Chapter 1

Occurrence of Endocrine Disruptor Chemicals in the Urban Water Cycle of Colombia

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Additional information is available at the end of the chapter

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Abstract

In developing countries such as Colombia, information on the occurrence of endocrine disruptors is still incipient. Bogotá, the capital of Colombia, has a complexity at an anthropogenic and environmental level that makes it particularly important to determine the possible presence of this type of compounds and the risks associated with its presence in aquatic environments. During the present study, the occurrence of endocrine disruptors, mainly pharmaceuticals, plasticizers, and hormones in different aquatic matrices including wastewater, surface water, runoff water, and drinking water was evaluated; the results show that phthalates present the highest occurrence followed by bisphenol A, with an important participation of carbamazepine (0.68–31.45 μg L^{-1}), the most commonly found compound is bis(2-ethylhexyl) phthalate (BEHP). It was also found in the drinking water, this leads to the conclusion that endocrine disruptors in Colombia and Bogotá are a reality and deserve attention from researchers to deepen their potential sources of generation and control strategies, as well as the provision must start generating policies in this regard.

Keywords: endocrine disruptors, occurrence, water pollution, hazard ratio, emerging contaminants

1. Introduction

The increased interest in the study of endocrine disruptors and other emerging pollutants in aquatic matrices that is evidenced in different scientific publications [1] arises from the evidence of their presence in components such as wastewater and its association with problems and effects on ecosystems. This is also due to the high production and commercialization of chemical products in the world with different uses that cause them to be in important concentrations in all matrices, including water [2]. However, both the occurrence studies and the ecotoxicological and risk studies have not been conducted with the same frequency throughout the world, with large differences in the amount of research conducted in the United States and Europe relative to that in Latin America or elsewhere in the world [3].

Although there has been a significant increase in research in this field, there is still a marked difference between the quantity of substances produced and the capacity to monitor, control and understand the totality of the transformations and impacts on the ecosystems they generate. Research and policy tools are lacking in many contexts around the world [2, 4]. Research on ECs encompasses multiple concepts and definitions that are related, including the concepts of micropollutants, personal care products, pharmaceuticals, disinfection byproducts, and flame retardants, among others [5].

To address the issue of endocrine disruptors, it is necessary to speak on emerging pollutants in the first instance, an EC or, preferably, a contaminant of emerging concern (CEC) is defined as any naturally occurring substance, chemical or artificial material that has been discovered or suspected to be present in various environmental compartments and whose toxicity or persistence is likely to significantly alter the metabolism of a living being [6]. The classification of ECs has also been the subject of discussion based on the aforementioned definitions; many of the so-called micro-contaminants are ECs, and even so-called nanoparticles are included. Some of the most widespread classifications include drugs, hormones, polymers, pesticides, stimulants, nanoparticles, and nanomaterials [7–10].

Endocrine disruptors (EDs) chemicals are a category within ECs associated with the type of health risk, such as those that are capable of disrupting the normal functioning of the endocrine system, responsible for all hormonal physiology in living beings [11]. There has been considerable research on EDs around the world, predominantly in Europe and the United States [12, p. 37, 13–16]. Studies have also been performed in Asia, specifically in China, where ED concentrations rarely exceed micrograms per liter [17, 18]. The risk and toxicity of the different ECs have been approached from different points of view, including controlled experimental trials, cohort studies, epidemiological studies of cases and controls, and ecotoxicological studies focusing on the chronic risk as EDs [19, 20]; one of the best known cases is that of bisphenol A, a recognized plasticizer of widespread use worldwide [21]. As part of what continues to be found regarding the level of the risk, contaminants appear on various lists around the world according to precautionary principle, and more than 56 were identified in a single sample of surface water [22]. One of the main sources of EDs in the aquatic environment is wastewater, where it is possible to find sufficient concentrations of these compounds to contaminate surface sources or subsequently contaminate soils or food when the compounds are used for irrigation [23]. This situation has even led water for human consumption exhibiting significant amounts of disruptors; according to a study by Plotan et al. [24], even in bottled and flavored water, it is possible to find concentrations of EDs such as β-estradiol (10 ng L^{-1}), testosterone (26 ng L^{-1}), progesterone (123 ng L^{-1}), and hydrocortisone (13.5 ng L^{-1}).

