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Occurrence of emerging contaminants in surface water bodies of a coastal province in Ecuador and possible influence of tourism decline caused by COVID-19 lockdown

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HIGHLIGHTS

- Emerging pollutants were measured in water from a coastal province in Ecuador.
- The influence of COVID lockdown in the occurrence of these contaminants was assessed.
- Acetaminophen, caffeine, Na diclofenac and trimethoprim were detected in water samples.
- The occurrence of caffeine and diclofenac decreased during lockdown.
- Frequency or concentration of emerging pollutants was generally lower during lockdown.

GRAPHICAL ABSTRACT

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ABSTRACT

Emerging contaminants in water bodies is an issue of concern due to their impact on the ecosystem and human health. The COVID-19 pandemic has forced the implementation of protective measures such as social distancing, lockdowns, and remote work, which have affected the tourism influx. This study aimed to evaluate the occurrence of emerging pollutants in bodies of water in Esmeraldas, a coastal province of Ecuador, before and during the COVID-19 pandemic in a highly touristic region. For this purpose, surface waters from 14 beaches and ten river mouths were sampled at two-time points in November 2019 and November 2020. Compounds widely consumed in Ecuador: acetaminophen, caffeine, sodium diclofenac, trimethoprim, and sulfamethoxazole were extracted from water samples by solid phase extraction SPE and detected with a UPLC-QTOF-MS system. We found a decrease in the occurrence of caffeine from 100 % to 4.2 % of caffeine and 25 % to 0 % of diclofenac, likely related to the decline in tourist afflux due to the lockdown measures. Most of the compounds diminished in terms of frequency and/or concentration; however, as COVID-19 treatments make use of different pharmaceutical compounds such as antivirals, antibiotics, antiparasitics, or glucocorticoids, future studies should include these to assess their environmental impact.

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1. Introduction

The occurrence of emerging contaminants (ECs), also called micropollutants, is derived from different sources (Galindo-Miranda et al., 2019). In many natural water systems, including rivers, lakes, and reservoirs, ECs have been detected (Wang et al., 2011; Wanda et al., 2017; Rivera-Jaimes et al., 2018), and their presence in aquatic environments is growing continuously every year (Agüera et al., 2013). Pharmaceutical products are widely used for human and veterinary-related health problems. However, due to incomplete metabolism, these drugs are excreted through defecation and the urinary system (Chander et al., 2016), thus reaching and being detected in aquatic (rivers, lakes, and reservoirs) (Wang et al., 2011; Wanda et al., 2017; Rivera-Jaimes et al., 2018) and terrestrial systems (Shaheen et al., 2022). The inadequate management of pharmaceutical waste and its incomplete elimination leads to these compounds reaching surface waters through the direct discharge of raw or treated wastewater from municipal, hospital, industrial wastewater treatment plants (WWTPs), landfill leachate, and confined animal farms waste (Shaheen et al., 2022). Municipal wastewater is considered one of the principal discharge sources for the emanation of ECs like nonpoint and point sources, industries and stormwater, wastewater from households, and water treatment facilities into the environment (Ternes et al., 2004). Although in recent years, a set of different physical, chemical, and biological techniques have been used to remove or decompose ECs (Zhang and Zhou, 2008; Grover et al., 2011), in Ecuador, as in many developing countries, only 70.1 % of municipal Decentralised Autonomous Governments (GAD in Spanish) treat their wastewater, while 26.3 % directly discharges wastewater to aquatic ecosystems (AME-INEC, 2019). At the national level, the treatment at wastewater treatment plants (WWTP) is secondary, that is, the organic matter present in the wastewater is mainly eliminated. But many toxic substances should still be removed (e. g. ECs, heavy metals, viruses, nitrates). Some Ecuadorian cities like Cuenca and Quito, which are in the Andean region, have WWTPs, but this is not the case for Esmeraldas, a coastal city whose drinking water sources are affected by wastewater discharge from Quito. A previous study has shown the presence of emerging compounds both in the effluents that reach the Esmeraldas River and, in this city's, drinking water (Voloshenko-Rossin et al., 2015).

