over the years, several research has been carried out in order to assess pollution levels, effects and impacts in aquatic ecosystems in Gulf of Urabá and nearby areas. Physicochemical parameters, pesticides and metals have been studied through the years in Gulf of Urabá, which have shown elevated contents of toxic compounds that deteriorate the aquatic ecosystem (Gallego Ríos et al., 2018; INVEMAR, 2017; Salas Tovar and Murillo Hinestroza, 2013).

Our laboratory has collaborated with some research where have been evaluated environmental problematic that affect aquatic ecosystem in Gulf of Urabá due to metal contamination in fish caught in the gulf (Gallego Ríos et al., 2018, 2017; Zuluaga Rodríguez et al., 2017). For example, the Atrato river is the main water current that reaches the Gulf of Urabá, and is highly polluted. Zuluaga et al. reported the presence of toxic metals in various fish species in the Atrato River delta in the Gulf of Urabá. They evaluated the concentration of iron (Fe), copper (Cu), and zinc (Zn) in 96 samples of the following eight fish species: *Centropomus undecimalis*, *Caranx hippos*, *Scomberomorus brasiliensis*, *Lutjanus purpureus*, *Caranx crysos*, *Megalops atlanticus*, *Elops saurus*, and *Epinephelus itajara* (Zuluaga Rodríguez et al., 2017).

Taking into account the above, we decided to monitor various emerging pollutants in the Gulf of Urabá, using UHPLC–MS/MS with triple quadrupole. In this paper, we assess triclosan, ibuprofen, diclofenac in seawater and several fish species samples typical of the area during nine sampling campaigns from the Gulf of Urabá. The above, corresponds to main contribution of this research, because levels of emerging pollutant in matrices such as seawater and fish from Gulf of Urabá have not been reported, and to the best of our knowledge, this is the first study.

In Colombia, only two studies related to the presence of emerging pollutants in surface and wastewater in Bogotá and Antioquia have been published (Botero-Coy et al., 2018; Gracia-Lor et al., 2012). Several pharmaceuticals products among them diclofenac and ibuprofen were analyzed in these studies, also were detected personal care products as benzophenone and methyparaben. However, compounds like triclosan that is one of the main component UV filters, disinfectants, and sunblock has not been included in Colombian researches. This research gap has motivated our study and constitutes one more contribution since the presence of triclosan in environment is unknown in our country.

2. Material and methods

2.1. Sampling

Nine sampling campaigns from the Gulf of Urabá were carried out between November 2018 and October 2019 in order to collect fish and water samples from the wet and dry seasons, as shown Table 1. Seawater samples were collected in four points located near bay of Turbo (Aduana spout, Casanova spout, Higinio spout and Waffe port) and one point out of the bay (Table 2). Spouts nearby the Turbo bay have depths slightly

Table 1. Date of collections for 9 sampling campaigns.

	Month	Sampling
Wet season	November-2018	M1
	May-19	M5
	July 2019	M6
	August 2019	M7
	September 2019	M8
	October 2019	M9
Dry season	February-2019	M2
	March-2019	M3
	April-2019	M4

Table 2. Location of the collection points of the water samples (9 sampling campaigns).

Sampling points	Abbreviation	Location
Aduana spout	AS	8° 4′ 25.0″ N 76°43′ 56.6 W
Casanova spout	CA	8° 4′ 25.0″ N 76°43′ 18.4 W
Higinio spout	HS	8° 4′ 51.8″ N 76°43′ 18.4 W
Waffe port	WP	8° 5′ 19.3″ N 76°44′ 00.0 W
Out of the bay	OB	8° 3′ 19.9″ N 76°44′ 17.4 W

greater than two meters, thus composite water sampling was carried out at different surface water depths (0.5 m, 1.0 m, 1.5 m and 2.0 m) with two replicates for each site. The two replicates of seawater samples were stored in 0.5 L amber glass bottles and kept at 4 °C during transport to the laboratory. Upon reception in the laboratory, the samples were stored at −4 °C, until extraction.