Another aspect that has presented challenges in the monitoring of EDs is the diversity of compounds that can affect the endocrine system and the techniques for measuring them, which are increasingly sensitive and robust; Mol et al. [25] proposed as a technique for the quantification of

EC gas chromatography-mass spectrometry, noting that this technique offers good results with respect to other methodologies used, such as supercritical fluid extraction, derived fluorescence followed by liquid-liquid microextraction, and other techniques of chromatography with mass spectrometry. This in turn has been proven to be a high precision technique with a sensitivity of 4–6 ng L^{-1}, except for hormones, for which the precision is 50–300 ng L^{-1} [26].

At the level of Colombia and specifically in the city of Bogotá, there have been no studies evaluating the occurrence of EDs in aquatic matrices or the associated ecosystem risk; thus, it is important to set a precedent taking into account the problems of domestic and industrial wastewater pollution in the primary cities around the country [27]. The city of Bogotá has chemically assisted coverage for the treatment of domestic wastewater of approximately 30% at the primary level, which implies the arrival of large amounts of organic matter and different compounds in surface waters such as rivers and channels [28]. On the other hand, the evaluation of photocatalytic treatments [29] or natural systems (wetlands) [30] for the treatment of some endocrine disruptors of general interest has been studied.

2. Study area

Colombia is a tropical country located north of South America and whose capital is Bogotá, has around 9 million inhabitants, also constituting the most important commercial and industrial city [31]. The main river that crosses the extension of the capital district is the Bogotá River that in turn receives as main tributaries the Tunjuelo, Fucha, and Arzobispo rivers that flow into the Northwest zone of the city; these present a significant pollution due to the discharge of wastewater and industrialists from all areas of the city.

Figure 1 shows the distribution area of the sampling points that included three points in the Bogotá River, in the mouths of its effluents, in three rainwater channels, three wetlands, the

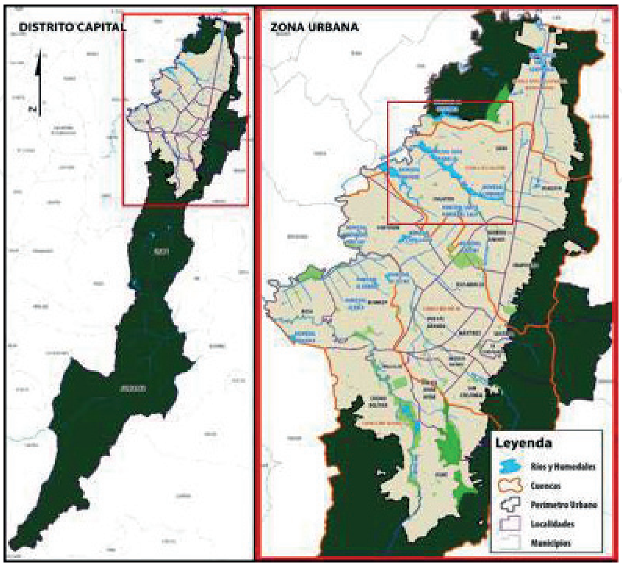

Figure 1. Distribution of monitoring points of EDs in the city of Bogotá.

main sources of supply for the city, and points of the water distribution network; the potable water points were selected according to their distribution from the three current supply systems in the city, including the reservoirs used to supply each system. As for the residual water points, the determination was made at the plant (northwest of the city) and at a sewage pumping station known as the San Benito lifting plant in the southeast.

The selection of the compounds for the monitoring of EDs was based on preliminary and secondary information that allowed us to know the possible sources and quantities generated, groups and commercially available categories, and availability of external standards used in the assembly of the standards and their corresponding calibration curves. These categories are as follows: pharmaceutical compounds (14 compounds), organophosphorus pesticides (20 compounds), hormones and steroids (8 compounds), and phthalates (14 compounds); all high-quality standards were obtained from RESTEK® (Pennsylvania, USA).

3. Sampling

The sampling sites were monitored at selected points according to the criteria of representativeness, access, importance, and physicochemical characteristics. In the points that had current such as rivers, sewers, and channels, composite sampling was carried out, whereas specific samples were taken in the dams and wetlands. **Table 1** shows the number of points and their description and observations.

