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Emerging Contaminants in the Northeast Andean Foothills of Amazonia: The Case of Study of the City of Tena, Napo, Ecuador

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Abstract

This work is a study on the occurrence of emerging pollutants in the northeast Ecuadorian Amazon. Emerging contaminants (ECs)—caffeine, triclosan, estradiol, acetaminophen, nicotine, and ibuprofen—were quantified by gas chromatography–mass spectrometry in rivers and streams of the Amazon basin near the city of Tena, Ecuador. For that, a total of 16 natural water samples were taken in 8 locations. Sampling sites included areas impacted by discharges from inefficient sewage networks in urban areas, wastes from fish farming and non-functional landfill, a stream with few threats, tap water, and treated sewage. Caffeine was found in the 38% of the samples studied while trimethoprim and acetaminophen had an occurrence of 13%. Caffeine was detected at two sites receiving untreated sewage and one site receiving treated sewage with mean concentrations that ranged between 19 and 31.5 µg L^{-1}. Acetaminophen (50.4 µg L^{-1}) and trimethoprim (2 µg L^{-1}) were only detected in the river receiving treated sewage effluent. This is the first assessment of emerging contaminants in the upper Ecuadorian Amazon basin, and our observations highlight the need for better sewage treatment and water quality monitoring in Amazonian cities.

Keywords Caffeine · Trimethoprim · Acetaminophen · Amazon basin · Pharmaceuticals

There is a worldwide concern about the so-called emerging contaminants (ECs) present in natural and drinking water. The ECs are chemical compounds, including antibiotics, pesticides, surfactants, caffeine, and illegal drugs, among other substances, that are not eliminated in conventional water treatments and, therefore, are released into the environment (Becerril 2009; Tran et al. 2018). Generally, ECs are found in low concentrations, but their continuous discharge into the environment is perceived as public health and environmental risk. Studies around the world have detected ECs in a surface, underground, and drinking water (Ali et al. 2018; Alvarez et al. 2014; Barceló et al. 2009; Birch et al. 2015; Diaz-Sosa et al. 2020; Pinos-Vélez et al. 2019; Sorensen et al. 2015; Sousa et al. 2019; Trabalón et al. 2017; Zhang et al. 2015). Common ECs found in rivers, and other surface waters include triclosan, sulfamethoxazole, diclofenac, ibuprofen, nicotine, acetaminophen, trimethoprim, and estradiol (Archundia et al. 2018; Jagini et al. 2019; Marques et al. 2016; Robles-Molina et al. 2014, p.; Seabra et al. 2016). Among them, the compounds of most significant concern are antibiotics, due to bacterial resistance, and endocrine disruptors such as triclosan and estradiol; endocrine disruptors are capable of mimicking the hormones and, therefore, altering the proper functioning of the body and negatively affecting our health (Lu et al. 2020; Sharman et al. 2016). In fact, some studies link cancers such as breast and prostate with its presence (Kim et al. 2020; Siddique et al. 2016). Endocrine disruptors are also related to hormonal alterations

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in fauna; for instance, the presence of intersex fish, where male reproductive tissues show evidence of feminization (Niemuth and Klaper 2015). Many studies have found ECs in marine environments and inland waters of large cities related to the consumption habits of the population (Naidu et al. 2016). To our knowledge, there are no studies on the detection of ECs in the Amazonas basin, perhaps because the technologies needed to analyze these compounds are still expensive and barely accessible for some Latin American countries.

Lack of wastewater treatment is a problem throughout Latin American countries. Discharge of untreated wastewater into rivers is a serious environmental challenge, resulting in widespread environmental pollution. Less than 30% of the cities in Latin America have sewage treatment (Rojas-Ortuste 2012; Hernández-Padilla et al. 2017). In the Ecuadorian Amazon region, only 25% of the wastewater is subjected to some type of treatment, and 56% of the untreated wastewater is discharged directly into rivers. Additionally, the few existing sewage treatment plants include only primary and secondary treatments focusing on the removal of nutrients, microbial contaminants, heavy metals, and other regulated compounds such as pesticides (Rodriguez-Narvaez et al. 2017). The study of the occurrence and risks of ECs is important to select which should be regulated for discharges and considered for its remotion in water treatments.