The COVID-19 pandemic had global economic, environmental, and social impacts (Atalan, 2020). According to the World Health Organisation data, by October 2020, Ecuador was one of the countries more seriously affected; the number of deaths per million inhabitants ranked Ecuador fourth place within the Americas and ninth place globally (Alava and Guevara, 2021). Several studies have evaluated the affections of the pandemic on different aspects, such as environmental, economic, and social. Regarding the environmental impacts, some studies have shown a reduction in air pollution (Kumari and Toshniwal, 2020) while others, an increase in the waste generated (Zambrano-Monserrate et al., 2020). However, there is not enough information regarding neither the occurrence nor the environmental impacts in aquatic environments, especially in Latin America (Vargas-Berrones et al., 2020).

The Esmeraldas province is located on the northwestern coast of Ecuador. It is a popular tourist destination, with beaches as the main attraction, the most popular Atacames C6, Súa C7, Muisne C12, and Same C8 (Fig. 1) (Zambonino-Rivadeneira, 2022). Before COVID-19 Esmeraldas housed 8.8 % of the total tourism in the country (Cisneros-Palacios et al., 2019). COVID-19 caused a severe economic impact in this province due to the primary income being tourism; it is estimated that the effects of the economic crisis due to the pandemic are even worse than the ones caused by the earthquake in April 2016 (Zambonino-Rivadeneira, 2022).

Our objectives were to identify and quantify acetaminophen, caffeine, sodium diclofenac, trimethoprim, and sulfamethoxazole, highly consumed compounds in Ecuador, according to the Ministry of Public Health, in the Esmeraldas surface waters during two time periods: the first one before the COVID-19 pandemic and the second one during the lockdown measures adopted worldwide by the COVID-19 pandemic. We hypothesize that the reduction in the tourist afflux caused a reduction in the concentration levels of the compounds measured.

2. Materials and methods

2.1. Study area

The Esmeraldas province is on the north-western coast of Ecuador and occupies an area of 161,32 km^2, with a population of ca. 644,000 inhabitants (Instituto Nacional de Estadística y Censos, 2020a, 2020b). Ten sampling sites in the mouth of some rivers (upstream of the estuary) were selected, including the five largest rivers of Esmeraldas (Santiago R1, Cayapas R2, Rioverde R4, Esmeraldas R6 and Muisne R10) and other smaller rivers (Fig. 1, Table 1). Fourteen sampling sites in coastal areas were selected along a range of urbanization. The percentage of urban land in a 2 km buffer around each sampling site was calculated from a land-use map published by the Ministry of Agriculture (2015) with Q-GIS (QGIS.Development Team, 2022).

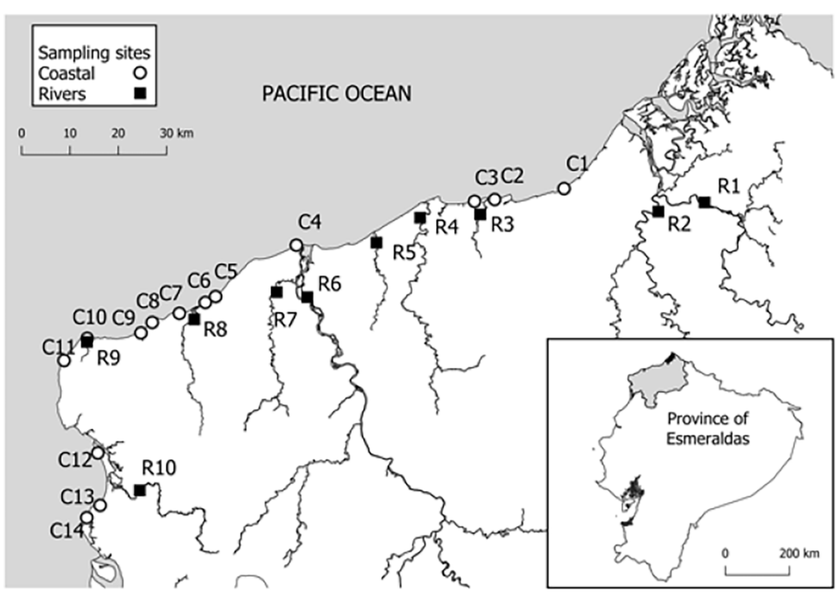

Fig. 1. Location of sampling points in coastal waters (C) and rivers mouth (R) in the study area.

