



Assessing the Presence of Petroleum Hydrocarbons in the Punta Carnero Estuary (Ecuador)

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Received: 3 August 2023 / Accepted: 22 January 2024 / Published online: 2 February 2024
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Abstract Chronic hydrocarbon spills are a threat to coastal ecosystems, and their impact on the water quality along watercourses should be characterised to medium long term in order to assess the risk and define cost-effective and sustainable remediation strategies. For this purpose, a methodology for the measurement of total petroleum hydrocarbons (TPH) on a spatio-temporal scale was designed, implemented and validated in the Punta Carnero estuary,

in the Santa Elena province, western Ecuador, which is affected by hydrocarbon pollution. The selection of monitoring stations was made according to the different inflows along the water system corresponding to the different anthropogenic activities in the area, in order to assess whether the effluents involve critical levels of pollution. Measurements of hydrodynamic, environmental and vegetation cover parameters were also carried out to assess their possible variations as a consequence of the impact of the spatio-temporal TPH concentrations. An increase in hydrocarbon concentrations was observed from 2013 to 2021. Mean annual TPH levels were above the maximum allowable limit for the protection of aquatic and other wildlife in estuarine waters according to the Ecuadorian regulation for environmental quality. An increase in mangrove tree cover could contribute to an exponential decrease in contamination levels. The methodology used in this study may support the quantifying of TPH content in future applications, which is a priority task for the restoration of degraded ecosystems.

Highlights

- Total petroleum hydrocarbon (TPH) was used to assess the level of oil pollution.
- Monitoring stations were selected according to different inflows along water system.
- Hydrodynamic parameters and vegetation cover were related with the TPH impact.
- TPH increased from 2013 to 2021 and exceeded permitted levels for estuaries.
- Red mangrove may be contributing to hydrocarbon trapping.

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Keywords Drainage canal · Environmental monitoring · Ecuasal wetland · Total petroleum hydrocarbons · Oil pollution · *Rhizophora mangle*

1 Introduction

The economy of Ecuador is mainly based on oil exports; these accounting for 39% of all exports in 2019 (8680 million US dollars) (Ministry of Production, Foreign Trade, Investments and Fisheries of Ecuador, 2021). As a result, the country is at risk of experiencing environment impacts of oil pollution from any stage of the management of this resource: exploration, production, transportation, storage and processing (Centeno-Bordones et al., 2021; Espinosa et al., 2021; Maurice et al., 2019), and, despite this situation, there is limited information about the possible alteration of surface waters in Ecuadorian coastal regions characterised by provide ecosystem services to society. A detailed evaluation and understanding of these coastal systems are needed to the health of these valuable ecosystems (Camacho-Ibar & Rivera-Monroy, 2014; Cetin et al., 2022a, b).

The province of Santa Elena, which contains the Salinas, La Libertad and Santa Elena cantons, is the most western geographical part of Ecuador (Fig. 1). Its coastal area is rich in biodiversity and is included in Ecuador's National System of Protected Areas (SNAPE) as the Puntilla Santa Elena Coastal Marine Fauna Production Reserve (REMACOPSE) (Ministry of Environment of Ecuador, 2009). Aguirre (2014) indicated that, in this region, tourism is a key activity for local people and a benchmark at the national level. The main ecosystems include coastal waters, coral and rocky reefs, sandy and mixed (sand and rock) beaches, cliffs, low-lying and coastal dry scrublands and coastal thorn scrublands.

Oil and oil derivatives are closely linked to the ancient and modern history of the Santa Elena Peninsula. Evidence has been found of the use of petroleum hydrocarbons by indigenous populations and traces of activities related to the extraction of oil, coal, kerosene and other bituminous materials date back to 1878. It is estimated that in the province, and more specifically in the Peninsula of Santa Elena, there is a network of 2882 wells in the Gustavo Galindo Velasco oil field (Chavarría & Salazar, 2006). This intense oil extraction activity is associated with oil seepage that contaminates soil and water bodies.

The most commonly used environmental quality parameter to assess the level oil pollution is TPH (total petroleum hydrocarbon concentration). According to Tran et al. (2021), TPH pollutants are hydrophobic recalcitrant compounds, which are part of complex mixtures of aliphatic, aromatic hydrocarbons, resins and asphaltenes. Petroleum-contaminated areas are common worldwide, due to the activities of oil exploration, extraction and refining as well as oil spills, underground oil storage tank leakage and runoff. Once in the soil, TPHs can alter its physical and chemical properties and disturb the biological

balance. These compounds are highly toxic, posing a risk to human health and ecosystems. Two large groups of petroleum hydrocarbons, aliphatic and aromatic hydrocarbons (ALHs and ARHs, respectively), are described (Veloz, 2013). The Environmental Protection Agency (EPA) of the USA included 16 of these polycyclic aromatic hydrocarbons (PAHs) in the list of priority pollutants. It is very difficult to identify each individual petroleum constituent, and therefore, the lumped parameter TPH is normally used to assess the degree of contamination by petroleum products (Sun et al., 2021).

Hydrocarbon pollution events have occurred in the Punta Carnero sector in the Salinas canton (Fig. 1) (Veloz, 2015). Specifically, seeps occurred in traditional salt production ponds of Ecuatoriana de Sal y Productos Químicos C.A. (Ecuasal), and the effluents moved through drainage canals to the estuarine zones and affected the marine ecosystem of the REMACOPSE reserve (Ministry of the Environment of Ecuador, 2010; Veloz, 2013). These salt production ponds are a hypersaline ecosystem, which hosts flourishing interacting communities of microorganisms that are the main food source for aquatic birds,