The species evaluated in this study were obtained from local fishermen and selected according to the interest of the fishing community, and those species that are highly commercialized and consumed locally. Fish samples above the mean size of sexual maturity were captured by fishermen in the same five points selected for water sampling, with a minimum catch size, male sex and 500 g portions. The fish bought by laboratory were transferred to a bucket filled with cooling gels and then immediately transported to the laboratory. The following species were included in this study (Table 3): king mackerel (*Scomberomorus cavalla*), leatherjacket (*Oligoplites saurus*), mullet (*Mugil incilis*), gafftopsail catfish (*Bagre marinus*), white sea catfish (*Genidens barbus*) and crevalle jack (*Caranx hippos*). Three replicates of each fish species were analyzed. On arrival at the laboratory, viscera were removed (discarding head, fins, tail, skin and fat), and the fish were crushed and homogenized. All tissues were immediately frozen at −20 °C until extraction.

All sampling points belong to the Turbo municipality (Figure 1), a tourist and commercial port where the most important banana crops in Colombia are located. This district is subject to various activities that cause pollution in aquatic ecosystems due to direct discharges into the Atlantic Ocean through the contributions of river currents (Turbo, Guadualito, Currulao, and Atrato rivers); solid waste; port activity; banana crops; gold mining; organic matter; nutrients; leachate; and domestic wastewater, since there is no adequate sewage system.

2.2. Extraction and cleanup

The extraction methods for triclosan, ibuprofen and diclofenac in water and fish muscle samples were developed in our laboratory using a modified methodology according to what is established in the EPA Method: 1694 (EPA, 2007). Briefly, 100 mL of water samples were vacuum filtered through glass wool (Agilent), then completed at 200 mL and extracted by solid-phase extraction, using Oasis HLB cartridges (60 mg, 3 mL, Waters). The cartridges were conditioned with 12 mL of methanol, followed by 3 mL of ultra-pure water at pH 2. The cartridge was then dried under vacuum to remove the excess of water, and each seawater sample was percolated through the cartridge. Elution was performed with 12 mL of methanol and 6 mL of methanol:acetone mixture (1:1, HPLC-grade solvents, Merck). Extracts were evaporated under a gentle stream of nitrogen and reconstituted with 1 mL of methanol–ultra-pure water (10:90, v/v).

Fish homogenate samples (~5 g) were spiked with a mixture of the analytes and subsequently subjected to the chosen extraction methodologies based on QuEChERS (quick, easy, cheap, effective, rugged, and safe), which involved extraction of the extract using anhydrous magnesium sulfate and sodium chloride as extraction salts. Subsequently, 10 mL of acetonitrile (HPLC-grade solvents, Merck) was added for the extraction, and the mixture was shaken intensively for 1min and centrifuged (5000 rpm, 5 min, 20 °C) to separate the organic and aqueous phases. Finally, a 500 μL of supernatant was injected, adjusting the volume to 1 mL with mobile phase.

2.3. Liquid chromatography and mass spectrometry (UHPLC–MS/MS)

The PPCPs in the extracts of seawater and fish muscle samples were analyzed using an Acquity UPLC system (Waters Corp., Milford, MA, USA), equipped with a quaternary solvent manager and a sample manager coupled to an Agilent 6460 triple quadrupole mass spectrometer with electrospray ionization (ESI) source in multiple reaction monitoring (MRM) mode. Nitrogen was used as a cone gas as well as a desolvation gas at 100 L/h and 1000 L/h, respectively. The capillary voltage was 3.5 kV, source temperature was 130 °C and the desolvation temperature was 350 °C. Chromatographic separation was performed using a C18 column (Waters, 2.1 × 100 mm, 2.7 μm particle size) at a flow rate of 0.3 mL/min. The mobile phase was C = 1 L ultra-pure water, 0.5 mL acetic acid, D = acetonitrile: methanol (1:1) (MS-grade solvents, Merck). The flow rate was 0.3 mL/min, the column was maintained at 40 °C, and the sample

Table 3. Summary of samplings fishes from Gulf Urabá (samplings performed M1-M9).