Table 1
Sampling sites characteristics.

	ID	Site	UTMX	UTMY	Urban (%)[a]
River mouth sites	R1	Santiago	733,903	10,118,580	<1
	R2	Cayapas	724,347	10,116,682	–
	R3	Ostiones	687,475	10,116,098	2
	R4	Rioverde	675,053	10,115,416	–
	R5	Colope	666,013	10,110,262	<1
	R6	Esmeraldas	651,683	10,098,965	4
	R7	Teaone	645,334	10,100,019	35
	R8	Atacames	628,292	10,094,371	16
	R9	Galera	606,086	10,089,716	1
	R10	Muisne	617,010	10,058,982	–
Coastal sites	C1	Las Peñas	704,830	10,121,448	5
	C2	África	690,473	10,119,175	<1
	C3	Paufí	686,303	10,118,794	<1
	C4	Las Palmas	649,427	10,109,728	65
	C5	Tonsupa	632,717	10,099,096	64
	C6	Atacames	630,588	10,097,869	54
	C7	Súa	625,225	10,095,623	18
	C8	Same	619,599	10,093,741	17
	C9	Tonchigüe	617,262	10,091,566	12
	C10	Galera	606,149	10,090,438	2
	C11	E de Plátano	601,359	10,085,849	2
	C12	Muisne	608,344	10,066,724	15
	C13	Mompiche	608,826	10,055,884	2
	C14	Portete	606,055	10,053,323	3

Coordinates are for the (Universal Transverse Mercartor) UTM 17S zone. Land uses categories were determined in a 2 km buffer around the sampling points.
[a] Percentage of urban land in a 2 km buffer around each sampling site is also shown.

2.2. Sampling

Two sampling campaigns were performed, the first in November 2019 and the second in November 2020 during the lockdown due to the COVID-19 pandemic. The Coronavirus disease 2019 (COVID-19) was characterized by the World Health Organisation as a pandemic in March 2020 (Adhanom Ghebreyesus, 2020), and the lockdown measures that were implemented to limit the transmission of the virus affected the daily life of many people all over the world.

A total of 24 surface water samples in each campaign (14 beaches and ten river mouths) were taken along the Esmeraldas Coast. Nearshore sampling sites were selected according to the level of urbanization, classified as high level (sites Las Palmas C4, Tonsupa C5, Atacames C6, Súa C7, Same, Tonchigüe C9, Muisne C12) and low level (sites Las Peñas C1, África C2, Paufí C3, Galera C10, Estero de Plátano C11, Mompiche C13, Portete C14) (Table 1). The river mouths (upstream estuary) sampled were the main hydrographic basins (Cayapas R2, Santiago R1, Rioverde R4, Esmeraldas R6, Teaone R7, Atacames R8 and Muisne R10) and the rivers that flow into the beaches selected (Colope R5, Ostiones R3, and Galera R9). The river mouth samples were taken in areas of current. Samples were taken 10 m from the shore at a water depth of approximately 1 m. Samples were collected in 0.5 L glass amber bottles previously washed with methanol and kept refrigerated until they were processed in the laboratory. Field blanks were prepared each sampling day by filling a 0.5 L glass bottle with deionized water at a randomly selected sampling location. The following physicochemical parameters were analyzed in situ: turbidity (HACH DR890), pH, conductivity, salinity, temperature, and dissolved oxygen and saturated (HACH HQ40d portable meter).