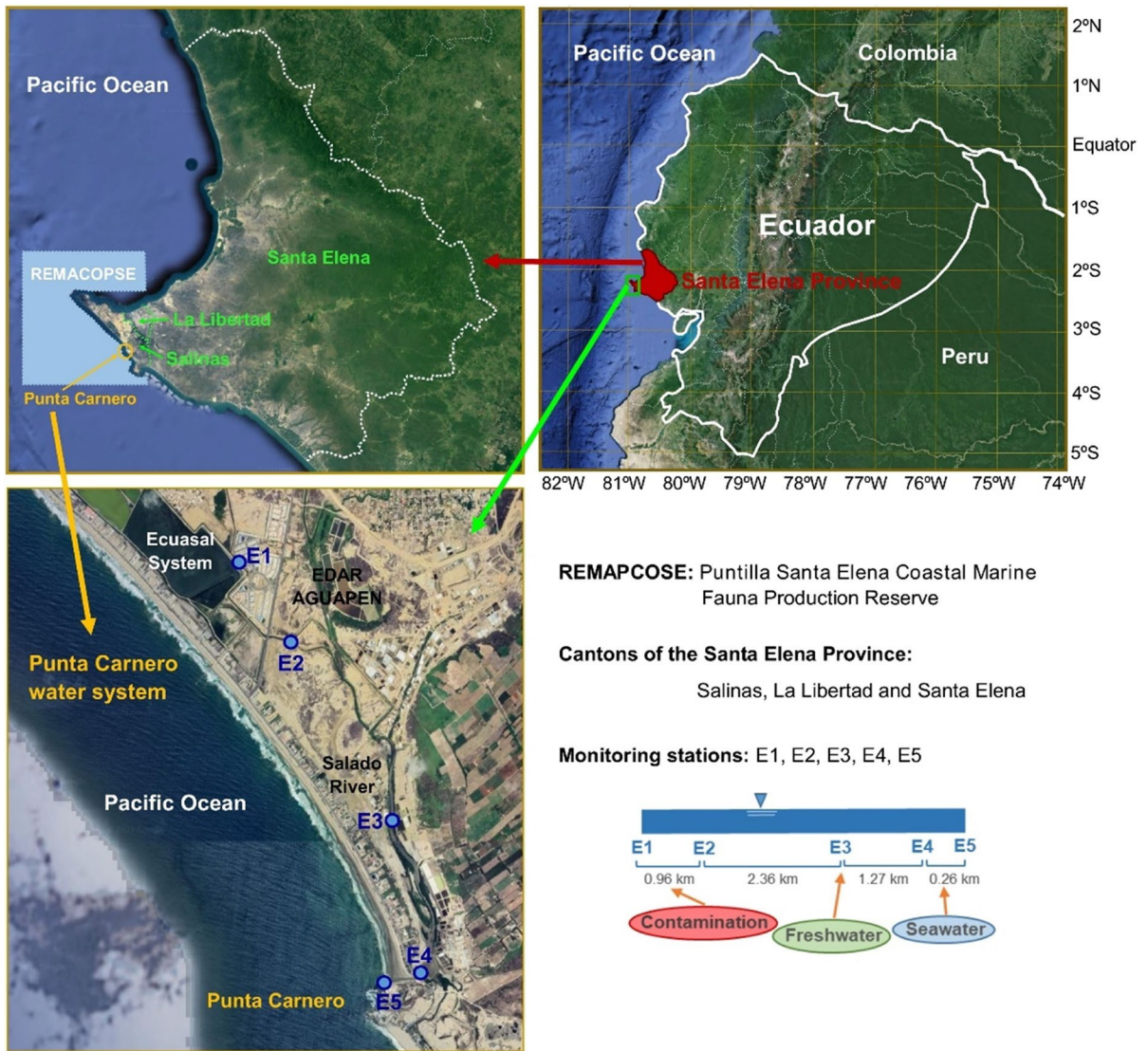


Fig. 1 The province of Santa Elena (Ecuador) that comprises the cantons of Salinas, La Libertad and Santa Elena indicating the Puntilla Santa Elena Animal Production Reserve (REMACOPSE)

being classified as Important Bird Areas (IBAs) and an Ecuadorian site of importance in the Western Hemisphere Shorebird Reserve Network (WHSRN) (Ágreda, 2012).

In this context, for this study, the Punta Carnero water system has been defined as a system composed of the following three sections. Section 1, called the “Ecuasal System”, is formed by two perimeter drainage canals, at the north and south of the Ecuasal salt evaporation and crystallisation ponds. The southern canal discharges into shrimp larvae laboratories, and

the northern canal is adjacent to the traditional salt production ponds where wells are made to obtain saline water from the phreatic zone, which tend to cause ruptures in hydrocarbon seals. These two canals meet downstream of the main flow. In Section 2, the flow receives the treated water from the sewage treatment plant (EDAR AGUAPEN), this joining the flow coming from the Velasco Ibarra Dam, which is mainly feed by waters from the Salado River, with a peak flow between January and April. In Section 3 called “Estero Punta Carnero”, the flow mixes with