Samples were taken at the defined points on the dates scheduled for four monitoring days during the periods of August to December 2015 and February to May 2016. The method used

Component	Number of points	Location	Observations
Surface water	3	Tributaries of the Bogotá River (Tunjuelo, Fucha, and Archbishop)	The main contributors of flow and pollutant load
	3	Rio Bogota entrance to Bogota, exit and intermediate point	The purpose is to observe the contribution of the city to the occurrence of EDs
	18	Wetlands (Jaboque, Juan Amarillo and La Conejera)	Within each wetland, samples were taken at different points (6 per wetland)
Drinking water	3	Inputs to the supply systems (Chingaza, Tibitoc, and Sumapaz)	Selected from stratification according to the coverage percentages of the three current supply systems (Wiesner [70%], Tibitoc [20%], and El Dorado [10%])
	49	Points in supply network	29 for Chingaza, 11 for Tibitoc, and 9 for Sumapaz
Sewage water	2	Entry and exit of Salitretreatment plant	Coverage of approximately 40% of the city's wastewater
	1	San Benito lift plant exit	High presence of companies for tanning of skins
Runoff waters	3	South zone, north zone, and center zone	Three channels of rainwater that are part of the city's sewage system.
Total	82		

Table 1. Number and type of points selected for each component of the urban water cycle of the city of Bogotá.

to determine the flow in terms of area by velocity was to take a sample every hour for a period of 8 h, recording the values of flow rates and parameters at the measuring site (pH, conductivity, salinity, and oxygen). In drinking water, it was necessary to seek the assistance of the users of the system, who were trained to take the samples in their homes; these samples were subsequently collected for analysis.

At the exit of the reservoirs used as sources of supply, rainwater channels, sections of the Bogotá River and its tributaries, we used windmills. In the wetlands, samples were taken at different points in the water mirror and in the exits and entries that could be identified, taking into account that the latter are composed of large areas of water and in some cases are fractioned. Two liters of water were taken for each sampling point in each campaign in amber glass bottles of 1 l capacity, refrigerated, and taken as soon as possible to the laboratory for preprocessing.

4. Results and analysis

The spatial occurrence of the pharmaceutical group was determined, in particular, the pharmaceutical compounds are of interest due to their pharmacological activity and their wide use in all contexts; recent studies catalog them as some of the compounds of greater occurrence in aquatic matrices [1, 3, 32]. As expected, the presence of this type of compound exhibits a regular behavior, indicating that these compounds come from sources of continuous contamination, possibly from domestic wastewater containing residues of these compounds that are not fully metabolized [33]. In general terms, the concentrations exhibit similar behaviors for compounds such as fluoxetine but higher in the case of trimethoprim, 860 ng L^{-1}, relative to a range of 10–120 ng L^{-1} [3, 34]. The presence of carbamazepine is striking, as it is known to pose a significant risk to ecosystems and public health [35]. Based on this descriptive information, the highest occurrences are seen for fluoxetine and carbamazepine compounds in runoff waters (12%) and trimethoprim (17%) and carbamazepine (26%) in wastewater and surface waters; these compounds are commonly used as antiepileptics and antidepressants. In the case of carbamazepine, which presents the greatest occurrences, its presence in all type of aquatic matrices has been previously reported [36, 37]; its presence is related to incomplete metabolism in the body, excessive use by people and its persistence in the environment [35, 36].

Figure 2 shows that the points with the highest occurrence of pharmacists are in the western part of the city, specifically in the points located in the Bogota River and the mouths of its tributaries Tunjuelito, Fucha, and Arzobispo; this makes sense since they receive the runoff from city waters and also domestic and industrial wastewater resulting from wrong connections to the sewage or combined sewer system.