2.3. Laboratory analysis

Information about the most sold pharmaceutical compounds in Ecuador was obtained through *Subsecretaría Nacional de Gobernanza de la Salud Pública*. Caffeine, acetaminophen, diclofenac, sulfamethoxazole, and trimethoprim were selected for analysis according to information obtained and the bibliographic revision; caffeine is not a pharmaceutical compound, but it was selected as it is present as an adjuvant in several medicaments. The samples were previously filtered by glass fiber filters (0.45 μm). 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, following the protocol from Glassmeyer et al. (2017). The cartridges were conditioned at a flow rate of 10 $mLmin^{-1}$ using 4 mL of methanol, followed by treatment with 6 mL of ultrapure water (type I). 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 in glass tubes. Extracts were concentrated to dryness with nitrogen, and the volume was reconstituted to 0.5 mL with methanol, filtered (0.22 μm), and transferred to vials for the chromatographic analysis. All samples were analyzed by 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 2). High purity analytical standards of acetaminophen, caffeine sodium diclofenac, trimethoprim, and sulfamethoxazole were obtained from Sigma–Aldrich and Supelco with a purity higher than 96.8 %.

2.4. Instrumental analysis

Determination of emerging compounds in water was performed in a Waters Model I-Class liquid chromatograph (UPLC) coupled to a mass spectrometer Waters Model Xevo G2 QTOF. The solvents used as mobile phases A and B were water and acetonitrile with 0.1 % formic acid, respectively. The established elution gradient was 5 % B over 1 min, 5 % to 100 % B over 9 min, then 100 % to 5 % B over 2 min, and finally, a re-equilibration of the column at 5 % B by 3 min. The analysis of emerging compounds in water was performed on an ACQUITY UPLC BEH C18 column (Waters, Millford, USA) (1.7 μm, 100 mm × 2.1 mm i.d.) operating at 25 °C with a flow rate of 0.3 $mLmin^{-1}$. Mass spectrometric analysis was performed with an electrospray ionization (ESI) source in a mass range of *m/z* 50 to 1000 Da in positive mode with a capillary voltage of 0.5 kV, 30 Lh^{-1} cone gas flow, 900 Lh^{-1} desolvation gas flow, 120 °C source temperature,

Table 2
Instrumental analysis conditions.

Compound name	Elemental composition	Ion	t_R (min)	Precursor (m/z)	Product ion (m/z)	CE (V)	R%	MQL ng L^{-1}
Acetaminophen	$C_{10}H_9NO_2$	$[M + H]^+$	2.64	152	109.9	20	80	6.3
					65.1	34		
					93	24		
Caffeine	$C_8H_{10}N_4O_2$	$[M + H]^+$	3.23	195	138	19	83	12.5
					110	22		
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	$[M + H]^+$	7.47	295.8	214.7	20	85	10.0
					249.9	12		
					277.6	8		
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	$[M + H]^+$	4.59	253.9	92	31	77	3.1
					155.8	14		
Trimethoprim	$C_{14}H_{18}N_4O_3$	$[M + H]^+$	3.43	291.2	230	25	90	18.8

