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Pharmaceutical and personal care products in domestic wastewater and their removal in anaerobic treatment systems: septic tank – up flow anaerobic filter

Presencia de productos farmacéuticos y de cuidado personal en aguas residuales domésticas y su eliminación en sistemas de tratamiento anaerobios: tanque séptico - filtro anaerobio de flujo ascendente

Juan P. Arrubla[1], Janneth A. Cubillos[2], Carlos A. Ramírez [3], Jhon A. Arredondo[4], Carlos A. Arias[5], and Diego Paredes[6]

ABSTRACT

In several countries around the world, Pharmaceutical and Personal Care Products (PPCPs) exist in aquatic environments, a fact that increases the awareness within the scientific community with respect to their possible fate and environment effects. This research presents a preliminary monitoring of use, consumption and presence of PPCPs in wastewater from a treatment plant in a rural area of Pereira (Colombia). Domestic sewage is treated in a septic tank followed by an Up-Flow Anaerobic Filter and its effluent is discharged into the Otún River, upstream of the water intake of the supply system of the city. The compounds monitored in this research included ibuprofen, naproxen, diclofenac, aspirin, ketoprofen, caffeine, galaxolide, tonalide and dihydrojasmonate. An adapted method of multi-residue analysis was used, which is based on solid phase extraction with hydrophilic-lipophilic balance cartridges, and determination by gas chromatography-mass spectrometry. The removal efficiencies demonstrated that the treatment plant could eliminate less than 50% of dihydrojasmonate, diclofenac and galaxolide existing in wastewater; concentration of aspirin, naproxen and tonalide could only be reduced in 15%; and caffeine, ibuprofen and ketoprofen were not removed. Results provided basic information to decide over the necessity of complementary treatments for effluents from systems with the mentioned units.

Keywords: Medicines, personal care, emerging pollutants, socio-demographic characteristics, domestic wastewater.

RESUMEN

En muchos países del mundo, los productos farmacéuticos y de cuidado personal (PPCPs) están presentes en el medio acuático, aumentando las preocupaciones entre la comunidad científica respecto a sus posibles destinos y efectos ambientales. Esta investigación presenta un monitoreo preliminar del uso y consumo de PPCPs y su presencia en las aguas residuales de una planta de tratamiento en zona rural de Pereira (Colombia), donde los vertimientos domésticos son tratadas en un sistema tanque séptico-filtro anaerobio y cuyo efluente se vierte en el río Otún antes de la bocatoma del acueducto de la ciudad. Los compuestos monitoreados en esta investigación incluyen ibuprofeno, naproxeno, diclofenaco, aspirina, ketoprofeno, cafeína, galaxolide, tonalida y dihidrojasmonato. Se utilizó un método de análisis multiresiduo adaptado, que se basa en la extracción en fase sólida con cartuchos de balance hydrophilic-lipophilic y determinación por cromatografía de gases-espectrometría de masas. La planta de tratamiento pudo eliminar menos del 50% del dihidrojasmonato, diclofenaco y galaxolida del agua residual; las concentraciones de aspirina, naproxeno y tonalida sólo fueron reducidas en un 15%, y la cafeína, ibuporfeno y ketoprofeno no fueron removidos. Estos resultados proporcionan información base para decidir sobre la necesidad de tratamientos complementarios para los efluentes de estos sistemas de tratamiento.

Palabras clave: Medicamentos, cuidado personal, contaminantes emergentes, características sociodemográficas, agua residual doméstica.

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Introduction

The role of medicines in human health is important, but they are only one of the determinants of people's well-being. Self-medication, non-authorized and inadequate prescription, and treatment mistakes are also aspects that influence quality of life. In Colombia these problems are present and obey to the common practice of sale of medication without prescription, lack of training for sale personnel, and commercial practices of the industry (World Health Organization, 2008). This situation has increased the consumption of medicines and the necessity of their final disposal when they are no longer needed.