The upper Amazon River system is one of the largest and most biodiverse aquatic systems in the Andean-Amazon region of Ecuador (Alexiades et al. 2019). It is considered that the rivers of the upper Amazon basin receive less agricultural, industrial, and domestic pollution than their counterparts in central Amazonia due to a lower population density and urbanization (Encalada et al. 2019). Nevertheless, local environmental impacts caused by the diversification of economic activities, the lack of proper waste management, and the flexibilization of environmental protection controls have intensified environmental pollution risks (Capparelli et al. 2020; Galarza et al. 2021; Lessmann et al. 2019; Lucas-Solis et al. 2021). Considering the lack of information regarding ECs in the Amazon basin, the aim of this study was to evaluate ECs in drinking water, wastewater, rivers, and streams of the upper Ecuadorian Amazon basin near the city of Tena to set a precedent for its environmental monitoring.

Materials and Methods

Study Area and Sampling Sites

The study area comprises about 7.000 ha in the Ecuadorian Amazonia, on the eastern Andean foothills, near the city of Tena (Fig. 1). Rivers and streams in the study area drain into the upper Napo River, which is the main Northern Ecuadorian Amazon River. The population in the study area is about 44,000, occupying both rural and urban areas, with a population density of 11.8 inhabitants/km^2 (INEC, 2010). Sampling points were chosen to reflect land uses and known pollution sources (Fig. 1): a small stream receiving fish farming wastes (1FF), a stream with few threats (2FTS), domestic tap water from the water distribution system of Tena (3TW), effluents of wastewater treatment plants (4TWW and 7TWW), urban drainages (5UP and 6 UP) and a small stream receiving landfill drainages (8LF).

Sample Collection

Water samples were collected in March 2020 during a period of low flows and hydrological stability. No precipitation above 15 mm per day was recorded in the five days prior to sampling nor in the sampling day (Meteorological Station of Ikiam University, http://meteorologia.ikiam.edu).

Sampling sites were chosen based on the presence of different contamination sources mapped by Capparelli et al. 2020. Wastewater and urban effluents (4TWW, 7TWW, 5UP, and 6UP) were sampled from the outlet pipes. Drinking water (3TW) was collected from the tap of a residence in the city of Tena. The streams that receive fish farming wastes (1FF) and landfill drainages (8LF) were sampled downstream of the effluent discharges. The stream with few threats (2FTS) was sampled at a location far from the urban center but downstream of small riverside communities without wastewater treatment. FT sites were locations distant from the main contamination sources identified.

Two water samples (500 mL) were collected in amber glass bottles at all sampling locations. Physicochemical parameters—temperature, conductivity (SpC), pH, color, turbidity, total dissolved solids (TDS), and residual chlorine—were measured in situ employing a HACH HQ11d. Samples were transported under refrigeration to the laboratory and were stored at 4°C for one day until analysis.

ECs Evaluated

Seven widely consumed compounds, whose characteristics taken from PubChem (2020) are shown in Table 1, were chosen for this study. Caffeine and nicotine have been chosen as lifestyle products. Acetaminophen and ibuprofen are both included in the most sold pharmaceuticals without prescription in Ecuador. Trimethoprim is a prescription antibiotic commonly used by the population and also used in veterinary products. Estradiol is a hormone included in contraceptives. Triclosan is used as a preservative and additive as well as it is part of cleaning products as an antibacterial. All this