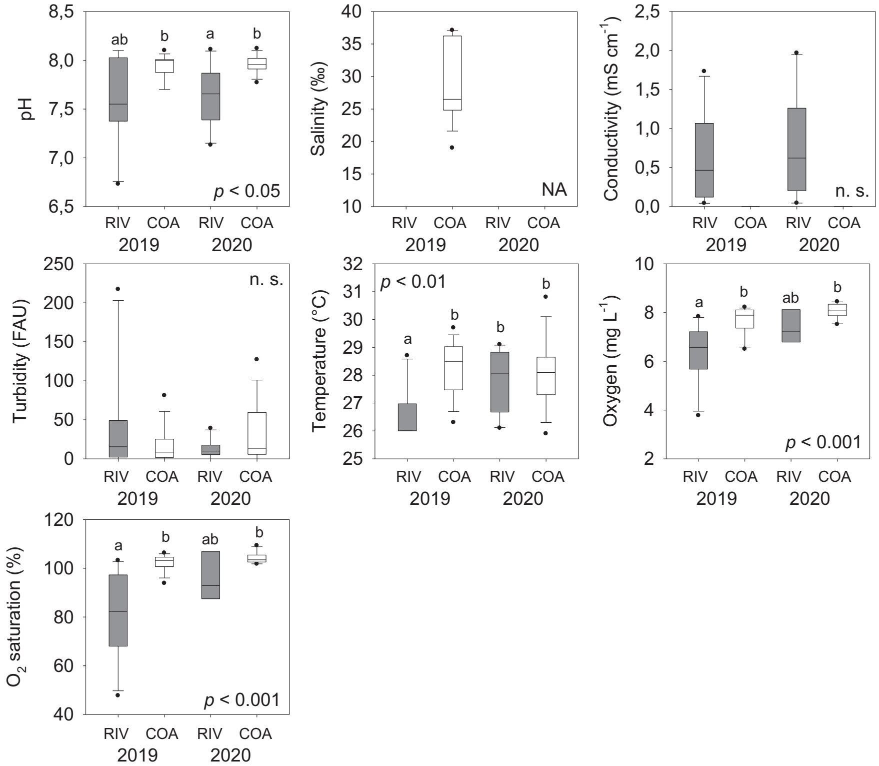

Fig. 2. Physical and chemical variables at the study sites. Results of the Kruskal-Wallis test and the Wilcoxon test for differences among the river mouth (RIV) and coastal (COA) samples are shown. There are no significant differences between levels with the same letter. (<DL, below detection level; NA, not applicable; n.s, not significance.)

450 °C desolvation temperature with sampling cone and source compensation at 40 and 80 V, the data acquisition method was MS^E with ramp collision energy (CE): low CE off and a high CE of 20 to 30 eV. The analytes quantification was performed using the precursor or product ion with the greatest intensity because the acquisition method provides the full information. The method quantification limits were determined according to Barwick et al. (2016) (Table 2).

2.5. Statistical analyses

Concentrations of emergent pollutants were compared by one-way Kruskall-Wallis analysis followed by the Wilcoxon test for multiple comparisons. Correlations between concentrations of emergent pollutants and the percentage of urban land area around each sampling site were also performed. All analyses were done in R (R Core Team, 2019).

3. Results

As seen in Fig. 2, except for turbidity, physical and chemical variables showed significant differences between river mouths and coastal sites before and during the pandemic. In the case of pH and dissolved oxygen, the differences occur between river mouths and coastal waters, as expected for these types of surface waters. Temperature values were significantly different both for the type of water bodies and for timepoints. In the case of conductivity, only the river mouths values between 2019 and 2020 are compared because there is an evident difference between river mouths and coastal sites due to salinity.

Among the considered substances, diclofenac was detected at two river mouths and four coastal sites before the COVID-19 pandemic (Fig. 3, Tables S1, S2), and its concentration ranged between 10.9 and 16.5 ng L^{-1}in the river mouth sites, and between 20.3 and 515.3 ng L^{-1}in coastal sites. During the COVID-19 pandemic, diclofenac was below detection limits at all sampling sites. The differences in diclofenac concentrations between river mouths and coastal sites before the COVID-19 pandemic were not significant (Wilcoxon test: $W = 60, p = 0.46$). Acetaminophen was detected at two river mouths and two coastal sites before the COVID-19 pandemic. Its concentrations ranged between 17.2 and 165.3 ng L^{-1}in rivers mouth and between 75.7 and 169.8 ng L^{-1} in coastal sites. During the COVID-19 pandemic, acetaminophen was detected at one coastal site with a concentration of 95.6 ng L^{-1}. The differences in acetaminophen concentrations between the river mouths and coastal sites and before and during the COVID-19 pandemic were not significant (Kuskal-Wallis test: $\chi^2 = 2.42$, df $= 3, p = 0.49$). Trimethoprim was detected at two coastal sites before the COVID-19 pandemic, and its concentrations ranged between 6.9 and 62.5 ng L^{-1}. During the COVID-19 pandemic, trimethoprim was below detection levels at all study sites. Sulfamethoxazole concentrations were below detection levels at all study sites before and during the COVID-19 pandemic. Finally, caffeine was detected at all the study sites before the COVID-19 pandemic, and its concentration ranged between 16.2 and 426.8 ng L^{-1} in river mouths and between 4.4 and 386.3 ng L^{-1} in coastal sites. During the COVID-19 pandemic, caffeine was detected at one coastal site with a concentration of 139.7 ng L^{-1}. The differences in caffeine concentrations between the river mouths and coastal sites before the pandemic were not significant, but there were significant differences in caffeine concentrations before and during the COVID-19 pandemic (Kuskal-Wallis test: $\chi^2 = 35.8$, df $= 3, p < 0.001$). There was a clear spatial relationship in the concentrations of ECs in coastal sites before the COVID-19 pandemic, as diclofenac, acetaminophen, trimethoprim, and caffeine were simultaneously detected at two of the coastal sites (C8 and C10).