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There are more than 3000 different substances used as medicines, including analgesics, antibiotics, contraceptives, beta blockers, lipid regulators, tranquilizers and medicines for impotence (Siegrist *et al.,* 2004). At the same time, there are thousands of chemical compounds present in products for skin, hair and teeth care products, and these are also present in soaps and sun blocking lotions (Daughton and Ternes, 1999). Some authors have suggested that up to 6 million of Pharmaceutical and Personal Care Products (PPCPs) are commercially available in the whole world, and the use of pharmaceutical products is growing from 3% to 4% in weight by year (Daughton, 2004).

Currently, pharmaceutical and personal care products have expanded importance on environment issues. They are a diverse group of chemical substances used every day in human and veterinary medicine, in agriculture and in cosmetic care (Ávila and García, 2015); they are included in the category of emergent contaminants which have been present in our lives for decades, but only a few years ago their presence in nature has been particularly confirmed in aqueous environments (Moreno *et al.,* 2014). Some of the sources of pollution are the wastewaters from hospitals, agriculture, industrial and domestic activities, which also are present in diffuse discharges as a result of run-offs in areas where human and animal wastes are not treated or confined.

Studies undertaken in North America have demonstrated that these contaminants are present in 80% of the rivers in the United States (Onesios, 2008) and in drinking water in cities, suggesting the existence of certain ecological damages that some PPCPs may cause (US-EPA, 2014).

These emergent contaminants may enter to the environment through the sewer network, by residues produced during the shower (US-EPA, 2014) and also by incomplete metabolic excretion from humans or bad disposal of these components in water (Kummerer, 2009). Once released in nature, many of these compounds persist in wastewater treatment plants (WWTP) and are transported to distant places away from the generating source (Wu *et al.*, 2009; Walters *et al.*, 2010). Many of the medicines that enter wastewater may be absorbed in the sludge produced in treatment systems, which represents a change of the contaminant state from a liquid phase to a solid phase, with low or null degradation (Gartiser *et al.,* 2007).

The medicines of greater consumption are generally the analgesics, due to their purpose of pain relievers. These type of pharmaceutical products are classified in narcotics, non-narcotic and non-asteroid anti-inflammatory (NSAID). The narcotics include codeine, methadone, morphine and oxycodone; the non-narcotic analgesics more used are the acetaminophen and aspirin; and the renowned NSAIDs are diclofenac, fenoprofen, ketoprofen, mefenamic acid, indomethacin, naproxen and ibuprofen (Nicholas-Bateman, 2012). Many of these compounds have been assessed in order to find the exposition routes in water and soil, and also the environment risk that they represent (Miege *et al.,* 2009).

The synthetic musks are chemical products used for the manufacture of fragrances, soap scents, home cleaning products, detergents, fabric softeners, shampoo, shaving lotions and even herbicides (Nair *et al.,* 1986; Gatermann *et al.,* 1995) with a high consumption in the whole world (Osemwengie and Gerstenberger, 2004). They have been found present in the environment because of their high degree of use and liberation, (Rimkus *et al.,* 1994). Due to their chemical structure and physicochemical properties they have a potential to bio-concentrate and bio-accumulate in the soil and the adipose tissue of aquatic organisms (Daughton and Ternes, 1999).

The polycyclic musks such as celestolide (ABDI), galaxolide (HHCB) and tonalide (AHTN) are commonly more used in greater amounts than nitrogenized musks; traseolide (ATII), phantolide (AHMI) and cashmeran (DPMI) are employed with lesser frequency (Daughton and Ternes, 1999). In general, the almost universal consumption of this kind of products results in a constant input to wastewater treatment plants and to the environment.

Caffeine is consumed in large amounts in beverages and in a lesser proportion in the analgesics form; however, its presence has been detected in different types of water: wastewaters (Sweden, Paxe´us, 1996; Spain, Matamoros, 2008); surface waters (Czech Republic, Franke *et al.,* 1995; in the United States, Gardinali and Zhao, 2002; Ontario and Erie lakes in Canada, Metcalf *et al.,* 2003; Spain, Huerta-Fontela *et al.,* 2008); seawaters (Canada, Weigel *et al.,* 2002; Comeau *et al.,* 2008); and in groundwater (Spain, Teijon *et al.,* 2010). In spite of this, the research over the distribution of caffeine in the aquatic environment initiated a few years ago, and it is found in rivers and aquifers in low concentrations in order of ng/L to mg/L.