	Sampling	Fish species		
Wet season	M1	Saw	Mackerel	Anchovy
	M5	Sea catfish	Stone head catfish	Anchovy
	M6			
	M7	Sea catfish	Stone head catfish	Anchovy
	M8	Sea catfish	Stone head catfish	Anchovy
	M9			
Dry season	M2	Saw	Shoemaker seven leather	Anchovy
	M3	Sea catfish	Stone head catfish	Anchovy
	M4			

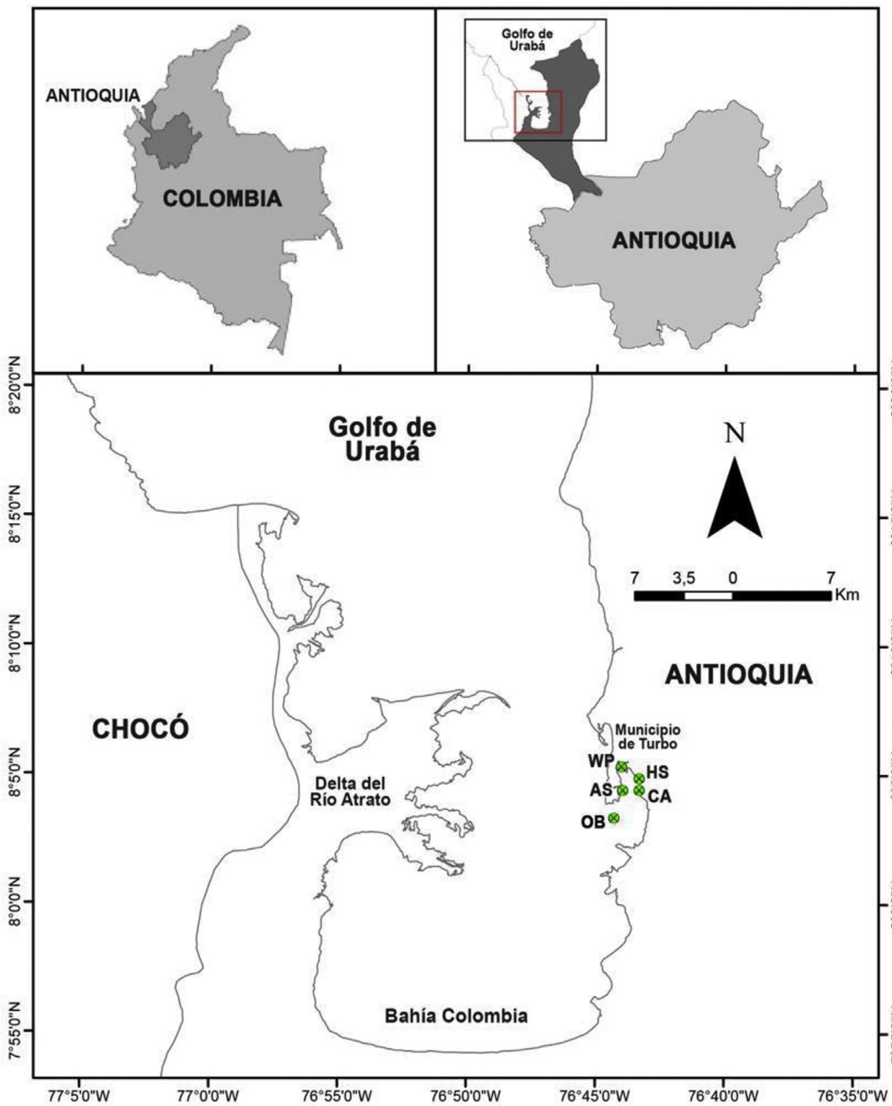

Figure 1. Study area Municipality of Turbo, Gulf of Urabá-Antioquia.

manager was maintained at 15 °C. Analysis run time was 7 min and the injection volume was 20 μL of sample. All data were acquired and processed using Masslynx v 4.1 software (Waters).