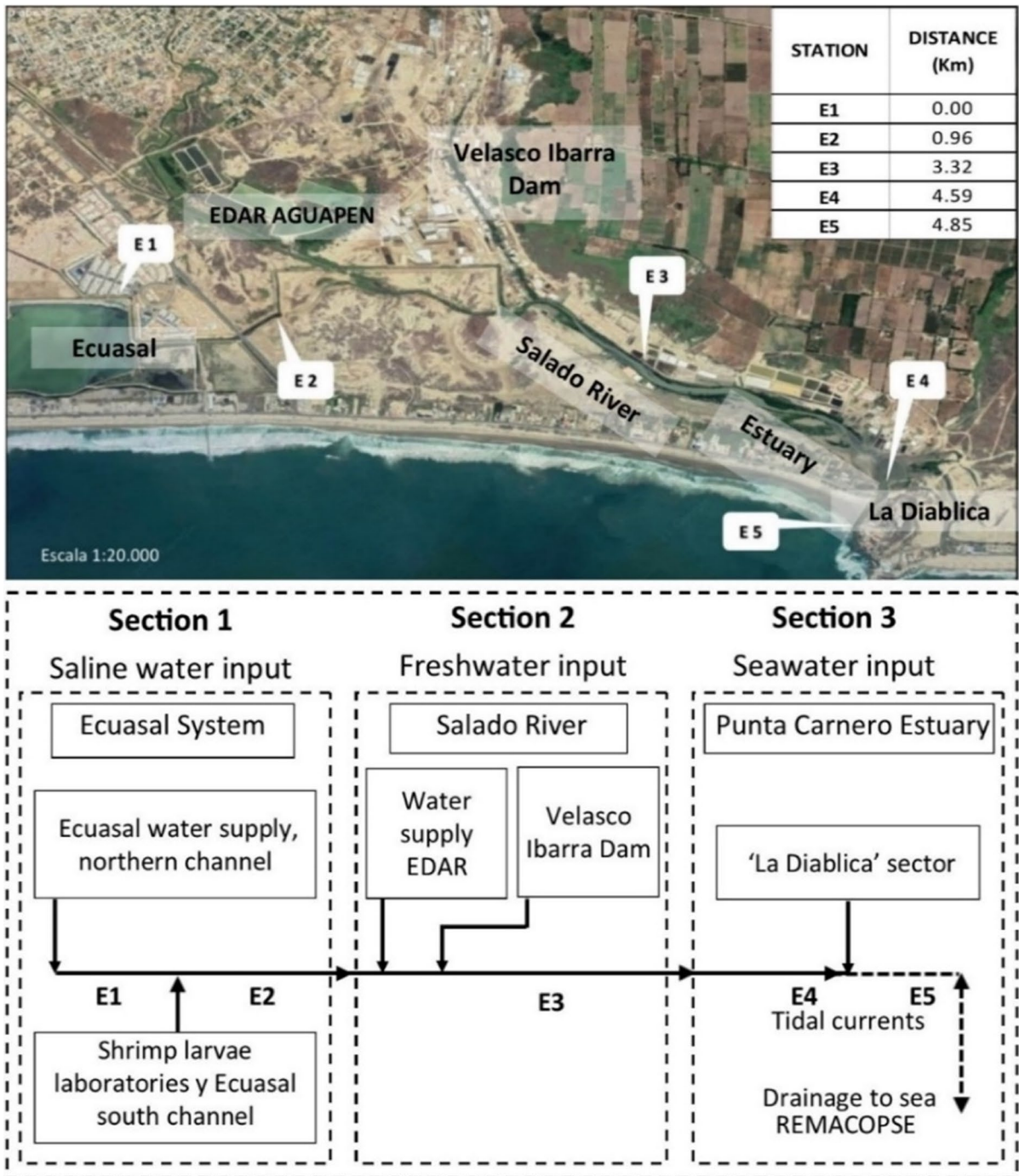


Fig. 2 Monitoring stations throughout the Punta Carnero water system (Ecuador). Station E1 is the first monitoring station defined as the 0 km point

seawater transported by tidal currents, coming from the REMACOPSE protected area. In this last section,

a brackish water flow is also incorporated, coming from the “La Diablica” sector (Figs. 1 and 2).

In Section 2, there is a large area of introduced vegetation, including forest of *Rhizophora mangle*, that extends as far as Section 3 in the estuarine area of Punta Carnero. Authors such as Taketani et al. (2010) and Moreira et al. (2011) in Brazil and Olguín et al. (2007) and Martínez-Hernández et al. (2021) in Mexico have reported an attenuation of the petroleum hydrocarbon contamination in the sediments of mangroves, particularly of *Rhizophora* sp., which can be attributed to physical and photochemical degradation (water cleansing and photooxidation) of crude oil in surface sediments and plant leaves (Ke et al., 2002). In this context, assessing petroleum hydrocarbon contamination in mangrove areas along the coast of Brazil, Araújo et al. (2020) found low levels of these compounds in the sediments associated with these ecosystems.

Against this background, the aim of this study was to analyse and characterise the petroleum hydrocarbon concentration throughout the Punta Carnero water system, comparing TPH measurements taken in three time periods at various different sampling stations and assessing the influence of mangroves on the quality of the water bodies studied. Hydrodynamic and environmental parameters were also measured at each monitoring station to analyse and understand the impact of TPH concentrations on the ecosystem processes of this estuary. The methodology followed and the results obtained for the determination the spatial and temporal variations of water quality could support decision-making about the effective and sustainable management of water systems disturbed by oil pollution and could contribute to the dynamic assessment of impacts on aquatic ecosystems (González et al., 2022; Koklu et al., 2010; Liu & Wirtz, 2007).

2 Materials and Methods

A methodology for the measurement of total petroleum hydrocarbons (TPH) on a spatio-temporal scale was designed with the objective of comparing and assessing the state of the pollution and changes therein along the Punta Carnero water system. Monitoring stations were set up at strategic points in relation to the different water inflows along the canal (Fig. 2).

2.1 Monitoring Stations

The sites for the monitoring stations were selected based on factors that may influence petroleum hydrocarbon levels. Specifically, E1 station was defined as the first station (0 km), at the outset of the contamination process in the canal due to natural seepage and/or oil field seal rupture associated with anthropogenic activities. Station E2 (at 0.96 km from E1 station) measures waters that included the outflow from the Ecuasal system and wastewater derived from the shrimp larvae production processes of the laboratories located on the southern bank of the canal. Station E3 (at 3.32 km from E1 station) measures the outflow from the sewage treatment plant (EDAR AGUAPEN) and the Velasco Ibarra Dam. Station E4 (at 4.59 km from station E1), located in the Punta Carnero estuarine zone, is influenced by tidal currents from the Pacific Ocean and receives brackish water from “La Diablica” sector. Finally, station E5 (at 4.85 km from station E1) is located in the area of discharge to the sea (Fig. 2).

2.2 Measurement of Petroleum Hydrocarbons

Samples for TPH analysis (mg/l) at three time points were collected: 10 January 2013, 8 October 2020 and 6 May 2021. TPH sampling was carried out following the protocols of the Ecuador’s technical standards (NTE INEN 2176:2013 and NTE INEN 2169:1998) (INEN, 1998, 2013) based on ISO standards 5667-1 and 5667-3 about water quality sampling. Samples were analysed using the TPH Method—EPA 418.1 (EPA, 1978) by PSI (Industrial Products and Services) laboratory accredited by the SAE (Ecuadorian Accreditation Service).

Levels of petroleum hydrocarbons were assessed by comparing levels measured with quality criteria defining levels allowed to protect aquatic and other wildlife in fresh, marine water and estuarine waters of the Ministerial Agreement No. 097-A issued by the Ecuadorian Ministry of the Environment (Ministry of the Environment of Ecuador, 2015).

2.3 Measurement of Hydrodynamic and Environmental Parameters

In order to understand and relate hydrodynamic, climatic and physicochemical processes in the Punta Carnero water system to the TPH concentrations found in the sampling carried out on 6 May 2021, at each sampling station, the variables current speed (m/s), flow (m³/s), water temperature (°C), salinity (‰), dissolved oxygen (mg/l), pH and turbidity (cm) were measured—either *in situ* or in the laboratory.