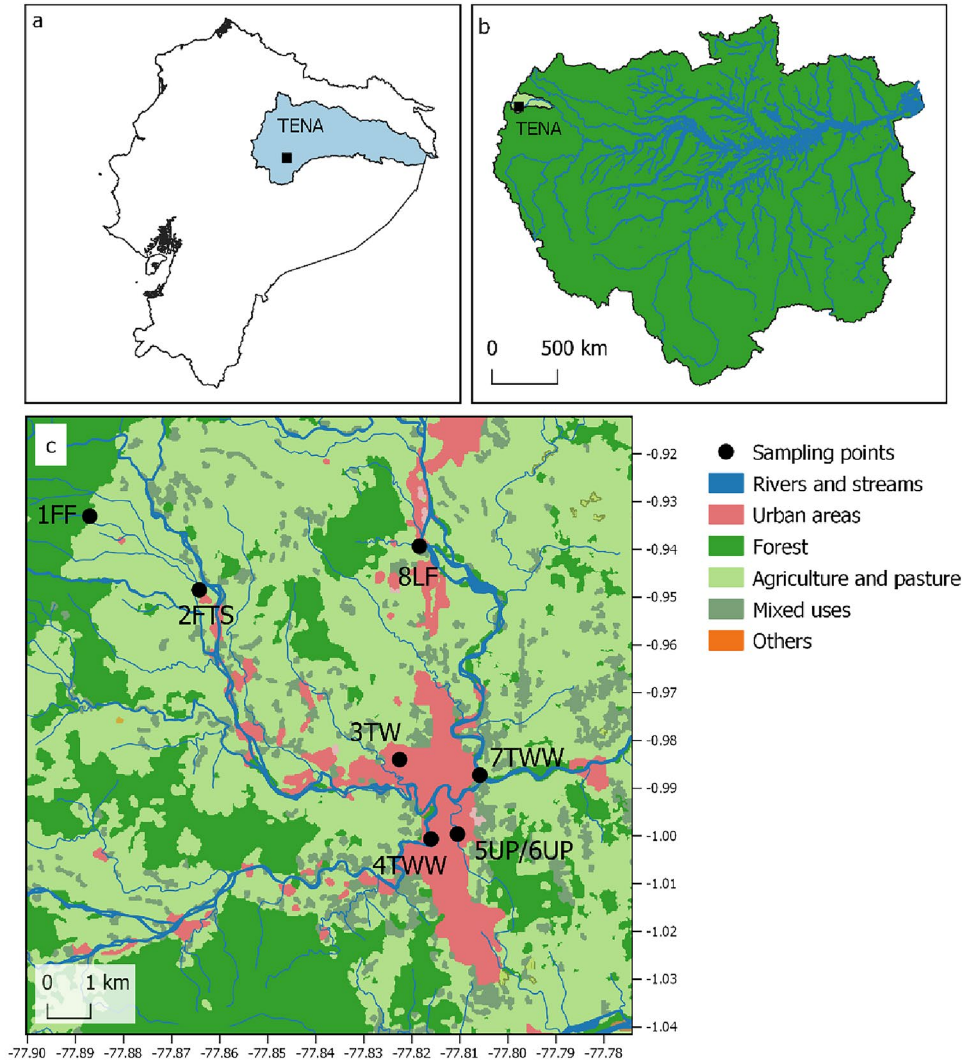


Fig. 1 **a** Location of Tena city and the Napo watershed in Ecuador. **b** Location of the study watershed within the Amazon basin. **c** Location of sampling points: 1FF, small stream downstream of fish farm (–0.9331, –77.8871); 2FTS, stream with few threats, Pashimbi stream (–0.9485, –77.8643); 3TW, domestic tap water (–0.9840, –77.8225); 4TWW, the effluent of wastewater treatment plant at Pano river (– 1.0006, –77.8160); 5UP and 6UP, urban drainages at Paushiyacu stream (–0.9996, –77.8105); 7TWW, effluent of wastewater treatment plant at Mishahuallí river (–0.9872, –77.8058); 8LF, small stream receiving landfill drainages (–0.9393, –77.8185)

information was obtained through Subsecretaría Nacional de Gobernanza de la Salud Pública del Ecuador (2019).

Sample Preparation

Following the protocol from Glassmeyer et al. (2017), analytes were isolated by solid-phase extraction (SPE) using a vacuum pump (Millipore, WP6111560), a manifold (27 × 17 × 9.5 cm), and Waters OASIS HLB cartridges with a capacity of 200 mg and 6 mL. The cartridges were conditioned at a flow rate of 10 mL/min using 4 mL of methanol followed by treatment with 6 mL of reagent water. After the elution of 500 mL of sample, the cartridges were dried for 10 min under vacuum, and analytes were eluted with 6 mL of methanol to glass tubes. Extracts were concentrated to 1 mL with nitrogen, filtered (0.22 µm), and transferred to vials for the chromatographic analysis. All samples were analyzed in duplicate. Quality controls included a field blank to check for contamination during sampling and extraction processes and a spiked sample of mean concentration level to evaluate the recovery percentage of each component (Table 1).