In this study the habits of consumption and disposal of PPCPs were assessed in a semi-urban area (La Florida) located upstream from the water supply system of Pereira city (Colombia); at the same time, how this compounds may be

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eliminated or not from the wastewater through a treatment system composed by a septic-tank followed by an anaerobic filter was also studied. Due to the innovation that this topic represents for Colombia, up to date this kind of studies have not been reported. It is necessary to characterize the population with emphasis on socio-economic variables, affiliation to the health system, house sanitation characteristics, and information of consumption of pharmaceutical and personal care products, in order to assess, in a later phase, their presence in domestic wastewaters and their removal in a wastewater treatment plant - WWTP.

Experimental Development

Consumption habits determination for Pharmaceutical and Personal Care Products

A descriptive transversal study was carried out through a population census in La Florida (n = 173 homes) located in the middle basin of Otún River, where a member of each house was interviewed with questions related to information of the family, general characteristics of the property, basic sanitation conditions, health and hygiene habits for the family members. After the verbally informed consent, participants answered a survey adapted from López *et al.,* (2007) through a mobile application (Memento Database Pro), in order to capture the field data of Census and Georeferenced Surveys on line. The aplication was developed by *El Centro de Sistematización Ambiental S.A.S*, Colombia.

Processing and descriptive analysis of data were carried out using the IBM SPSS software (version 20), and the construction of graphs was made through Excel 2010.

Water samples

To determine the reduction in concentrations of the studied compounds in wastewaters, a monitoring campaign was achieved in the wastewater treatment plant (WWTP) of La Florida, which is located in the coordinates 4° 45′ 36.64″ N and 75° 36′ 37.52″ E, upstream of the water intake structure of the aqueduct system of Pereira. The average intake flow rate of the wastewater system treatment is 2.97 L/s, and it receives a primary treatment by a Septic-tank and a secondary one in an Up-Flow Anaerobic Filter.

All system treatment has a total hydraulic retention time of 15 h, suggesting that the system is overload. To estimate the efficiency of the system and its removal of PPCPs, a 4 L sample was taken at the inflow and outflow during four sampling events. Each sampling was made during a composition period of 6 h and the assessment of the units was carried out during dry season to avoid the affectation by rain events. The collected water samples were stored at 4 °C in amber color glass containers to be processed in the Gas Chromatography and Mass Spectrometry laboratory at Universidad Industrial de Santander during the following seven days. Wastewater was also analyzed for common organic parameters such as COD, BOD_5 and TSS in order to recognize the efficiency of the treatment plant.

Chemicals and Reagents

All of the pharmaceutical products (ibuprofen, naproxen, diclofenac, aspirin, ketoprofen), stimulants (caffeine), and personal care products (galaxolide, tonalide, methyl dihydrojasmonate) that were used in the analytic techniques of this study were imported reference materials from Sigma-Aldrich, Steinheim, Germany.

Solid Phase Extraction (SPE)

The SPE was adapted from the method reported by Matamoros *et al.,* (2006). All the water samples were filtered through a fiberglass paper with a pore size of 0.45 µm and a 47 mm diameter in order to be acidified later to a pH 2 with concentrated chloride acid. A sample volume of 500 mL was percolated in a polymeric cartridge Strata X, previously set with 5 mL of n-hexane, 5 mL of ethyl acetate, 10 mL of MeOH, and 10 mL of Milli Q water. The filtration rate was adjusted to approximately 10 mL min^{-1}. After that, the cartridges were dried and, finally, the analytes were eluded with 5 mL of ethyl acetate. The extract was evaporated until it dried under a soft flow of reconstituted nitrogen in 175 µL of methanol.

Gas Chromatography Analysis and Mass Spectrometry

As a consequence of the low concentration of PPCPs (generally found at trace level in the environment), high polarity, thermic instability, and their interaction with complex aqueous matrixes, reliable and precise analytic processes to measure these compounds are required. The use of gas chromatography systems (GC) or a high-performance liquid chromatography separator (HPLC), and the use of qualitative and quantitative analyses with different detectors has been the best option.