In this work, in order to ensure the reliability of the data published some quality control samples (QCs) were included in every sampling batch (as shown Table 4). QCs consisted in prepared randomly by selecting one of the blank samples and samples spiked at known concentration (70% or 30%, 140μL and 60μL of 10 ppm of a mixture of three contaminants, respectively) within each sampling and were analyzed according to analytical procedure described for water and fish samples. Tolerance for QCs (50–120 %) were calculated according to percentage recoveries for acceptance criteria for PPCPs (EPA, 2007). In the light of our data, two MS/MS transitions were acquired and the identification was carried out by evaluating the ion ratios between the quantification and confirmation transitions. Relative standard deviation percentages (% RSD) also were calculated in order to satisfy a value below 20.3%.

3. Results and discussion

In this research, two pharmaceuticals and one personal care products were studied. The choice of diclofenac and ibuprofen was based on their high use in Colombia, given that these analgesics re sold without a prescription (Gracia-Lor et al., 2010). On the other hand, triclosan is the main component of UV filters, preservatives, fragrances and sunblock and it was selected due to their wide use and to their potential harmful effects on human and aquatic organisms (Pedrouzo et al., 2011).

3.1. Concentrations of PCPs in seawater samples

The method developed in the laboratory and described in the previous section was used for the analysis of the selected PPCPs in seawater samples. With regard to recoveries for acceptance criteria for PPCPs individual recoveries were in the range 50–120%, which is consistent with method EPA-1694 for the determination of PPCPs in environmental samples (EPA, 2007). In Table 5 shown the limit of quantification (LOQ) for seawater samples. All three pharmaceuticals were detected, the total concentrations of PPCPs in different sampling sites ranged from 0.10 to 1.54 μg/L in surface water. The mean concentrations of diclofenac and ibuprofen were in the range of 0.12–1.54 μg/L and 0.12–0.46 μg/L, respectively. For triclosan, the mean concentration ranged from 0.10 μg/L to 0.79 μg/L. Among the pharmaceuticals analyzed, diclofenac was found at the highest concentration while ibuprofen was found at the lowest concentration. Therefore, it can be considered that the method used in the laboratory was successfully applied in the determination of low levels of PPCPs in these kinds of samples. On the contrary, Ngubane et al., obtained higher concentrations for ibuprofen (0.17 μg/L) than for

Table 4. Compounds investigated and analytical conditions using UHPLC–MS/MS (MW: monoisotopic molecular weight in Da, MF: molecular formula).

Compound	Family/Function	MF	MW	Confirmation Transition	Quantification Transition
Diclofenac	Anti-inflammatories	$C_{14}H_{11}$	295.0	295.81 > 252	2941 > 249.98
Ibuprofen		$C_{13}H_{18}$	206.1	205.12 > 161.1	205.12 > 161.1
Triclosan	Antibacterial agent	$C_{12}H_7Cl$	287.9	286.9 > 35	288.9 > 35 288.9 > 37

naproxen and diclofenac, when analysing samples of seawater in Durban, South Africa (Ngubane et al., 2019). In this study, naproxen and ibuprofen were detected up to 0.16 and 0.17 μg/L respectively (Ngubane et al., 2019). Concentrations of emerging pollutant observed in our study were compared to those reported in several countries. Diclofenac and ibuprofen levels detected in Atlantic Ocean (Portuguese coast), Eastern Mediterranean Sea and Santos Bay in Brazil corresponding to 0.24 and 0.22 μg/L; 0.02 and <LOD and 0.02 and 2.09, respectively (Alygizakis et al., 2016; Ngubane et al., 2019; Paíga et al., 2015; Pereira et al., 2016).

Triclosan was the compound most frequently (44.4%) found in 20 samples, which indicates the wide use of personal care products in the Urabá region. This is not in accordance with Colombian regulations that restrict and prohibit the use of triclosan in the manufacture of cosmetics for hygiene and personal care (Comisión de la Comunidad Andina, 2017). On the other hand, diclofenac (22.2%) and ibuprofen (6.7%) were detected to a lesser extent in all samples analyzed (Figure 2). In Colombia, self-medication of ibuprofen and diclofenac is normal, also these pharmaceutical products are sold without a prescription.