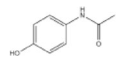
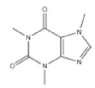
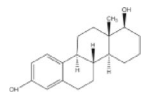
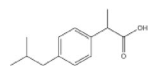
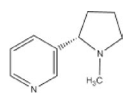
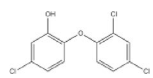
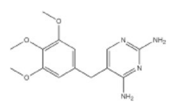
Reagents and Chemicals

High purity analytical standards of acetaminophen, caffeine, estradiol, ibuprofen, nicotine, triclosan, and trimethoprim were obtained from Sigma–Aldrich and Supelco with a purity of 99.9%, 99, 96.8%, 99.7%, 98.9%, 99.9%, and 99.8%, respectively.

Instrumental Analyses

Methanolic extracts were analyzed using a gas chromatograph coupled to a mass detector (GC–MS Agilent 7890/5977) under EI mode. The column used was a DB-5 ms, 30 m × 320 µm × 1 µm. The temperature ramp was 5°C for 2 min, 28°C/min up to 170°C, 4.9°C/min up

Table 1 Properties of target emerging contaminants

ECs (CAS)	Description	Chemical structure	Molar mass g mol^{-1}	Water solubility at 25°C, mg L^{-1}	pKa	log Kow	LOQ µg L^{-1}	LOD µg L^{-1}	Recovery %
Acetaminophen (103-90-2)	Analgesic		151.17	14,000	9.38	0.46	0.4	0.14	72
Caffeine (58-08-2)	Stimulant		194.19	21,600	14	− 0.07	0.02	0.007	92
Estradiol (50-28-2)	Hormone		272.38	3.60 at 27°C	10.27	4.13	1.14	0.38	75
Ibuprofen (15687-7-1)	Anti-inflammatory		206.28	21	4.91	3.97	0.14	0.05	76
Nicotine (54-11-5)	Stimulant		162.23	1,000,000 miscible	8.5	1.17	0.14	0.05	85
Triclosan (3380-34-5)	Antibacterial Fungicide		289.54	10 at 20°C	7.9	4.76	0.14	0.05	88
Trimethoprim (738-70-5)	Antibiotic		290.32	400	7.1	0.91	2.8	1	71

to 280°C, 6.3°C/min up to 30°C/min and then 300°C for 10 min. Before sample analysis a SIM method was developed using standards for the following components: caffeine, triclosan, estradiol, acetaminophen, nicotine, ibuprofen. LOQ and LOD values are included in Table 1. All samples were analyzed in a single batch using a SCAN method (30–500 m/z) and the SIM method previously developed. Spectral deconvolution software (AMDIS) was used to process the data. Extracts from each sampling site were screened using the NISTDRUG library. Compounds with a matching factor (> 80) were considered for further analysis; this non-targeted screening approach was performed to assess additional types of toxic and persistent pollutants that could be present.

Data Analyses

Physicochemical parameters were compared to water quality guidelines established by Ecuadorian legislation (MAE-TULSMA 2015), the US Environmental Protection Agency (USEPA 1996), and the Canadian Environmental Quality Guidelines (CCME 2002). k-Nearest Neighbors (kNN): The non-parametric kNN (Kowalski and Bender 1972) technique classifies a sampling site based on its k closest neighbors in the space defined by physicochemical parameters and ECs concentration. kNN is an appropriate classification method when dealing with non-linear class separation. In this study, physicochemical parameters and ECs concentration were pretreated by means of autoscaling, and the Euclidean metric was used to measure distances between samples. Classification performances were evaluated by means of the class precision (Pr) and sensitivity (Sn) (Ballabio et al. 2018). The precision of the g th class is defined as the purity of such class, i.e., the ability of the classifier to reject molecules from other classes. On the other hand, the sensitivity of the g th class (Sng) or true positive rate characterizes the model's ability to correctly recognize sampling sites belonging to the class. From these two primary class measures, it is possible to calculate global indices to evaluate the performances of the kNN classifier, such as the average precision and average sensitivity also known as the non-error rate (NER). Classes are formed based on the level of similarity. Sites that do not have a high level of similarity can be considered "a class", a group of the unclassified.