On the other hand, it should be noted that the point observed in the eastern part of the city corresponds to the main point of supply of the drinking water network (wiesner about 70% in coverage), this was presented for the carbamazepine compound that was found in two of the samples corresponding to this point. There is no evidence of contamination sources close to this source of supply, but an alert is generated in this regard that should lead to greater monitoring, mainly to one of the reservoirs that supply this system that is known as the

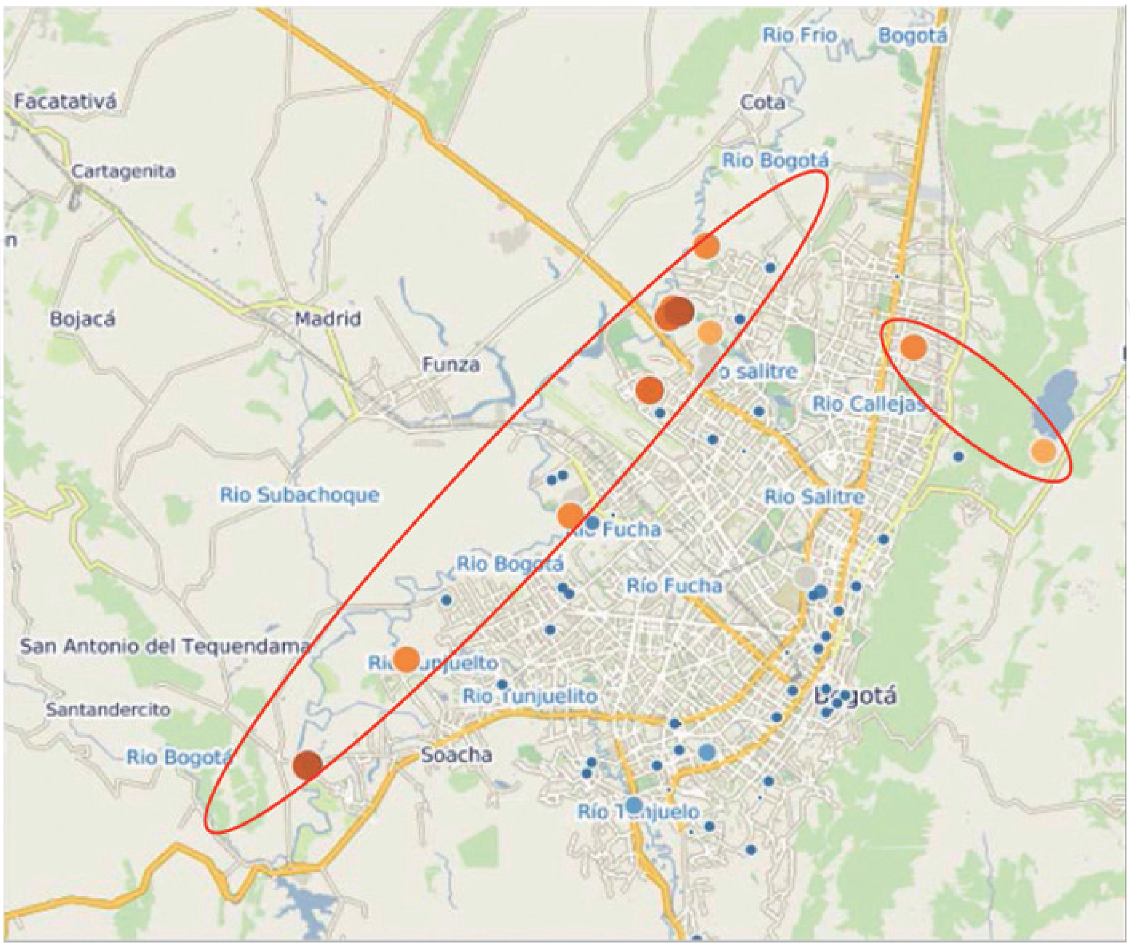

Figure 2. Spatial distribution of occurrence of pharmaceutical compounds.

San Rafael Reservoir, which is very close to inhabited areas and also to lands where agriculture is carried out.

Within the group of phthalates, a much more uniform distribution of these is observed within the city, which implies its distribution not only geographically speaking but in the different matrices evaluated, that is, runoff water, surface water, waste water, and drinking water. Of particular interest is the magnitude of the phthalates in the water supply network of the eastern part of the city, where it can be seen in **Figure 3** that the red color is darker, which represents a higher concentration of the compound bis(2-ethylhexyl) phthalate (BEHP). The area corresponds to the oldest part of the city, where the buildings are the oldest and there are also the oldest internal storage networks.