The current speed was calculated using Lagrangian tracers based on distance and time elapsed. The flow was calculated using the current speed value and the cross-sectional area of the canal. The water temperature was measured with a Kahlsico oceanographic thermometer. The salinity was measured with a LAQUAtwin Salt-11 refractometer calibrated *in situ* with distilled water. The dissolved oxygen was measured with a YSI Pro20i oxygen metre previously calibrated in the laboratory. The pH was measured with a portable Hanna HI 98127 pH metre, previously calibrated in the laboratory. And the turbidity was measured with a Secchi disk.

The values related to flow at stations E2, E3, E4 and E5 were obtained by multiplying water speed by the cross-sectional area of the canal. For station E1, we employed the cube method to measure the flow, using a container with levels marked in litres to establish the volume filled as a function of time.

Weather and tide gauge data from the study area were also used. Weather data (precipitation, air temperature and wind speed) were obtained from the Oceanographic Institute of the Navy of Ecuador (INOCAR) and the National Institute for Meteorology and Hydrology of Ecuador (INAMHI). Sea surface temperature (SST) data in the marine sector off the study area were obtained following the procedure described by Chavarría (2015), who extracted data from 765 charts obtained from the website of the Peruvian Institute of the Sea (IMARPE) corresponding to 16 years of data (2000–2015). Tidal data were obtained from the tide tables from INOCAR, these only being used for planning the monitoring process. The area of tidal influence in the estuary was determined by Lagrangian tracking during a rising tide, with the support of a Mavic 2 Pro DJI drone.

2.4 Vegetation Cover

Additionally, a temporal analysis consisting of the image comparison of the vegetation cover using satellite image time series was carried out. Historical images from Google Earth 2013, 2017 and 2021 were used and complemented with aerial photographs as well as images and videos from drone flights carried out *ad hoc* for the study. Areas of vegetation cover using polygons were described by sectors between monitoring stations and for the drainage canal overall during the study periods. These polygons were manually created using the Google Earth Ruler tool for surface estimation, configured in square metres and then converted to hectares.

2.5 Statistical Analysis

The time series analysis was performed using Student's *t* test for comparing means with 95% confidence intervals. The mean petroleum hydrocarbon levels were compared for the longest period between 2013 and 2020, due to its extension, would imply greater changes in the concentration of the contaminant.

Spatial analysis was carried out using the annual means (2013, 2020 and 2021) of TPH at each monitoring station. Linear and exponential regressions were performed to obtain relationships between location of monitoring stations and annual mean TPH concentrations. Analysis of variance (ANOVA) was also made, using the software IBM SPSS Statistics 26.0, to evaluate if there are significance differences in mean annual TPH concentrations between monitoring stations.

3 Results

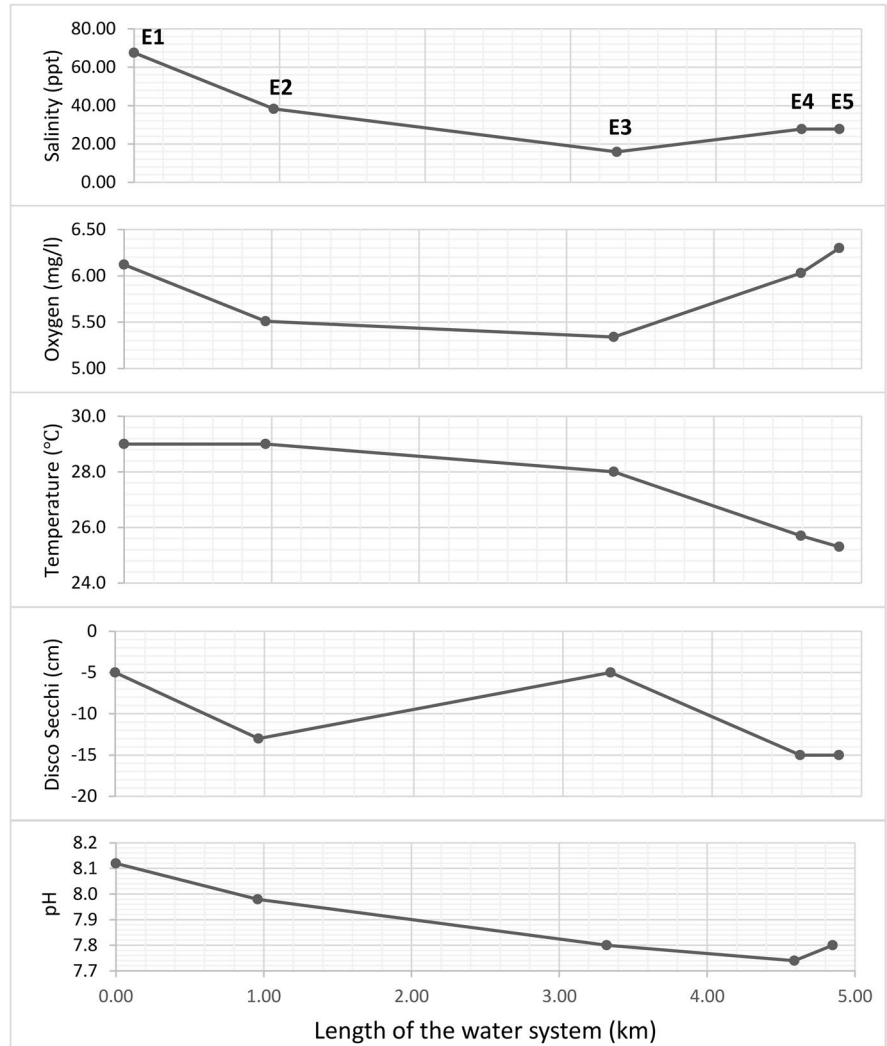
3.1 Analysis of the Environmental and Hydrodynamic Variables

Table 1 shows the mean monthly values of SST in the sector off the area of study in the period 2000 to 2015. In the wet season (January to April), SST was 25–26 °C higher than the values of around 22–23 °C in the dry season (May to December). There are significant differences in precipitation between these seasons for the period 1975–2006 in the study area.