4. Discussion

The COVID-19 pandemic has forced the implementation of some measures such as social distancing, lockdown, or remote work, among others; measures that have affected the environment in different ways; regarding the aquatic environments, the reduction of tourists on the beaches is directly related to a pollution decrease as has been observed in some of the most popular beaches around the world (Zambrano-Monserrate et al.,

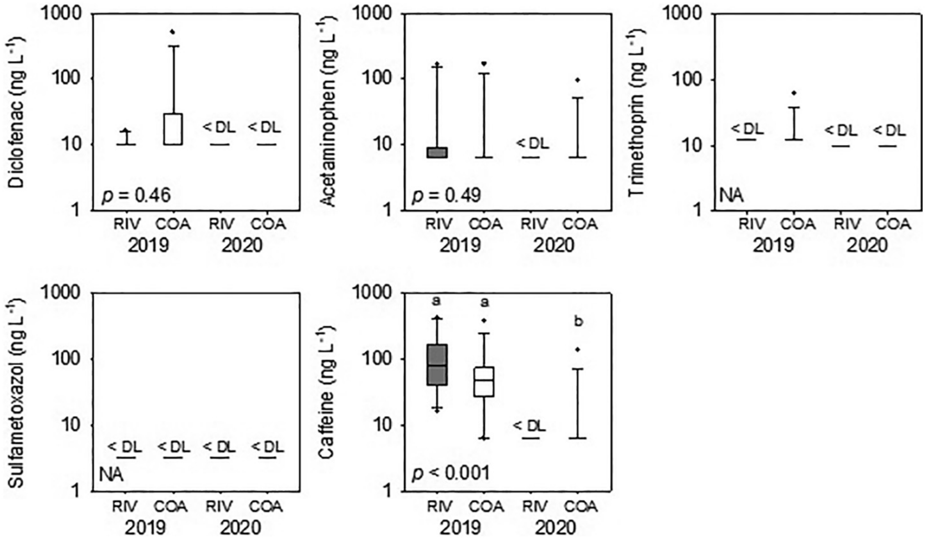

Fig. 3. Concentrations of five emerging contaminants along the coast of Esmeraldas. Results of the one-way Kruskal–Wallis analyses and multiple comparisons with the Wilcoxon test are also shown. There are no significant differences between levels with the same letter (<DL, below detection level; NA, statistical analysis not applicable; RIV, river mouths; COA, coastal).

2020; Ormaza-Gonzaìlez et al., 2021). In this study, we found a decrease in the occurrence of the compounds measured during the pandemic, which suggests a relation between the lack of visitors observed during the lockdown (Figs. S1, S2) and the occurrence of these compounds in the coastal and river mouths analyzed.

The physicochemical measures did not show any relation with the occurrence of ECs. Principal component analysis (Fig. S3) separates the river mouths from the beaches and the three beaches with the highest level of urbanization, but caffeine did not enter the main components. No physicochemical variable is related to differences in caffeine concentration. Conductivity values between river mouths before and during the pandemic did not show a significant difference; the 2019 values are slightly lower compared with 2020 values. This coincides with the rainfall data (Fig. S4), which shows the monthly precipitation over Ecuador during the sampling periods; a similar trend is observed in the temperature values, indicating that the 2019 sampling period was drier than in 2020.