Aldana and Lopéz [31] ensure that the supply network of Bogotá presents a high complexity due to the variety of diameters, materials, unions, etc., which makes it extremely difficult to associate what is found to a particular factor; however, it is interesting to see the occurrence so high in all the matrices evaluated. Only some points of the drinking water network did not present any of the phthalates, the occurrence of this group of compounds was 100% in wastewater, runoff water, and surface water. The concentrations of the main compounds can be observed in **Figure 4**.

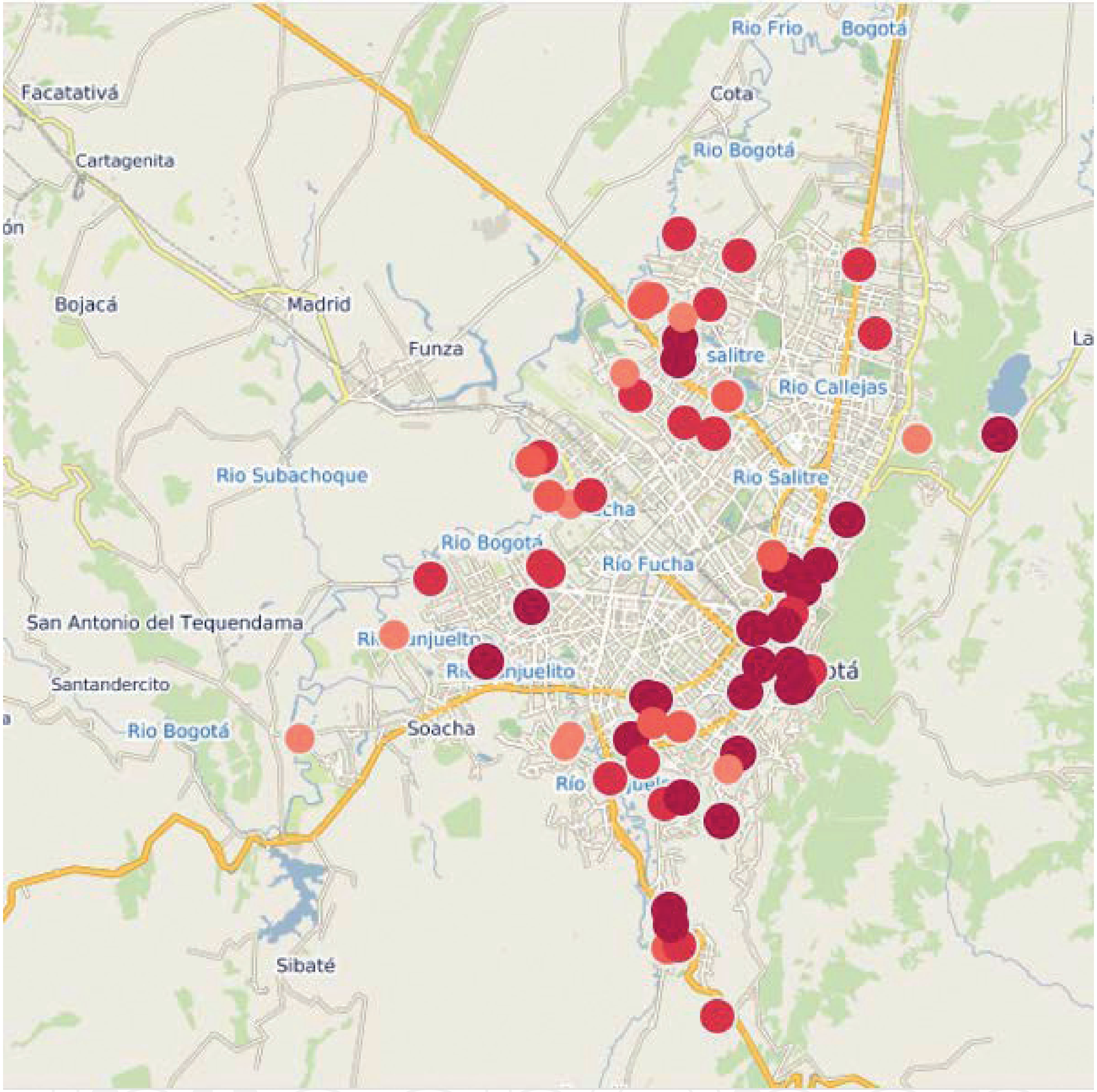

Figure 3. Spatial distribution of occurrence of phthalates.