Table 1 Mean monthly values of sea surface temperature (SST) off the area of study in the period 2000–2015

SST (°C)/wet season				SST (°C)/dry season								SST (°C)
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean
24.3	25.6	25.9	25.6	24.4	23.0	22.2	21.6	21.0	21.7	22.0	22.9	23.3

Fig. 3 Spatial variation in the environmental variables registered on 6 May 2021 in the petroleum hydrocarbon monitoring stations E1, E2, E3, E4 and E5 along the Punta Carnero water system



In the wet season, the mean precipitation was significantly greater (325 mm), this being associated with higher air temperatures. In contrast, in the dry season, there was less precipitation (50 mm), associated with cooler air temperatures. The mean, maximum and minimum values of the annual temperature are 23.6 °C, 29.7 °C and 17.81 °C, respectively. Wind speed was fairly moderate (mean, 3.9 m/s; maximum,

4.1 m/s), and winds were predominantly from the southeast.

The readings from 6 May 2021 obtained for salinity, dissolved oxygen, temperature, turbidity and pH in the water bodies through the canal at the different monitoring stations are shown in Fig. 3. Hypersaline conditions were observed at station E1 (0 km), with salinity values twice as high as those of normal sea conditions due to the fact that, at this point, there is

Table 2 Flow rates recorded on 6 May 2021 along the Punta Carnero water system

Stations	Distance (km)	Flow rate (m ³ /s)
E1	0.00	0.003
E2	0.96	0.496
E3	3.32	0.063
E4	4.59	0.340
E5	4.85	0.389

an inflow of wastewater from the evaporation salt production ponds. Also, it is highlighted that there is relatively high oxygen concentration due to the turbulence caused the discharge of the water towards the canal through various different discharge pipes. The station E1 was characterised by the damming of water in this section of the canal and subsequent discharge through gooseneck pipelines. At this station, there a clear alkaline pH, characteristic of sea waters, as well as high turbidity characterised by the Secchi depth, with light penetration of the water column of barely 5 cm.

The data series of Fig. 3 show the variability in the environmental parameters along the canal. It is highlighted that salinity significantly decreases at station E3, due to the freshwater inflow from the AGUAPEN sewage treatment plant, the water in the canal regaining characteristics of sea water by stations E4 and E5 with the tidal influence. Station E3 also has the lowest concentration of dissolved oxygen (5.34 mg/l).

The water surface temperature from station E1 to station E3 is influenced by solar radiation that affects the narrow water column which has a maximum depth of 50 cm at E3. At stations E4 and E5, the height of the water column in the canal is variable due to tides. In these monitoring stations, water temperature is influenced by the sea temperature.

Turbidity in the canal is variable with a peak at station E3 due to the inflow of freshwater from the sewage treatment plant, reaching its greatest depth at this point and decreasing in the areas influenced by the tides, where this parameter is more closely associated with the sand dispersion dynamics in the water column, characteristic of coastal processes. On the other hand, pH varies in line with the dilution effect occurring along the canal, the water generally being alkaline.

Flow rates recorded at the monitoring stations are presented in Table 2. The flow rate is the lowest

(0.003 m³/s) at station E1, due to the damming of water in this section of the canal and subsequent discharge through gooseneck pipelines. It then increases due to the inflow of water from the shrimp larvae laboratories and output of the Ecuasal, reaching 0.496 m³/s at station E2. Then, despite the inflow from the sewage treatment plant, the flow rate falls to 0.063 m³/s at station E3, this being attributable to having reached a natural drainage channel with a wider canal, the existence of meanders and the interaction with tidal rising currents. Flow rates at stations E4 and E5 are influenced by tidal currents and a drainage canal coming from the east, from a sector known as “La Diablica” (Fig. 2).

3.2 Evaluation of Vegetation Cover

Based on satellite images, the presence of vegetation in the Salado River sector, Punta Carnero estuary, was observed, corresponding to the Section 2 of the water system, from stations E2 to E4 (Fig. 2). In the sampling at station E3, the vegetation corresponded to a mangrove forest, specifically red mangrove (*Rhizophora mangle*). Considering the importance of this ecosystem in natural attenuation of hydrocarbon contamination, the images were analysed. There was emerging mangrove vegetation in 2013, and this then considerably expanded, as can be seen in the images from 2017 to 2021. In 2021, relatively dense vegetation cover was observed, with trees that reached a mean height of at least 4 m.

In Fig. 4, it is shown that the difference between 2013 and 2017 of vegetation cover images in the section of the Punta Carnero water system, corresponding to the final area of Salado River, is not pronounced, and hence, the estimation and comparison of areas of mangrove coverage were only carried out between 2013 and 2021. In Fig. 5, it is shown that the area of forest on the banks of the section Salado River-Punta Carnero estuary had trebled during the 8 years between the two samplings.

3.3 Spatial and Temporal Analyses of Hydrocarbon Concentration

The TPH concentrations at each monitoring station during the years of sampling are shown in Fig. 6 where the maximum permitted level of 0.5 mg/l, corresponding to the water quality criteria established



Fig. 4 Vegetation cover images in the section of the Punta Carnero water system corresponding to the final area of Salado River: **a** mangrove cover in December 2013, **b** mangrove cover in May 2017 and **c** mangrove cover in April 2021

in the Ecuadorian regulations to protect aquatic and other wildlife in fresh, marine and estuarine waters, is indicated (Ministerial Agreement 097-A, Ministry of the Environment of Ecuador, 2015).

The comparison of the mean TPH concentrations measured in 2013 (0.62 ± 0.362 mg/l) and 2020 (1.36 ± 0.463 mg/l) showed statistically significant differences both in mean values and the data series at each of the stations ($R = 0.638$; t statistic = -3.006 ; $p < 0.05$). Specifically, an increase in hydrocarbon concentration between 2013 and 2021 was observed.

The relationship between mean annual TPH concentrations, considering the measurements in 2013, 2020 and 2021, and the location x of the monitoring stations in the water system on study indicated a linear downward trend with a coefficient of determination of $R^2 = 0.8478$: $[\text{TPH}] \text{ (mg/l)} = -0.3403 \times (\text{km}) + 2.0923$. The analysis of variance (ANOVA), with 95% confidence intervals, showed significance differences in mean annual TPH concentrations between monitoring stations ($F = 16.71$; $p < 0.05$).