Regarding the occurrence of these pollutants (Figure 2), it can be seen that emerging pollutants frequently detected (>66%) in seawater samples were commonly found in four of the sampling points (OB, AS, CA, WP), while in Higinio port they were detected less frequently (55%). PPCPs only appeared in six of nine campaigns sampling. The higher occurrence of pollutants may be linked to those areas with the highest number of people, nearby navigation port and the main disposal zone, corresponding to Aduana spout, Casanova spout and Waffe spout.

All the emerging pollutants are detected in M1 sampling (Figure 2). On the contrary, none of the target compounds was detected M4, M5 and M8. Triclosan occurred most frequently in the sampling (>40%), and was detected in M1, M2, M3, and M9, while diclofenac and ibuprofen were only detected in three samplings (M1, M6, M7) and two samplings (M1, M3), respectively. In the seawater collected in M2 (0.27 μg/L) and M3 (0.35 μg/L) the concentrations for triclosan showed an increase in mean levels. Similarly, M6 (0.24 μg/L) and M7 (0.81 μg/L) also exhibited increase in diclofenac mean contents throughout the two sampling months. Similarly, to our results, a study has reported that of pharmaceuticals of abuse concentrations commonly increase over time (Bijlsma et al., 2016).

As expected, of the five sampling points Waffe spout exhibited the highest levels of diclofenac and triclosan. This spout is located towards the center of the urban area, in the Turbo bay, and is used as the passenger dock and loading and unloading place that connects Turbo with the local, regional and national towns (Salas Tovar and Murillo Hinestroza, 2013). It is characterized by slow waters, high turbidity and high concentrations of muddy sediment, fecal coliforms, fats, oils, nutrients

Table 5. Summary of mean concentrations (μg/L) of detected target compounds in seawater samples from Gulf Urabá (sampling months M1-M9).

			OB	AS	CA	HS	WP
Wet season		Triclosan	0.54	0.50	0.63	0.56	0.79
	M1	Ibuprofen	0.46	nd[a]	nd[a]	nd[a]	nd[a]
		Diclofenac	0.57	nd[a]	nd[a]	nd[a]	nd[a]
		Triclosan	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]
	M5	Ibuprofen	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]
		Diclofenac	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]
		Triclosan	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
	M6	Ibuprofen	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
		Diclofenac	0.12	nd[b]	0.47	nd[b]	0.63
		Triclosan	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
	M7	Ibuprofen	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
		Diclofenac	0.24	0.85	0.83	0.59	1.54
		Triclosan	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
	M8	Ibuprofen	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
		Diclofenac	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
		Triclosan	0.13	0.18	0.49	0.12	0.20
	M9	Ibuprofen	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
		Diclofenac	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
Dry season		Triclosan	0.24	0.24	0.17	0.43	0.26
	M2	Ibuprofen	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
		Diclofenac	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
		Triclosan	0.28	0.27	0.35	0.10	0.75
	M3	Ibuprofen	nd[b]	0.15	nd[b]	nd[b]	0.12
		Diclofenac	nd[b]	nd[b]	nd[b]	nd[b]	nd[b]
		Triclosan	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]
	M4	Ibuprofen	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]
		Diclofenac	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]

nd: not detected (<LOQ = 0.10 μg/L)[a] and (<LOQ = 0.50 μg/L)[b].

and solids, which affects the physical conditions of the water and its operation. A state of eutrophication affects the physical conditions of the water and its operation as an ecosystem and habitat for diverse biological groups of ecological and economic importance (Salas Tovar and Murillo Hinestroza, 2013). The waters bodies are highly contaminated by activities such as intensive deforestation, the use of agrochemicals and fertilizers and the continuous discharge of solid wastes contributed by domestic and industrial activities together with the dumping of fats and oils resulting from the transit of the arriving vessels. Similarly, this spout receives direct discharges of wastewater and solid waste from 8 nearby neighborhoods. In addition, other spout (Tranca and Veranillo spouts) and rivers such as Turbo, León, Currulao flow into it, bringing with them the pollutants discharged by activities in their respective areas of influence (Salas Tovar and Murillo Hinestroza, 2013).