Caffeine was found in 100 % of samples analyzed before the pandemic while it was found only in 4.2 % during the pandemic. These results suggest a relation between the reduction in the concentration of caffeine and the pandemic, which coincides with some studies that refer to caffeine as a direct indicator of human activity in natural environments due to its presence being related to domestic effluent inputs into the surface waters (Siegener and Chen, 2002). Other studies have shown a decrease in the consumption of coffee related to the pandemic. However, there is no available information for Ecuador; this could be another reason for the low occurrence of caffeine found in the coastal and river mouth samples during the pandemic (Bakaloudi et al., 2022). The concentrations of caffeine found in this study in river mouths (16.2 ng L^{-1} to 426.8 ng L^{-1}) coincide with the values reported in other studies where the values found in surface water ranged from <10.0 to 373.0 ng L^{-1} (Choi et al., 2008). In the case of coastal points (4.4 ng L^{-1} to 386.3 ng L^{-1}), the literature concentrations vary widely from 2 ng L^{-1} to 5000 ng L^{-1} (Rodriguez del Rey et al., 2012). The high occurrence of caffeine in the samples analyzed has been attributed to the proportional relation between the concentration of caffeine and salinity (Rodriguez del Rey et al., 2012). However, in this study, this relation was not observed. Fig. S5 shows that neither the conductivity in the river mouths nor the salinity in coastal sites can explain the differences in caffeine concentrations. Although caffeine has been used as a wastewater pollution marker and to track population density (Buerge et al., 2006), in the case of tropical regions, as is the case of Esmeraldas, caffeine can be present naturally due to coffee bean or guayusa plantations, which could difficult its use as a marker (Knee et al., 2010).

Although sulfamethoxazole is one of the antibiotics of most frequent appearance in the studies reviewed (Alygizakis et al., 2021), in this study, it was not present in any of the points analyzed. Some studies suggest a stable concentration of sulfamethoxazole (Fisch, Waniek, and Schulz-Bull, 2017), this could be the case in this study, the sulfamethoxazole concentration was stable and below the detection limit of this study. Additionally, the occurrence of trimethoprim in the coastal sites in this study (8.3 % and 0 % before and during the COVID-19 lockdown, respectively) was lower compared with similar studies (Alygizakis et al., 2021). The results obtained coincide with the low occurrence of sulfamethoxazole as these two antibiotics are commonly joined in the commercial formulations, even in the formulations used for veterinary (Alygizakis et al., 2021).

Diclofenac was the second compound with the highest occurrence in this study, with 25 % in the samples before the pandemic and 0 % during it. Although the range of concentrations in river mouths found in this study (LOQ-16.5 ng L^{-1}) coincide with the values found in other studies (Ismail et al., 2019); the concentration reported at point C8 is five times higher than the maximum value reported by Alygizakis et al. (2021). Diclofenac inhibits the oocyte maturation in the estuarine Crab Neohelice Granulata (Lofrano et al., 2022) and oxidative stress and neurotoxicity in fish and marine polychaetes (Nunes et al., 2020). Additionally, affections on the osmoregulatory ability of green shore crabs (*Carcinus maenas*) have been observed (Eades and Waring, 2010). Increased exposure to diclofenac raises health concerns for aquatic organisms and higher plants but also causes serious threats to mammals (Sathishkumar et al., 2020).

Acetaminophen had an occurrence of 16.6 % in the samples before the pandemic, and together with caffeine, it was the only compound detected in one sample during the pandemic. The concentrations found in river mouths (17.2–165.3 ng L^{-1}) are lower than those reported in previous studies (243–530 ng L^{-1}) (Silva et al., 2011), while the concentrations found in the coastal samples (75.7–169.8 ng L^{-1}) are twice higher than the previously reported (4.7–72.3 ng L^{-1}) (Alygizakis et al., 2021).