A better goodness of fit was obtained with the exponential regression analysis for the relationship between the mean annual TPH concentration, considering the measurements from 2013, 2020 and 2021, and the sites of the monitoring stations in the water system (Fig. 7). In this case, a determination coefficient of $R^2 = 0.9299$ was obtained showing that the TPH concentration throughout the Punta Carnero water system decays exponentially with distance from station E1 where the petroleum hydrocarbons seep up.

4 Discussion

The drainage canal studied has the distinctive characteristic of being a body mass with combined characteristics of an anthropogenic and a natural environment, the first part being a drainage canal for wastewater from the salt production industry and shrimp larvae laboratories, with additional inflow from the sewage treatment plant outflow, before joining the waters of the Salado River. Against this background, the results showed that the waters at the start can be considered a hypersaline environment, later becoming estuary-like for around 60% of the length of the canal studied.

4.1 Mangrove Ecosystems for Hydrocarbon Trapping

This estuary-type environment is favourable for mangrove ecosystems. There was no mangrove vegetation in this area until 2008 when red mangrove (*Rhizophora mangle*) was planted, with the support of the Ministry of the Environment of Ecuador, in two phases in 2008 and 2012. The environmental conditions from this period to 2021 have enabled the mangrove forest to spread to cover an estimated area of 88.42 ha at the time of this study, this representing an increase of 213% from 2013 to 2021.

The greater coverage of red mangrove (*Rhizophora mangle*) experienced in recent years could be justified on the basis of greater foliar development produced by the same growth of the plant and also to an expansion of the vegetation cover propitiated by the expansion of the flooded area, due to an expected increase in the volume of water transported by the water system in response to the generation of water from the WWTP, due to the population increase. Monroy-Torres et al. (2014) found that there is a greater development of red mangrove (*Rhizophora mangle*) in permanently flooded areas.

Various research studies (Araújo et al., 2020; Foroughbakhch et al., 2004; Hong et al., 2021; Ke et al., 2002; Molina, 2015; Moreira et al., 2011; Olgún et al., 2007; Pernía et al., 2019; Samara et al., 2020; Taketani et al., 2010; Villate-Daza et al., 2020) have reported that mangrove forest provides an area for natural attenuation of contaminants including petroleum hydrocarbons, heavy metals and organic and microbiological loads that occur in areas with high levels of anthropogenic activity. This may be happening in the sector of Salado River and the Punta Carnero estuary. In this way, the tourist zone with primary contact waters presents certain preservation conditions that would make it, for the moment, suitable for these purposes, although this should be further investigated.

Pinto et al. (2015) and Sanches-Filho et al. (2017) in Brazil, Zhou et al. (2014) and Li et al. (2019) in China, Vane et al. (2020) in the USA and Ashok et al. (2019) in various different locations in the Persian Gulf in the Middle East have shown that petroleum hydrocarbons and heavy metals easily lodge in the sediment of the estuarine vegetation, which, in turn, retains hydrocarbon films, stopping their flow through the water systems studied. In line with this, Wang

et al. (2012) described that the sediments trap, not only oil and heavy metals but also a large variety of hydrocarbons which, though not often considered in the planning of monitoring processes (mainly focused on parameters assessed by conventional methods), but which would be of importance to analyse in order to minimise future environmental risks.

With these considerations, it is plausible to suggest that TPH concentration attenuation in the study area is associated with the natural processes of (1) trapping in existing vegetation, mainly red mangrove (*Rhizophora mangle*), and (2) sedimentation in the substrates of the meanders and edges and banks throughout the Punta Carnero water system.

4.2 Environmental Conditions in Water System

From the point of view of environmental quality, the results of this study were compared to levels stipulated in Ecuadorian regulations (Ministerial Agreement 097-A, Ministry of the Environment of Ecuador, 2015). Notably, oxygen saturation as a function of temperature and salinity in the study area was within the limits in all the monitoring stations. The lowest levels were found at station E3, which receives the inflow from the sewage treatment plant outflow, and this may be attributed to the high organic load of this outflow reducing oxygen saturation. In line with this, Revilla et al. (2017) indicated that that oxygen conditions depend on natural factors related to the normal functioning of such estuarine systems (photosynthesis, respiration, nitrification, diffusion, etc.) as well as to anthropogenic factors (discharge with a high organic content and presence of petroleum hydrocarbons, chemicals, etc.).

Although the pH values measured in the monitoring stations are within the maximum permitted levels (Ministerial Agreement 097-A, Ministry of the Environment of Ecuador, 2015) and the waters were alkaline, the pH between the stations E2 and E5 does not reach levels that are characteristic of marine waters. The reduction observed in pH values is attributable to dilution with the waters coming from the sewage treatment plant. Nonetheless, the relatively low pH values at station E5 make us wonder whether there is an acidification process in the canal.

Regarding turbidity, measured indirectly with a Secchi disk, none of the stations reached levels

approved for primary contact waters in the environmental regulations. On the other hand, given that primary contact activities are carried out mainly at stations E4 and E5, these are not critical values given that turbidity would in any case be caused by the strong tidal currents in the area that move sand to the water column.

4.3 Hydrocarbon Concentration Evaluation Over Time and Along the Water System

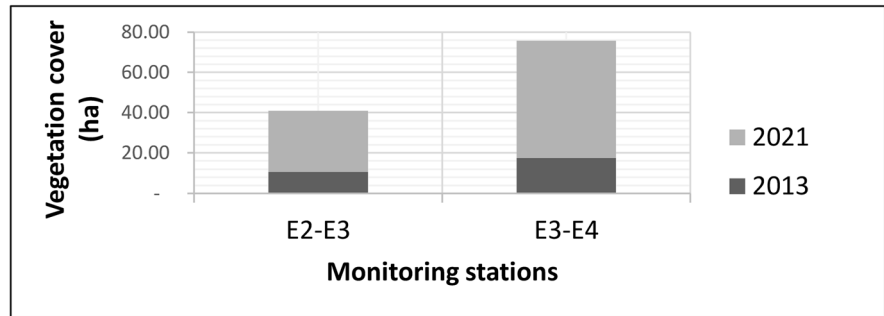
In the context of petroleum hydrocarbon contamination, the nature of the seepage is not clear. On some occasions, seepage is natural, while on others, it is due to human intervention as a consequence of activities in the soil such as the drilling of wells and even small-scale excavation for canals and clearing of vegetation. The high level of human activity over many years on the Santa Elena Peninsula, which has permeable soils with micro-fissures with evidence of petroleum hydrocarbons on the surface, makes think that most of the seepage is related to anthropogenic factors (Veloz, 2015).