Pollution problems in the area have increased substantially due to overcrowding, lack of basic sanitation systems, and inadequate operation of the wastewater treatment plants in the municipality of Turbo. Besides, the Gulf of Urabá is a semi-closed water body and its mobility and replacement rate of water is relatively slow. The influence of human activities (tourist, residential and commercial) in areas near this bay seems clear in the case of PPCPs, but more research and information would be required to understand the fate and behavior of pharmaceuticals in this aquatic environment. Therefore, the results suggest that PPCPs into Waffe spout are distributed towards the bay, contaminating all bodies of water. There are no previous reports on PPCP studies in seawater samples from the Gulf of Turbo, therefore it is not possible to compare the results obtained in this article. However, our results are related to the high levels of pollution in Turbo bay. Physicochemical studies (suspended solids, turbidity, pH, dissolved oxygen, chlorine, phosphates, nitrates, coliforms, fats, among others), ecological studies, and studies of pesticides and metals (Hg, Pb, Cd, among others) in seawater and fish samples from the Gulf of Urabá have shown elevated contents of toxic compounds that have impaired the aquatic ecosystem (Gallego Ríos et al., 2018; INVEMAR, 2017; Salas Tovar and Murillo Hinestroza, 2013). It is important to highlight that environmental management measures are currently being carried out in order to reduce the pollutant load and guarantee the conservation of its environmental resources. These results can contribute to entities such as the municipal administration and environmental corporation of Urabá region (CORPOURABÁ), can develop and implement environmental management measures in order to reduce the pollutant load and guarantee the conservation of its environmental resources. Similarly, it is important to continue with this kind of research in order to monitor, determine concentrations and locate possible sources of contamination in this region.

3.2. Seasonal variations in seawater samples

The climate of the Urabá region is governed by the Intertropical Convergence Zone (ZCIT), in which the climate normally fluctuates between 26 and 28 °C, but frequently exceeds 35 °C. In addition, in this zone there are no regular seasons, although there is a dry period from the end of December until April, and a wet season that begins in May (Chevillot et al., 1993; Ortiz et al., 2003). Most PPCPs in the surface water had important variation in the different seasons, as shown in Figure 3. Three PPCPs showed higher concentrations in the wet season than those in dry season. In particular, the concentrations of diclofenac in the wet season were approximately twice as high as those in dry season. Diclofenac and acetaminophen are two widely consumed analgesics in Colombia, since they are very easy to buy as they are sold without a prescription. However, there is a lack of knowledge about the implications of its high consumption (Jaramillo et al., 2004). On the other hand, ibuprofen presented the lowest levels in both climatic seasons. In the wet season, the highest content (0.46 μg/L) of this pharmaceutical was obtained, while in the dry season the lowest value (0.12 μg/L) was obtained (Figure 3). This results are in accordance with those of Ngubane et al., who detected minimum levels of ibuprofen (0.17 μg/L) in seawater at the Glen Ashley beach in South Africa during sampling in September 2018 (Ngubane et al., 2019). For triclosan, slight differences between the wet and dry seasons were found. Mean concentrations between 0.4 μg/L for the dry season and 0.6 μg/L for the wet season were detected, which might be related to a weaker degradation rate. Due to the high level of sun exposure in this region, personal care products (deodorants and antiperspirants, sunscreen, pesticides, insect repellant, and others) that contain triclosan are frequently used by the general population (Huang et al., 2016).

Depending on the season, the results showed variability in concentrations for compounds, which might be explained by their degradation rates being higher in the dry season because of higher temperatures (Du et al., 2019). Some research has shown increased concentrations of PPCPs in surface water during the rainy season based on the mechanisms mentioned above (Daneshvar et al., 2010; Vieno et al., 2005). For example, Jiang et al. found that 16 kinds of PPCPs in water had higher