Phthalates had a much higher occurrence in all evaluated matrices, including potable water points, both at source supply points and network points. Phthalates are widely extended compounds and are therefore found in all spheres of the environment [38]. However, their use as plasticizers in consumer products or industrial activities ensure that in cases such as drinking water, their presence tends to increase, specifically in the case of compounds such as N-diethylhexyl phthalate (BEHP), which is used as an additive in PVC pipes [39, 40]. In total, five compounds were found during the monitoring in all matrices, namely, DEP, DPP, BEHP, DnHP, and BnBP. For DEP, the highest occurrence was found in drinking water (28%); however, the highest occurrences in drinking water were measured for DPP and BEHP, with values higher than 80%. These compounds also showed wide variability in

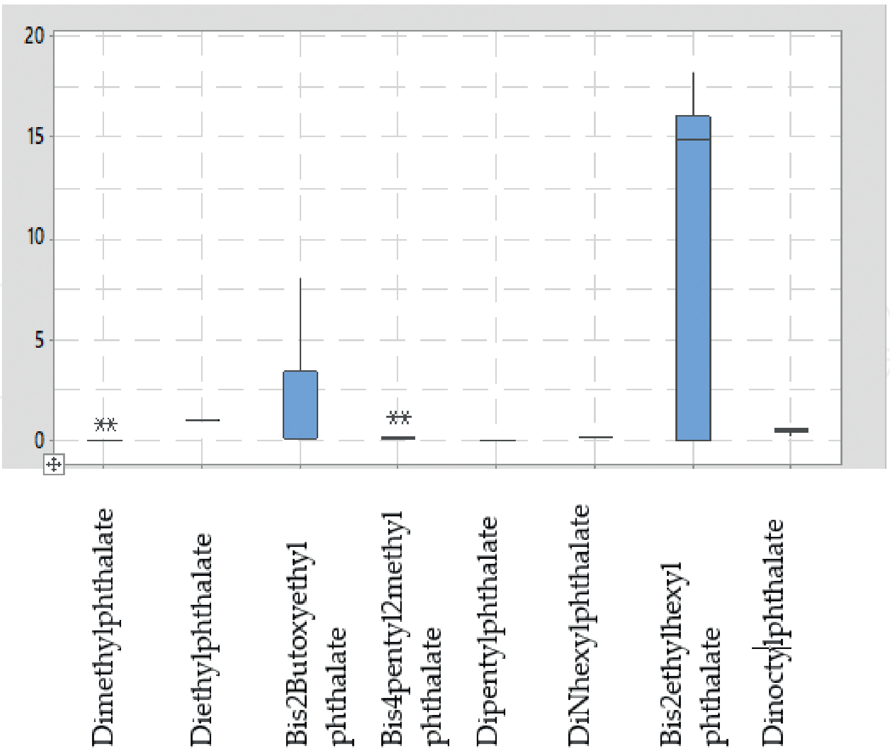

Figure 4. Concentration (μg L^{-1}) of phthalates in wastewater.

concentration, with most being below the concentration considered to have a negative effect on ecosystems and health [41].

It should be noted that the only wastewater treatment plant in the city of Bogotá works with the technology of advanced primary treatment or chemically assisted, this plant does not present high efficiencies for the removal of emerging contaminants, for which it would be required the implementation of other secondary or tertiary treatments such as membrane bioreactors [42] or constructed wetlands [43].

It is not surprising that the behavior observed in the surface waters composed of the Bogotá River and its tributaries (**Figure 5**) is similar to that observed in wastewater, since, as mentioned previously, these are the receptors of most of the city's pollution, including domestic waste water and in some cases industrial waste water.

In the case of the concentrations of pharmaceutical compounds, the presence of this type of compound exhibits a regular behavior, indicating that these compounds come from sources of continuous contamination, possibly from domestic wastewater containing residues of these compounds that are not fully metabolized [33]. In general terms, the concentrations exhibit similar behaviors for compounds such as fluoxetine but higher in the case of trimethoprim, 860 ng L^{-1}, relative to a range of 10–120 ng L^{-1} [3, 34]. The presence of carbamazepine is striking, as it is known to pose a significant risk to ecosystems and public health [35] (see **Figure 6**).