Mass spectrometry (MS) presents high selectivity, specificity and sensitivity advantages in order to analyze the PPCPs; this is the reason why the GC-MS and LC-MS have become an indispensable tool in the investigation of these type of compounds in environmental matrixes (Hao *et al.,* 2007).

The methodology used for the analyses was GC-MS adapted from Matamoros *et al*. (2005) where the obtained extracts in the SPE were analyzed in a Gas Chromatograph AT 6890 Series Plus (Agilent Technologies, Palo Alto, California, USA.) coupled to a mass selective detector operated in ion selective monitoring mode (SIM) (MSD 5975 Inert XL Agilent Technologies, Palo Alto, California, USA). The column used was HP-5 capillary (5 % phenyl, 95 % dimethyl-polysiloxane) (30 m × 0.25 mm ID, 0.25 µm thickness phase); the He gas running was 1.0 mL min^{-1}; the injection volume was 2 µL in split less mode. Methylation of the carboxylic acid group was carried out on line in a hot gas injector supplied with 2 µL of trimethylsulfonium hydroxyl solution, TMSH (0.25 mol/L in methanol) at 50 µL of sample before the injection.

In the selective ion monitoring mode the following ions were selected: methyl ester Ibuprofen, 161/162/177/220; methyl ester naproxen, 170/185/186/244; methyl ester diclofenac, 214/216/242/309; methyl ester ketoprofen, 191/209/210/268; galaxolide, 213/243/244/258; tonalide, 201/243/244/258; caffeine, 82/109/165/194; dihydrojasmonate, 83/153/156/226; and methyl ester acetylsalicylic acid, 92/120/121/152.

Statistical Analysis

The results of the removal study were analyzed with the statics package IBM SPSS version 20.

Results

Socio-economic characterization of the population

Each home has an average of 3.4 inhabitants, and the typical range of member ages found were between 19 and 59 years old with a 54 % of frequency. The inhabitants above 60 years were 20 % of the population, and the infants below 2 years were less than 3 % of the total analyzed population.

The children between 2 and 12 years old were represented by approximately12 %, as well as the adolescents between 13 and 18 years. 60 % of the residents were associated with the contributive official health system (persons with wage pay for health services in the official government system) while 37.5 % belong to the subsidized regime (people covered by the official health system). Only 2.5 % of the interviewed homes were found lacking any health protection.

51 % of homes reported an income between COP $190.000 and COP $600.000, 36 % between COP $616.000 and COP $1.232.000, 2 % between COP $1.232.000 and COP $1.848.000, and only 3 % had an income above COP $1.848.000. 8 % of the homes informed to be living with an income below COP $190.000 (the corresponding exchange rate from USD to COP for 2014 was $2000.33).33.3 % of the people interviewed declared that their income is not enough to cover their basic needs, 58.3 % of the total declared that their income barely allows them to survive, and only 8.3 % affirmed that their wages went beyond the basic needs.

When inquiring about the socio-economic classification, it was found that 19 % of homes were in strata I (low-low), 76 % were in strata 2 (low) and only 5 % of the homes were classified in strata 3 (medium- low). These data represents the typical condition of people from rural zones in Colombia.

Regarding access to water and sanitation services, 98 % of the interviewed homes had water from the local aqueduct system, and only 2 % were supplied by a water spring. 83 % of properties discharge their wastewater in the sewer system and 12 % treats it through an individual decentralized treatment plant (55 % of these homes know how to perform maintenance to their systems, while the remaining 45 % does not know how to do it); only 5 % of homes directly discharge the effluents to a surface source and to the ground. Just 91 % of the homes confirmed that they deliver the solid wastes to a collection vehicle.

La Florida is a semi-urban community with a great deal of population belonging to low socio-economical classification, good basic sanitation indexes, a high rate of affiliation to health system, and a low level of education.