Results and Discussion

Physicochemical Parameters

Physicochemical parameters were compared with the Ecuadorian standards of quality criteria for preserving aquatic and wildlife and the discharge of effluents into freshwater bodies (MAE-TULSMA 2015). The temperature values exceed the maximum permissible limit (25°C) at all sampling locations except for the treatment plant effluent (7TWW, 25°C). 1FF, 5US, 6 UP, 7TWW and 8LF, are below 80% of dissolved oxygen (DO) which is the minimum permissible limit for the preservation of aquatic life, being 8LF the lowest (8%). Regarding SpC and TDS, none of the stations exceeded the maximum allowable limits; however, treatment plants, urban rivers, and sanitary landfill values (locations 4, 5, 6, 7 and 8) were higher to locations 1, 2 and 3. The pH values from all samples were within the recommended range between 6.5 and 9, except for sampling point 4TWW, which had an acid pH of 5. The urban rivers (5UP and 6UP), the treatment plant effluent (7TWW), and the landfill stream (8LF) exceed up to 18 times the maximum permissible turbidity limit (10 NTU). Moreover, Ecuadorian regulations do not include the color of effluents in Pt–Co color units, but these values are high for urban rivers and the sanitary landfill according to international guidelines. Finally, the residual chlorine does not exceed the maximum permissible limit (0.5 mg L^{-1}), but concentrations between 0.03 and 0.05 mg L^{-1} were observed for the 4TWW and 8LF locations, respectively. The sample 2TW, was evaluated with the standard for water for human consumption (NTE INEN 1108 2020); according to this guideline, the chlorine concentration is insufficient (0.3–1.5 mg L^{-1}).

Emerging Contaminants

Caffeine was detected at 5UP, 6UP, and 7TWW sites in mean concentrations that ranged between 19.3 to 31.5 µg L^{-1}. Acetaminophen and trimethoprim were only detected at site 7TWW, in mean concentrations 50.5 and 2 µg L^{-1}, respectively (Table 2). Caffeine found in sampling points 5 and 6 may reflect local consumption habits as guayusa tea (*Ilex guayusa* Loes leaves), native to the Andean Amazon, has high caffeine concentrations (Sequeda-Castañeda et al. 2016) and is massively consumed in the region. Besides, caffeine is one of the most frequently found compounds in emerging pollutants studies, usually in high concentrations (Pinos-Vélez et al. 2019), in fact it is considered ubiquitous. This compound can be found in coffee and other massively consumed beverages and it has a high solubility in water under ambient conditions. Sites 5 and 6 (UP) are located close to urban areas where previous studies showed high concentration of metals and poor quality of water (Capparelli et al. 2020; Galarza et al. 2021).

The stream with few threats (2FTS) and tap water (3TW) did not show ECs. Site 2FTS receives water from riverside communities without sewage treatment. For this reason, it is suggested the continuous monitoring of these sites, as in the future they may experience an increase in the presence of contaminants and an overall worsening of water quality, if they continue without adequate sewage treatment. On the other hand, Tena has a single drinking water treatment plant, which distributes tap water to the city. The water is taken directly from a pristine area, which explains the good water quality and the lack of ECs in 3TW.

Table 2 Emerging contaminants and physicochemical parameters of the analyzed water samples from each of the eight sampling points located on different Napo River tributaries in the Napo province, Ecuador (see Fig. 1 for site location)

	Collection sites							
	1 FF	2 FTS	3 TW	4 TWW	5 UP	6 UP	7 TWW	8 LF
Compound (ug L^{-1})								
Caffeine	*	*	*	*	19	30	31.5	*
Acetaminophen	*	*	*	*	*	*	50.5	*
Trimetropin	*	*	*	*	*	*	2	*
Nicotine	*	*	*	*	*	*	*	*
Ibuprofen	*	*	*	*	*	*	*	*
Triclosan	*	*	*	*	*	*	*	*
Estradiol	*	*	*	*	*	*	*	*
Parameters								
T (°C)	26	22	26	28	28	28	25	28
DO (%)	78	121	114	94	50	30	50	8
SpC (µS cm^{-1})	43.6	27	37	377	340	282	300	312
TDS (g L^{-1})	21.5	14	18	188	169	141	175	156
pH	6.9	7.5	7.5	5	7	7	7	7.5
Turbidity (NTU)	7.8	0	0	0.32	180	20	78	16.8
Color (Pt–Co units)	39	12	0	9	110	115	45	240
Cloro (mg L^{-1})	0	0	0	0.05	0	0	0	0.03

Collection sites are classified as fish farming (FF), a stream with few threats (FTS), waste discharge in urban areas (UP), landfills (LF), tap water (TW), and treated sewage (TWW). Values reported for ECs are the mean (n = 2)