The results by the type of water evaluated show that the highest occurrences are seen for fluoxetine and carbamazepine compounds in runoff waters (12%) and trimethoprim (17%) and carbamazepine (26%) in wastewater and surface waters; these compounds are commonly used as antiepileptics and antidepressants. In the case of carbamazepine, which presents the greatest occurrences, its presence in all type of aquatic matrices has been previously reported [36, 37]; its presence is related to incomplete metabolism in the body, excessive use by people

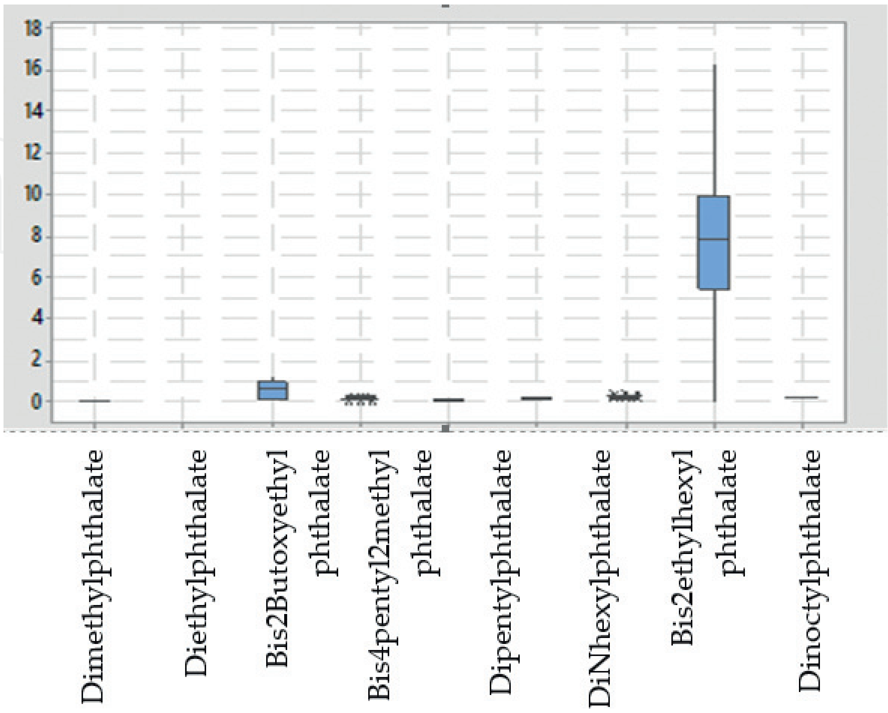

Figure 5. Concentration (μg L^{-1}) of phthalates in surface water.

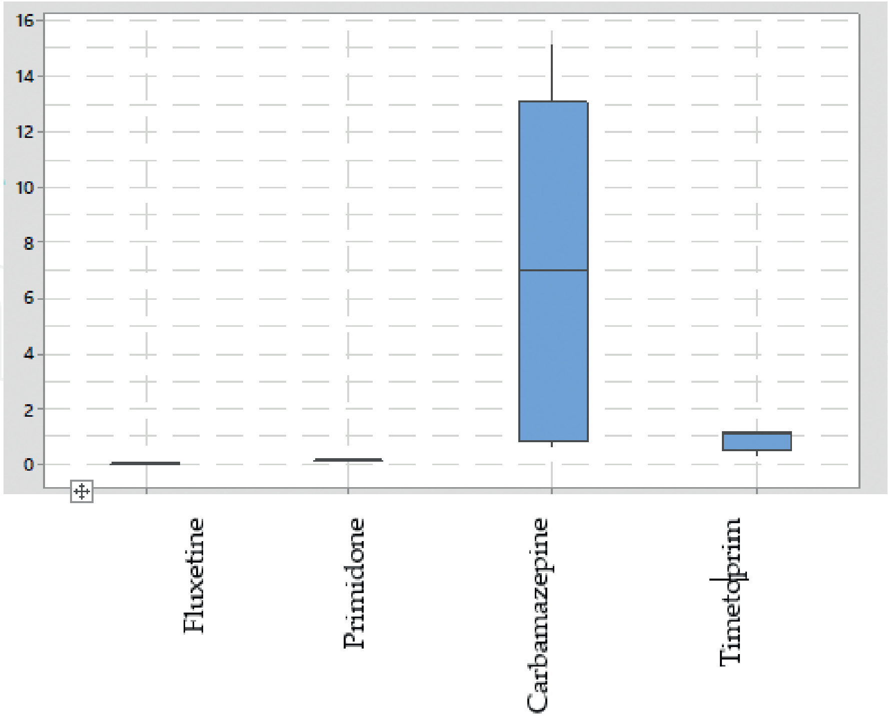

Figure 6. Concentration (μg L^{-1}) of pharmaceuticals in wastewater.