Pharmaceutical and personal care products consumption habits

Concerning health habits, 79 % of the inhabitants of the surveyed homes consume medicines, while 21 % indicated that they do not. The consumption habits are divided in equal parts (50 %) among those who have a daily use and those who only use them when symptoms arise. Among the criteria used to buy a medicine, the medical prescription is prevalent (69 %), followed by self-medication (27 %), and mixed prescription/self-medication (4 %). Regarding consumption orientation, 79 % of the interviewed people declared that the doctor gives them a prescription, 13 % were oriented by family suggestions, and 8 % by the pharmacist, friends or publicity.

The interrogated people reported a total use of 37 medicines: 1. Acetaminophen (paracetamol), 2. Aspirin (acetylsalicylic acid), 3. Alapril (halazepam), 4. Alercet (cetirizine), 5. Amiodarone, 6. Amlodipine, 7. Amoxicillin, 8. Astonin (fludrocortisone), 9. Atorvastatin, 10. Bromide of Ipratropium, 11. Buscapine (paracetamol and scopolamine), 12. Calcium, 13. Cephalexin, 14. Descongel (paracetamol, loratadine, phenylephrine), 15. Diclofenac, 16. Dinitrate Isosorbide, 17. Dolex (acetaminophen, phenylephrine), 18. Furosemide, 19. Glibenclamide, 20. Hydrochlorothiazide, 21. Hydrocortisone, 22. Ibuprofen, 23. Insulin, 24. Ketoprofen, 25. Metformin, 26. Metoprolol, 27. Naproxen, 28. Metformin, 29. Nifedipine, 30. Noraver (ibuprofen, phenylephrine, levocetirizine), 31. Noxpirin (paracetamol, caffeine, cetirizine), 32. Piroxicam, 33. Prednisolone, 34. Robitusin (dextromethorphan, hydrobromide), 35. Salbutamol, 36. Saline solution, and 37. Tyrosine.

Medicines of greater consumption in the population are non-asteroid anti-inflammatory (NSAIDs). Among these, the most popular is acetaminophen (medicine with analgesic properties) with a 27 %: medicines sold without medical prescription such as aspirin (6.5 %), ibuprofen (4.5 %), naproxen (2.4 %) and diclofenac (2.4 %) were also featured.

Other medicine groups that are highlighted are those prescribed for high blood pressure treatment (amlodipine-5 %; enalapril-7 %; losartan-11 %); for treatment of hyperthyroidism (levothyroxine-3 %); for lowering cholesterol level (lovastatin-10 %); and for use as diuretics (furosemide-3 %; hydrochlorothiazide-7 %). Medicines used for diabetes control are also reported (insulin-2 %; metformin-5 %), and for the treatment of common cold (noxpirin-3 %).

The reported dosages differ from each medicine consumed, and depend on the purpose of each one. As an example, acetaminophen is administered orally in every case with dosages varying between 250 to 500 mg from one to three times per day. The same occurs with medicines used to treat common colds such as noxpirin (paracetamol, caffeine, and cetirizine), dolex (acetaminophen, phenylephrine) and descongel (Phenylephrine hydrochloride, loratadine, and acetaminophen) that have treatments up to three days with a dosage of pills every 8 to 12 hours. On the other hand, the medicines used for the treatment of blood pressure vary between 20 and 150 mg in doses per day during a lifetime treatment as well as the treatment for kidney illness and diabetes. The antibiotic treatments with amoxicillin were reported under a dosage of 500 mg for three times a day during one week period. In general, the most common doses were administered orally, and the least common administration is the injection, reported for medicines such as insulin and diclofenac. The NSAIDs were testified as occasional use and their treatment depends on the response from the patient.

Once the medical treatments are finished, it is very common for people to dispose the leftover medicines. Most of them (59 %) dump the products with the domestic solid wastes while 9.3 % disposes them through the sanitary unit. 17 % of the people gives the medicines as a gift to other people, and the remaining 15 % reported taking them to a pharmacy for their appropriated and controlled disposal. It is assumed that at least 37 active different pharmaceutical principles (apart of their degradation metabolites) are incorporated into the domestic wastewater due to the use of medicines. Currently, the mentioned compounds are not monitored in Colombia, neither are there laws in the country to monitor and control this.