*Below detection limit

The site 4TWW did not present ECs in the treated water, unlike site 7TWW, which received effluents with the presence of caffeine, paracetamol, and trimethoprim. It can be inferred that 7TWW may not have ECs treated efficiently. The physicochemical parameters (Table 2) suggest that the treatment plant might not be functioning properly, or it is linked to another source of untreated wastewater before joining the stream. Since site 7TWW had a lower DO level (50%), higher turbidity (78 NTU), and color (45 Pt–Co units) in comparison with site 4TWW, a low performance in the aeration and filtration process is deduced (Liu et al. 2010; Zhao et al. 2009). In 2015, the Environmental Technical Processes Company (Protecmed 2015) installed two urban wastewater treatment plants (4TWW and 7TWW sampling sites), using a membrane biological reactor (MBR) system, that treats 4300 m^3 per day for the city of Tena. The sewage treatment using a MBR consists of membrane filtration, combined with biological degradation using sludge, achieving both the physical retention of pollutants and their biodegradation (Clemente et al., 2013). MBR treatments can reduce micropollutant concentrations by 20%–50%; nevertheless, studies have shown that this type of treatment can remove over 80% of emerging compounds such as hormones, and some pharmaceuticals (e.g., acetaminophen and ibuprofen), lifestyle products (e.g., caffeine and nicotine), among others. However, MBRs are not effective to remove recalcitrant compounds such as antibiotics (e.g., trimethoprim) (Barceló et al. 2009; Grandclément et al. 2017). Given the characteristics of the studied compounds, it is justified that they have not been found at the sampling site since the treatment plant should be sufficient to eliminate them. Nevertheless, we suggest more studies to verify the efficiency of MBRs to remove emerging contaminants.

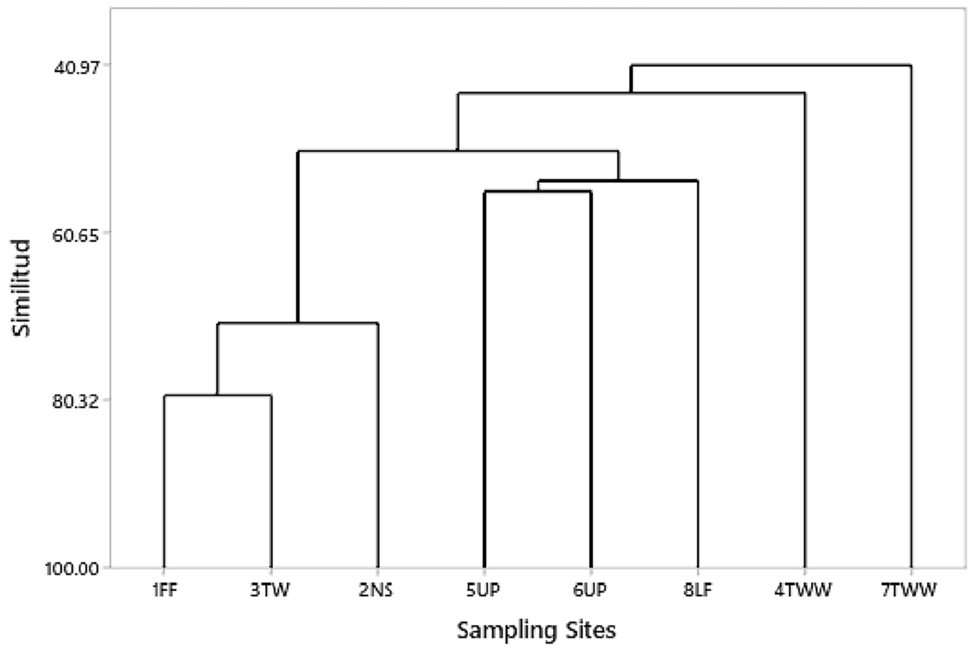
Fish farming (FF) and sanitary landfills (LF) are important sources of many types of contaminants in the studied region. High metal contamination (Capparelli et al. 2020) and low water quality (Galarza et al. 2021) were detected in these collection sites located at the drainage of the sanitary landfill. This landfill has already reached its upper capacity and the drainage system has exceeded its maximum limit, producing a leachate that flows directly into a small stream located nearby. Fish farming sites (FF) are in rivers that flow directly from the Colonso-Chalupas Biological Reserve (CCBR) and are used to fill and to receive about 20 fish farming pools (0.2 ha each). However, fish farming is not a source of ECs according to the data of the present study. The fact that some studies prove frequent use of ECs in aquaculture (Done and Halden, 2015) and that LF site contains untreated hospital effluents (Capparelli et al. 2020), leads us to suggest that these areas should be included in future monitoring.