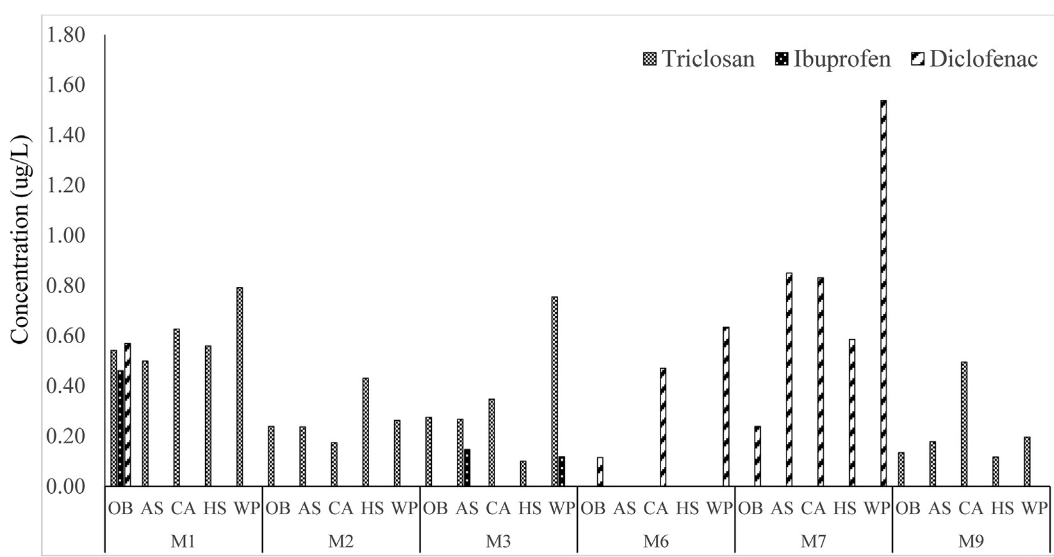

Figure 2. The spatial distribution of PPCPs in surface seawater from Gulf Urabá.

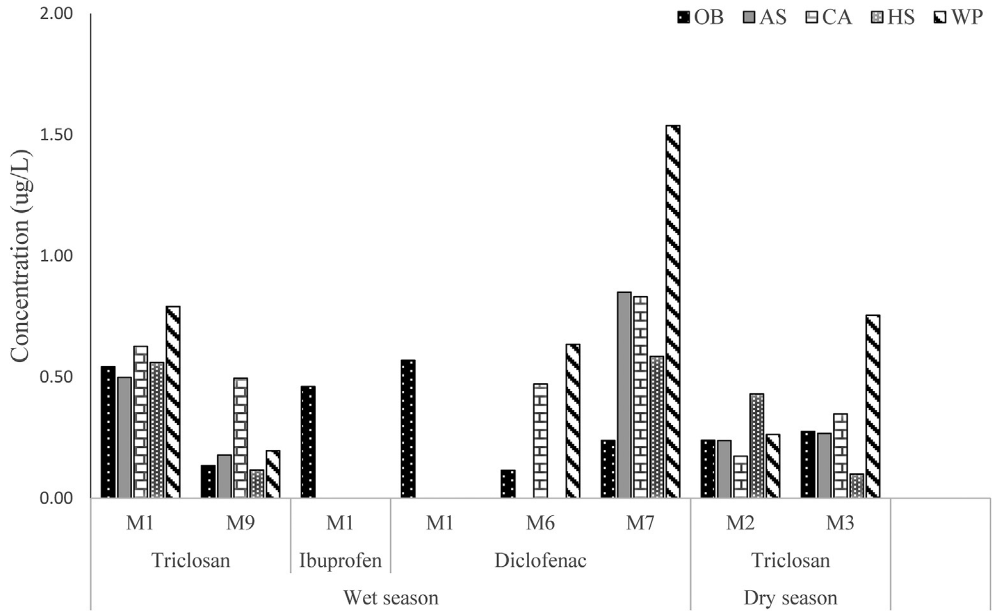

Figure 3. The seasonal variation of PPCPs in surface seawater from Gulf Urabá.

concentrations in winter, while 9 had higher concentrations in summer (Jiang et al., 2019). In addition, biodegradation and photodegradation are two type of natural elimination process for PPCPs, which can be significantly more effective due to stronger irradiation and greater activity of microorganisms (Cui et al., 2019; Du et al., 2019). Moreover, dilution did not exhibit an important effect for the seasonal variation obtained in this work (Cui et al., 2019). It is possible that certain factors that occur regularly in nearby areas to Turbo Bay and are related to agricultural activity such as rotations of banana, pineapple and other crops, irrigations of controlled and uncontrolled chemical products, high demand and other activities that involve tourist cruises that arrive at gulf can generate the differences between the levels of PPCPs.