According to data, there was no difference between the income and the type of medicines consumed, neither any correlation between consumption characteristics by family group and the reported income in this study case.

On the level of personal care products, the people interviewed were asked about the frequency of use, amount and purchase frequency. From the answers, it was possible to recognize that the daily use of ten personal care products and their emergent contaminant molecules are probably discharged in domestic wastewaters (Table 1).

A wide range of chemical compounds such as personal care products, surfactants, plasticizers and industrial additives are not included in the current monitoring of water treatment programs, but they are incorporated as new chemical compound synthesis that needs changes in the use and disposal, because up to date there is a limited available information on the effect that they may cause on human health and on the environment (Smital, 2008).

Table 1. Information of consumption of personal care products and possible contaminant molecules

Product	Size buy	Freq.* of use	Freq.* of purchase	Emerging contaminant molecules
Shower soap	120 g	Daily (98.2 %)	Monthly	Anionic surfactants and bactericides (triclosan, triclocarban, triclorocarbamide and cloroxilenol); EDTA (some soaps)
Tooth paste	125 mL	Daily (93.1 %)	Monthly	Sodium Laurilsulphate, triclosan
Deodorant	150 mL	Daily (92.6 %)	Monthly	Tetrachlorohydrexiglicinate of aluminium, triclosan, ciclohexene carboxaldehyde and BHT
Body cream	250 mL	Daily (78.7 %)	Monthly	BHT, methylparabene, propilparabene, phenoxyethanol, octasulfate of aluminium.
Perfume	100 mL	Daily (68.8 %)	Semester	Nitro musk (xylene and cetone; musk abelmosco, muscade and tibetan - in lesser proportion). polycyclic musks (galaxolide and tonalide)
Mouth wash	125 ml	Daily (57.4 %)	Monthly	Triclosan and chlorhexidine (antbacterial); nonilphenol (surfactant)
Shampoo	500 mL	Daily (52.8 %)	Monthly	Surfactants (salts of amonium quaternary); biocides (methylisotiazolinone)
Hair dye	100 mL	Monthly (43.4 %)	Monthly	Phenyl methyl pirazolone, quaternary ammonium salts, 2 methyl resorcinol, methyl paraben, resorcinol
Shaving cream	200 mL	Weekly (24.8 %)	Semester	Sodium Methylparaben and triethylenamin; triclosan.
Hair conditioner	500 mL	Daily (22.2 %)	Monthly	Quaternary ammonium, methylisotiazoline, xilensulphonates and methyl-chloroisothyazolines

***Freq.:** Frequency.

PPCPs Presence in wastewater

Based upon the collected information from the surveys and on different studies that report the presence of PPCPs in wastewater, it was decided to evaluate the products related in Table 2, and their possible removal from wastewater in the treatment system of the rural area of La Florida (Pereira). The assessed medicines are free-sale products and commonly used by the assessed population. On the other hand, the selection of compounds derived from personal care products is due to their presence in daily use elements reported by people (Table 1).

Table 2. Influent and effluent concentrations of assessed PPCPs

Parameter	Influent			Effluent		
	Max.	Min.n.	Ave.	Max.	Min.	Ave.
Aspirin (μg/L)	5.5	3.9	4.3	4.8	3.9	4.1
Caffeine (μg/L)	11.1	0.1	5.5	15.2	1.0	8.1
Cis-MDJM (μg/L)	31.8	4.7	15.7	11.5	7.4	9.1
Diclofenac (μg/L)	78.7	1.1	21.6	13.6	1.1	5.3
Galaxolide (μg/L)	39.2	5.7	16.0	17.6	0.1	7.2
Ibuprofen (μg/L)	0.7	0.1	0.3	2.1	0.1	0.9
Ketoprofen (μg/L)	1.7	0.8	1.3	2.4	0.8	1.5
Naproxen (μg/L)	2.0	0.4	1.1	4.8	0.9	2.3
Tonalide (μg/L)	6.3	2.2	3.4	6.6	2.2	3.4

Measured PPCPs presented trace level concentrations (µg/L) in the influent and effluent of the treatment systems (Table 2), and this has been commonly reported for this type of organic micro-contaminants existing in wastewater (Verlichi *et al.,* 2012). The described concentrations are in a wide range of values due to use/consumption variations of those products and their metabolism degree in humans (Miège *et al.,* 2009).