Through the non-targeted screening analysis, we presume the possible presence of the following pharmaceuticals: diethyltoluamide (main compound of mosquito repellent), lidocaine (a commonly use local anesthetic), carbamazepine (a widely used anticonvulsant), phenacetin (a pain-relieving and fever-reducing drug). Additionally, we identified plant-derived molecules: theobromine (alkaloid of the cacao plant), cannabinol (in cannabis plants), piperine (alkaloid from the *P. longum* fruits) and lupanine (alkaloid present in the genus Lupinus, locally consumed legume); these four compounds were only found in samples with a high contamination load. Although this study was only focused on volatile and semivolatile compounds, the presence of ECs at the studied sites highlights the need for a more detailed assessment of ECs at lower quantification levels in the future.

k—Nearest Neighbors analysis allows grouping the studied sites into 2 classes. Class 1 is composed of sites 1FF, 2 FTS, and 3TW. Class 2 comprises sampling locations 4TWW, 5US, 6US, 7TWW and 8LF. In Fig. 2, a dendrogram with separation of the sites as a function of the distance between them is shown. The calculated precision and sensitivity of the model are 1 and the non-error rate is also 1, thus this is a model with an ideal classification capacity. The locations with the worst physical–chemical water parameters were grouped, and in most cases presented ECs, which leads us to conclude that urban locations with a lack of adequate water treatment are the most susceptible to the presence and impacts of ECs and that should continue to be monitored.

Some studies conducted in Latin America have found ECs such as caffeine, acetaminophen, and trimethoprim in rivers; the highest concentrations have been found in sites close to the discharges of treated or untreated sewage being much higher when the water has not been treated (Pinos-Vélez et al. 2019). The concentration reported for caffeine ranged between 0.05 μg L^{-1} in Argentina to 1000 μg L^{-1} in Costa Rica (Elorriaga et al. 2013, Spongberg et al. 2011; Voloshenko-Rossin et al. 2014), values within the range of our study (Table 2, mean concentration: 19–31.5 μg L^{-1}). For acetaminophen, the values ranged from 13 μg L^{-1} for Costa Rica (Spongberg et al. 2011) to 31 μg L^{-1} in Esmeraldas River, Ecuador (Voloshenko-Rossin et al. 2014), both much lower concentrations than found in our study (Table 1, mean of 50.4 μg L^{-1}). Trimethoprim was found in Costa Rica at a maximum concentration of 0.12 μg L^{-1} and in Bolivia a mean concentration of 0.16 μg L^{-1} (Archundia et al. 2018). In our study, higher concentrations of trimethoprim were found despite Tena being a small city (Table 1, mean of 2 μg L^{-1}). The presence of these compounds in the city of Tena, a low population density area, raises concerns about the occurrence of ECs and their magnitude in comparison to more contaminated and populated areas. Caffeine was found in 3 of the 8 studied sites. Although this compound is not considered to be highly toxic the effects of its presence in high concentrations in sensitive habitats such as

Fig. 2 Dendrogram of the distribution of the sites according to their similarity. The conformation of the classes was considered, for the samples that have a similarity greater than 50% (class 1) and those that have a similarity less than 50% (class 2)



the Amazon are unknown. We recommend carrying out studies to assess the risk of this contaminant in Amazonian species. The locality called treated sewage (TWW) was the one that presented most of the compounds found. Our assessment of the ECs contamination at Tena, Napo provides a baseline information about its occurrence in one small city at the upper Amazon basin, Ecuador. The presence of caffeine, acetaminophen, and trimethoprim requires controlling efforts to treat these compounds and raises the question about the need for proper sewage treatment in Amazonian cities. More complete ECs monitoring in this area is urgently needed, as we report here a small part of an undocumented issue. This includes further studies on the ECs removal capacity of wastewater plants and management actions towards global sewage treatment. The absence of waste management in Amazonian cities may result in pervasive ECs contamination of freshwater ecosystems and potential adverse effects to aquatic biota and human health. We strongly suggest the continuous monitoring of the ECs at the upper Amazon basin.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could influence the present investigation.

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