The analysis of the flow rate shows that the TPHs are held in the surface layer at station E1. Nonetheless, the bottom water that goes through the goose-neck pipe still contains hydrocarbons, as we have seen through the samples of TPHs and the presence of visible grease and oil films at stations E1 and E2. This dammed water does not undergo any treatment and may pose a risk of contamination when there is overflow following high rainfall.

The TPH measurements obtained in 2013 found that levels only exceeded permitted levels at stations E1 and E2, while TPH concentrations remained at acceptable levels in terms of environmental quality at the other stations. In contrast, the analysis carried out in 2020 and 2021 showed that TPH levels exceeded the maximum permitted levels at all stations, especially at stations E1 and E2. The statistical analysis confirmed the hypothesis that the level of TPH increased between 2013 and 2021.

It was found that the decay in the concentration of TPH along the canal may be expressed using an exponential equation with a very good good-of-fit. This exponential trend of pollutant with the distance to the source has been described by other authors (Abdelhady et al., 2019; Wang et al.,

Fig. 5 Comparison of red mangrove (*Rhizophora mangle*) cover in the Salado River section within the Punta Carnero water system between 2013 and 2021



2015), and, in this study case, the reduction in the concentration of TPH could be favoured by the presence of mangroves along a considerable length of the canal. In relation to this, Suprayogi and Murray (1999), Zhang et al. (2004), Olgún et al. (2007) and Moreira et al. (2011) reported that the high productivity of mangroves and the high level of organic matter make them a preferential place for the accumulation of hydrocarbons and indicated that mangrove soils and adjacent areas are a substrate for the accumulation and attenuation of petroleum hydrocarbons.

Hence, given the relatively low concentration of hydrocarbons that manage to reach the water system after the confined area, it seems that the area of the mangrove serves as a substrate for the degradation of hydrocarbons, both at the leaf and root levels and in the sediment, with a reduction in levels of the concentration of TPH towards the Punta Carnero estuary. Nonetheless, the data indicate that the values recorded in the monitoring stations exceed the legal levels, and as a consequence, it would be advisable to carry out measures aimed to achieve better control of contamination at its source. Potential measures include the creation of an artificial dam with red mangrove (*Rhizophora mangle*) in the stretch after station E1. Another potential treatment would be the use of bacterial consortia in the confined area, as described by Phulpoto et al. (2020) who indicate that bacterial consortia would accelerate the potential degradation of petroleum hydrocarbons in a contaminated environment. There is a need to assess the cost-benefit relationship of the aforementioned possible measures and other options.

5 Conclusions

Statistical analysis of the temporal characterisation of petroleum hydrocarbon concentration data showed an increase from 2013 to 2021. Regarding spatial characterisation throughout the canal, TPH levels are high at stations E1 and E2, and decrease significantly towards the end of the canal, in an exponential manner. This spatial reduction could be explained by dilution with other water sources, together with the presence of mangroves along a considerable stretch of the canal, which would be producing a substrate that retains and helps degrade the petroleum hydrocarbons that reach the sector, reducing TPH concentrations towards the end of the canal in the estuary.

Given that the TPH concentration exceeds legally permitted levels throughout the canal would be necessary to establish management measures in the estuary to reduce chronic presence of hydrocarbons. Some future proposals could be the implementation of a system involving an artificial dam with red mangrove (*Rhizophora mangle*) or an alternative method that would make it possible to control the contamination by petroleum hydrocarbons from their source.

This study has not assessed other factors, which have emerged during the analysis, such as the quality of the output waters of the sewage treatment plant and its microbiological characteristics, as well as the potential impact on the use of these waters when they mix with the estuarine waters for tourism and agricultural purposes. These factors should be considered in future works to establish an integrated management to improve water quality by reducing pollution and minimising release.

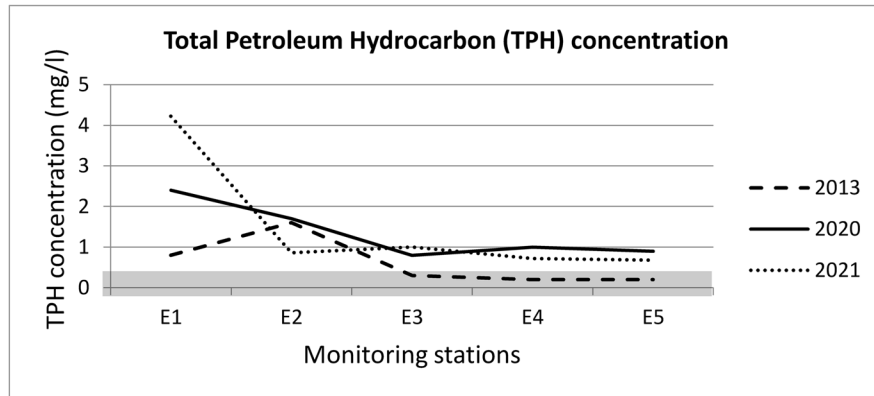
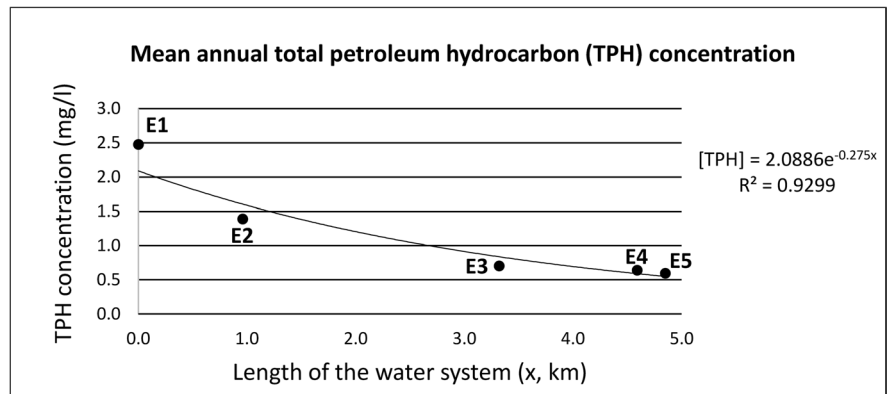