The compounds that present higher average concentrations in the treatment system are diclofenac (21.6 µg/L), methyl-dihydrojasmonate (15.7 µg/L) and galaxolide (16 µg/L). The remaining group of assessed compounds presents concentrations below 6 µg/L. For all PPCPs evaluated, the removal efficiencies may be estimated as low. Comparing influent and effluent concentrations (Figure 1), the removal rates were below 50 % for compounds such as methyl-dihydrojasmonate, diclofenac and galaxolide; below 15 % for aspirin, naproxen and tonalide, and no removal rates for caffeine, ibuprofen and ketoprofen. This fact agrees with the information reported by other authors in which conventional treatment systems do not have a wide removal capacity for this type of emerging contaminants (Suarez *et al.,* 2008; Dordio *et al.,* 2010).

It is difficult to say that the reported efficiencies are typical for the system assessed, since results in different investigations show a high variation in the removal percentages in conventional treatment systems. Such uncertainty is attributed to the variability in the rate of PPCPs consumption, the metabolism of the consumers, the wastewater generation rates, the persistence in the environment of such substances, and the efficiency in the treatment processes (Petrovic *et al.,* 2009; Jelic *et al.,* 2012).

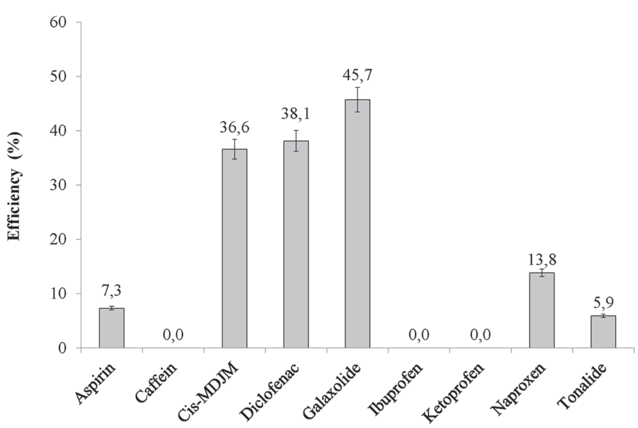

Figure 1. Removal efficiency of PPCPs (error level = 5 %)

The removals of galaxolide and tonalide are close to the average values mentioned by Luo *et al.* (2014), who report removals of galaxolide and tonalide between 15 and 30 % with biological degradation as one of the responsible mechanisms. Low removal rates of ibuprofen and naproxen may be presumably attributed to their low adsorption of sludge particles in primary treatment units. Regarding ketoprofen and diclofenac, low removals may be indorsed to compound structure characteristics (aromatic rings in ketoprofen and chloride molecule in the structure of diclofenac) that turns them into recalcitrant compounds (Matamoros *et al.,* 2009), and therefore difficults their removal. Caffeine is commonly informed as the most abundant PPCP in wastewater, reaching removal efficiencies above 80 %; however, for the assessed case, no reduction concentration was reported.

Several authors agree that the principal removal mechanisms of PPCPs in water treatment systems are biodegradation, sorption in filtering media/particulate material, filtration, chemical oxidation and volatilization (Miège *et al.,* 2009; Guerra *et al.,* 2014); those mechanisms may be either favored or not by the operational conditions of each system and the characteristics of the wastewater to be treated. This is the reason why it is difficult to confirm the persistence of each component in the studied treatment system and it is suggested to undertake more investigations that allow to identify the possible routes and removal mechanisms involved in this kind of treatment system.