Diclofenac, acetaminophen, trimethoprim, and caffeine were simultaneously detected at two of the coastal sites (C8 and C10), which suggest point sources of these pollutants near the sampling sites. However, the presence of these contaminants in coastal waters was not related to urbanization as both sites showed a low percentage of urban land around them (17 and 2 %, respectively). Similarly, caffeine concentrations before the COVID-19 pandemic showed no correlation with the percentage of urban land near the sampling points. The beach of Same (C8) showed the highest concentrations of ECs along the coast of Esmeraldas. In a previous work (Capparelli et al., 2021), the Same beach also showed high microplastic concentrations; although there is no relationship between the substances studied and microplastic, this is evidence of a greater accumulation of pollution in the area. Wastewater discharge from a large holiday resort located about 1 km north of the sampling site is the most likely source of these pollutants. ECs were also detected at the beach of Galera (C10), a small coastal community in the Galera-San Francisco Marine Reserve that lacks wastewater treatment facilities. The combination of mass tourism and ineffective or non-existent wastewater treatment in coastal towns and resorts poses a big threat to water quality, human health, and protected coastal areas of Esmeraldas. On a local scale, tourism relies on ecosystem services such as providing clean water for bathing and access to biodiversity (Holden, 2017). However, tourists use more water and produce more wastewater than the local population of touristic areas (Cullen et al., 2004; Becken, 2014; Gabarda Mallorquí et al., 2016) and, without proper environmental controls, both the sustainability of tourism and the well-being of the coastal communities in Esmeraldas are at risk in the long-term.

In developing countries such as Ecuador, the occurrence of emerging contaminants in surface waters is mainly due to wastewater that is released without treatment or after treatment that is not capable of effectively removing them (Pinos-Vélez et al., 2019). However, around the world, some initiatives have been proven to remove this type of pollutants; for instance, adsorbents such as natural or modified clays, bio sorbents, nanospheres have been used to remove pollutants such as caffeine, acetaminophen, sodium diclofenac, sulfamethoxazole, and trimethoprim (Aryee et al., 2021; Khan et al., 2022; Okoro et al., 2022; Pérez-González et al., 2021; Toniciolli-Rigueto et al., 2020). Moreover, different catalysts such as nanoparticles of transition metals oxides, semiconductors such as titanium or zinc oxides, and composite materials of different geometries and sizes have also been tested in advanced oxidation processes where photocatalysis stands out; the removal percentages oscillate between 95 and 99 (Cai et al., 2021; Castañeda et al., 2022; Jiang et al., 2021; Krawczyk et al., 2022; Muthukumar et al., 2020; Wang et al., 2022). Although promising, some of these solutions have disadvantages such as an expensive setup, and the need for changes and in pH, UV light, among others that make it difficult to scale up. Some ternary processes as advanced oxidation processes are currently used in developed countries, nevertheless; the possibility of their implementation in developing countries seems remote considering that they still do not even cover the need for primary and secondary treatments to eliminate organic matter and nutrients.

5. Conclusions

This study has shown a reduction in the studied emerging pollutants, mainly caffeine, diclofenac, and acetaminophen, related to the restrictive measures adopted during the COVID-19 lockdown period. These restrictions reduced the influx of tourists to the main spas in the Esmeraldas Province. This was a unique opportunity to assess the tourist impact and the need to implement environmental controls and future wastewater treatment plans to assure the sustainability of tourism and the well-being of the coastal communities in Esmeraldas. Additionally, there is an urgent need to increase the number of studies not only on the occurrence of emerging compounds but also on their environmental impacts; future approaches should consider including pharmaceutical contaminants like antivirals, antibiotics, antiparasitics, or glucocorticoids most used as a treatment against COVID-19 affection.

CRediT authorship contribution statement

Isabel Cipriani-Avila: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Funding acquisition, Supervision, Writing – original draft, Writing – review & editing. **Jon Molinero:** Conceptualization, Formal analysis, Investigation, Supervision, Writing – original draft, Writing – review & editing. **Marcela Cabrera:** Methodology, Validation, Formal analysis, Writing – review & editing. **Evencio Joel Medina-Villamizar:** Methodology, Validation, Formal analysis. **Mariana V. Capparelli:** Conceptualization, Investigation, Writing – review & editing. **Eliza Jara-Negrete:** Methodology, Formal analysis, Investigation, Writing – review & editing. **Verónica Pinos-Velez:** Methodology, Formal analysis, Investigation, Funding acquisition, Writing – review & editing. **Sofia Acosta:** Formal analysis, Writing – review & editing. **David Leiva Andrade:** Formal analysis. **Miren Barrado:** Formal analysis, Writing – review & editing. **Noroska G.S. Mogollón:** Funding acquisition, Supervision, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.161340.

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