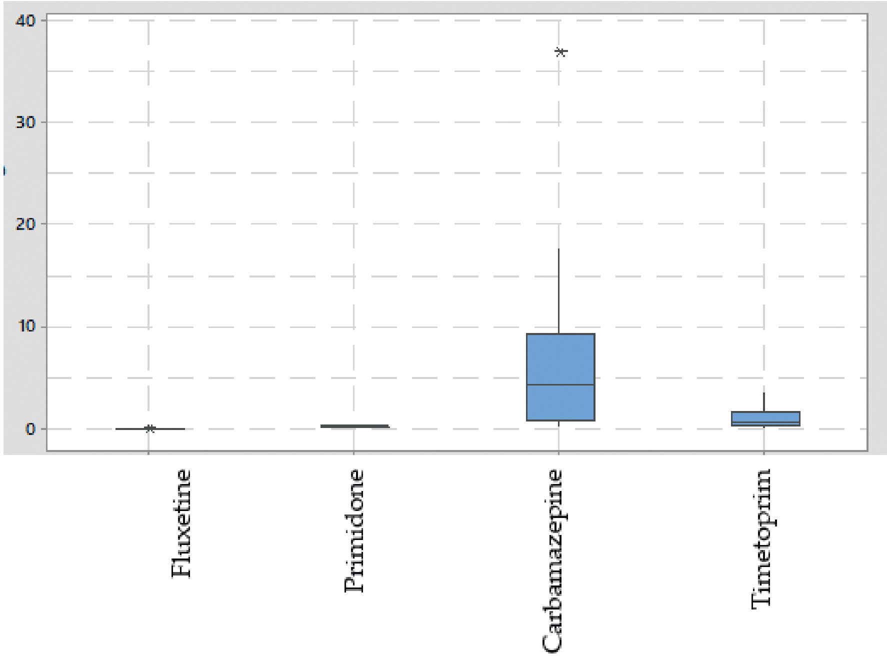

Figure 7. Concentration (μg L^{-1}) of pharmaceuticals in surface water.

and its persistence in the environment [35, 36]. Pharmaceutical compounds again behave similarly in terms of occurrence and concentration in both wastewater and surface water, **Figure 7** shows this behavior.

Studies of emerging pollutants with the potential to act as endocrine disruptors have been carried out in other important cities of Colombia such as Cali [44], which shows the importance of expanding the information and generating new lines of research that allow clarifying the possible effects and impacts of this type of compounds on environmental health.

5. Conclusions

The studies of occurrence imply the first step to be able to dimension a problematic one; in this case of environmental type, for it, it is seen the need to identify that compounds can generate risk as endocrine disruptors, in where and in what magnitude they are. This in order to compare the current situation in countries like Colombia that have little information, with what has already been defined in other contexts and in this way to be able to define better research, control, and regulatory tools.

The study of occurrence in the urban water cycle of the city of Bogotá revealed that endocrine disruptors do represent a problematic to be taken into account at the management level and that compounds such as bis-2(methylhexyl)phatalate and carbamazapine are found in important concentrations and should continue to be investigated in this respect.

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Abbreviations

ECs	emerging contaminants
EDs	endocrine disruptors
BPA	bisphenol A
CBZ	carbamazepine
TMP	trimetoprim
P4	progesterone
DMP	dimethylphthalate
DEP	diethylphthalate
BMHP	bis(2-methoxyethyl) phthalate
DIHxP	bis(4-methyl-2-pentyl) phthalate
DPP	dipentylphthalate
DnHP	di-n-hexylphthalate
BBP	benzylbutylphthalate
BnBP	bis(2-n-butoxyethyl)phthalate
BEHP	bis(2ethylhexyl) phthalate
DnOP	di-n-octylphthalate

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