The reported removals in this investigation are not surprising when considering that the assessed biological treatment system (ST-UFAF) is designed for the removal of conventional parameters such as BOD_5, COD and TSS, that present concentrations in the level of de mg/L (Ratola *et al.,* 2012; Patiño *et al.,* 2014), but not for the removal of organic micro-contaminants and their metabolites (Igos *et al.,* 2012). The wastewater treatment plants are considered in fact as a retention point and later liberation of PPCPs to the environment (Jelic *et al.,* 2012b; Wang *et al.,* 2015), because the physical and chemical properties of the PPCPs (solubility, volatility, absorbability, absorbability, biodegradability, polarity and stability) vary considerably in wastewater and depend on the operational conditions of the treatment systems (Verlichi *et al.*, 2012; Yunlong *et al.,* 2014).

On the topic of organic matter parameters used to assess the wastewater treatment systems operation, the arrangement of septic tank and anaerobic filter units in this research displayed an efficiency removal higher than 50 % for CDO, BOD and TSS, as presented in Table 3. These data represent a low efficiency in this kind of systems treatment since the typical percentage for organic matter removal in this combination units is reported between 80 and 90 % (Sperling, 2012).

Table 3. Organic loads and efficiency removal

Parameter	Organic loads		% efficiency ST-AF
	Influent Septic Tank	Effluent Anaerobic Filter	
BOD (kg/d)	56,7	28,3	50,09
COD (kg/d)	27,4	11,9	56,80
TSS (kg/d)	25,2	10,4	58,71

According to the results found in this study, the presence of PPCPs after the discharge on Otún River of the treated wastewater in La Florida is expected; however, we must emphasize that these pollutants, despite the current importance worldwide, are not yet considered as priority compounds for evaluation within the existing regulatory framework in Colombia. In this sense, we should not rule out the need to continue researching on these traces of emerging contaminants and the potential technological alternatives that can be implemented for their removal in wastewater.

Conclusions

In the rural area of La Florida it is recognized that the use of medicines and personal care products are due to consume practices not only by medical prescription but also by self-medication, which encourage the indiscriminate use of these products. As a consequence, and due to the lack of monitoring of PPCPs in the discharges of domestic wastewater, the uncertainty about the effect of the active components that are not absorbed by the human body and later discharged to the water sources increases.

The medicines consumed by the people from the evaluated area in this research are principally used as anti-inflammatories, analgesics, blood pressure control, diuretics, and for diabetes and high cholesterol treatments. Therefore, it was found that around 37 active pharmaceutical principles and their degradation metabolites can be incorporated into the domestic sewages that feed the anaerobic system treatment used in the study area.

All the analyzed personal care products and their active principles are defined as emerging contaminants. The purchase volume and frequency of use makes their concentrations in the effluents constant in time, causing an environment contamination risk that must be studied in detail. Even the persistence and risk for the water supply system downstream of the WWTP in the city must be evaluated.

The PPCPs of the produced wastewater in the study area were founded in typical concentration ranges; however, their reduction through the ST-AF system did not show to be very significant for most of the emergent contaminants assessed, mainly for caffeine, ibuprofen and ketoprofen, which are medicines with common use due to their wide usefulness and ease of access. The compounds with more reduction concentration in the treatment system were methyl-dihydrojasmonate, diclofenac and galaxolide, but nevertheless they did not reach removal efficiencies higher than 50%. This result might be complemented by the operation conditions of the treatment plant, which showed organic matter removal between 50 and 60%. This state should be checked due to the necessity to extend the hydraulic retention time from each treatment unit, as well as to allow better environments for the biological processes that occur inside reactors and perhaps contribute to PPCPs removal mechanisms.

Nowadays in Colombia, the monitoring of these kind of compounds is scarce and no regulations on these discharges are present in the laws; hence, it is suggested that national researchers invest in efforts to assess new depuration systems that allow the removal of this substances that are arriving to the domestic and industrial effluents, and that may indirectly be passed to the supply systems of drinking water.

It is recommended to start investigations on alternative treatment systems in order to reduce the concentrations of these contaminants in water. At the same time, a continuous monitoring campaign must be undertaken to allow an adequate control over the contaminant discharges of PPCPs in the water supply systems of the City of Pereira.

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