3.3. Concentrations of PCPs in fish

For the five sampling sites of the Gulf of Urabá, PPCPs frequently detected in surface water samples were not found in fish tissues. Indeed, all fish species analyzed reported mean concentrations below the detection limit (<LC = 20 μg/kg). These results are surprising, since some pharmaceuticals widely detected in surface water, even at relatively low concentrations (≤85.3 ng/L), have also been reported to bioaccumulate in fish (Liu and Wong, 2013). Tanoue et al., reported that disinfectants and insect repellents in the surface water (870 ng/L) in a stream in Ehime, Japan that receives effluent from WWTPs, were also commonly found in muscle, liver and bile in wild fish samples (Tanoue et al., 2015).

Although there is research that indicates that some contaminants in the environment can be accumulated by aquatic organisms due to exposure, there are other studies show particular PPCPs that were not detected in fish tissues despite being frequently detected in the surface water, which is in accordance with our results (Chen and Ying, 2015; Subedi et al., 2012). Ibuprofen and diclofenac are hydrophilic, (log K_{ow}: 1.90 for diclofenac and 2.48 for ibuprofen) (Scheytt et al., 2005), which does not favor their bioaccumulation in fish. In the case of triclosan, it is ionized at a pH above 7.9 (Aldous et al., 2009), since it has a pKa between 7.9 to 8.1, but below a pH of 7.9 it is a lipophilic compound (log K_{ow} of 4.76) (Aldous et al., 2009), and therefore it can bioaccumulate in the fatty tissues of fish.

Is important to mention that bioaccumulation is the result of the competing process of all routes of uptake and elimination, which means that contaminants can be directly accumulated by the liver but not by muscle (Lahti et al., 2011). Therefore, some pollutants can be directly accumulated by the liver and be partially or completely metabolized instead of be accumulated muscles (Escarrone et al., 2016).

4. Conclusions

We assess several temporal and spatial variation trends of emerging pollutants in fish and seawater in order estimate the concentration levels and understand the possible contamination sources of these compounds in the Gulf of Urabá. The results of this study show that PPCPs can be included in the extensive list of contaminants present in Turbo bay. This specific location is considered a high pollution area because it receives direct discharges of wastewater, solid waste, rivers, and due to the lack of basic sanitation systems and operation of the wastewater treatment plants in the municipality of Turbo.

In general, all three pharmaceuticals in different sampling sites were detected and total concentrations ranged from 0.10 to 1.54 μg/L in surface water. In addition, a high variability in triclosan, ibuprofen and diclofenac concentrations according to the season of sampling was found.

Better removal was presented in the dry season, due to stronger irradiation and greater activity of microorganisms. Diclofenac exhibited the highest levels, while ibuprofen showed the lowest contents in the analyzed seawater samples. Meanwhile, triclosan was the compound most frequently found in all samplings, which indicates the wide use of personal care products in the Urabα region.

On the other hand, emerging pollutants content in fish muscle was not detected in this study, likely due to detection limit of the method. These results can be explained due to bioaccumulation process contaminants can be directly accumulated by the liver instead of fish muscle. Therefore, the effects on the liver and other tissues should be investigated in the future, and their possible human health risks evaluated. To the best of our knowledge, the evaluation and monitoring of emerging pollutants in Urabα-Colombia have not been reported, and this is the first publication providing data on these kind of compounds. We propose more comprehensive and complete investigations of PPCPs in marine aquatic ecosystems in Urabα or similar areas from Colombia should be carried out, in order to expand controls and improve restriction strategies for this type of pollutants that are not yet regulated.

Declarations

Author contribution statement

Diana Pemberthy M: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Yisela Padilla: Performed the experiments.

Andrés Echeverri: Conceived and designed the experiments; Performed the experiments.

Gustavo A. Peñuela: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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