Fig. 6 Spatial and temporal characterisation of total petroleum hydrocarbon concentration throughout the Punta Carnero water system. Comparison with the maximum permitted limit of 0.5 mg/l from the table of quality criteria for protecting aquatic

and other wildlife in freshwater, marine and estuarine waters in Ecuador (Ministerial Agreement 097-A, Ministry of the Environment of Ecuador, 2015)

Fig. 7 Mean annual total petroleum hydrocarbon concentration vs distance x in the Punta Carnero water system canal. The downward exponential trend of the data series was represented



Acknowledgements We would like to thank Ecuasal for allowing access to part of the channel and obtaining the data necessary to carry out this study. =

Author Contribution Investigation: EV, JCh and IP-C; conceptualisation: EV and IP-C; methodology: EV and JCh; formal analysis: EV and IP-C; resources: JCh and IP-C; writing—original draft: EV and IP-C; writing—review and supervision: EV and IP-C. All authors have read and agreed to the published version of the manuscript.

Funding Funding for open access publishing: Universidad de Huelva/CBUA.

Data Availability Data will be made available on request.

Declarations

Competing Interests The authors declare no competing interests.

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References

- Abdelhady, A. A., Khalil, M. M., Ismail, E., Mohamed, R. S. A., Ali, A., Snousy, M. G., Fan, J., Zhang, S., Yanhong, L., & Xiao, J. (2019). Potential biodiversity threats associated with the metal pollution in the Nile-Delta ecosystem (Manzala lagoon, Egypt). *Ecological Indicators*, 98, 844–853. <https://doi.org/10.1016/j.ecolind.2018.12.002>
- Ágreda, A. (2012). Plan de Conservación de las Piscinas Artificiales de Ecuasal y Estudio de Capacidad de Carga Turística. In C. A. Ecuasal (Ed.), *Ecuatoriana de Sal y Productos Químicos y Aves y Conservación-BirdLife Internacional* (1st ed.).
- Aguirre, Z. (2014). *Sistema Nacional de Áreas Protegidas del Ecuador–SNAPE*. Área Agropecuaria y de Recursos Naturales Renovables, Carrera de Ingeniería Forestal, Universidad Nacional de Loja, Ecuador
- Araújo, M. P., Hamacher, C., de Oliveira, C., Martinho, P., de Oliveira, F., & Gomes, M. L. (2020). Assessment of Brazilian mangroves hydrocarbon contamination from a latitudinal perspective. *Marine Pollution Bulletin*, 150, 110673. <https://doi.org/10.1016/j.marpolbul.2019.110673>
- Ashok, A., Cusack, M., Saderne, V., Krishnakumar, P. K., Rabaoui, L., Qurban, M. A., Duarte, C. M., & Agustí, S. (2019). Accelerated burial of petroleum hydrocarbons in Arabian Gulf blue carbon repositories. *Science of the Total Environment*, 669, 205–212. <https://doi.org/10.1016/j.scitotenv.2019.01.437>
- Camacho-Ibar, V. F., & Rivera-Monroy, V. H. (2014). Coastal lagoons and estuaries in Mexico: Processes and vulnerability. *Estuaries and Coasts*, 37, 1313–1318. <https://doi.org/10.1007/s12237-014-9896-0>
- Centeno-Bordones, G., Labrador, H., Lara, G., & Jiménez, Y. (2021). Efficiency in the reduction of oil organic matter combining solar advanced oxidation processes and the biological reactor of a WWTP. *Ingeniería del Agua*, 25(4), 257–270. <https://doi.org/10.4995/la.2021.14874>
- Cetin, M., Aljama, A. M. O., Alrabiti, O. B. M., Adiguzel, F., Sevik, H., & Zeren-Cetin, I. (2022a). Determination and mapping of regional change of Pb and Cr pollution in Ankara City Center. *Water, Air, & Soil Pollution*, 233, 163. <https://doi.org/10.1007/s11270-022-05638-1>
- Cetin, M., Aljama, A. M. O., Alrabiti, O. B. M., Adiguzel, F., Sevik, H., & Zeren-Cetin, I. (2022b). Using topsoil analysis to determine and map changes in Ni Co pollution. *Water, Air, & Soil Pollution*, 233, 293. <https://doi.org/10.1007/s11270-022-05762-y>
- Chavarría, J. (2015). *Macro y microzonificación del mar ecuatoriano para el desarrollo de la maricultura de pargo (Lutjanus guttatus) y huayaipe (Seriola rivoliana)*. Doctoris Philosophiae en Ingeniería y Ciencias Ambientales, Universidad Nacional Agraria La Molina.
- Chavarría, J., & Salazar, D. (2006). *Monitoreo, modelamiento, inventario georeferenciado y evaluación de los pasivos e impactos ambientales y sociales de las actividades hidrocarbúrficas en la Península de Santa Elena*. Centro de Estudios Integrales del Ambiente, Universidad Estatal Península de Santa Elena.
- EPA. (1978). *Method 418.1. Petroleum hydrocarbon, total recoverable. Spectrophotometric Infrared*. United States Environmental Protection Agency.
- Espinosa, C. I., Reyes-Bueno, F., Ramírez, M. I., Arévalo, A. P., Bailon-Moscoco, N., & Duncan, D. H. (2021). Vulnerability of human populations to contamination from petroleum exploitation in the Napo River Basin: An approach for spatially explicit risk assessment. *Sustainability*, 13(16), 9230. <https://doi.org/10.3390/su13169230>
- Foroughbakhch, R., Céspedes, A. E., Alvarado, M. A., Núñez, A., & Badii, M. H. (2004). Aspectos ecológicos de los manglares y su potencial como fitorremediadores en el Golfo de México. *CIENCIA UANL*, VII, (2), 203–208.
- González, J., Fernández, E., & Figueiras, F. G. (2022). Assessing the effect of oil spills on the dynamics of the microbial plankton community using a NPZD model. *Estuarine, Coastal and Shelf Science*, 265, 107734. <https://doi.org/10.1016/j.ecss.2021.107734>
- Hong, H., Zhang, B., & Lu, H. (2021). Seasonal variation and ecological risk assessment of heavy metal in an estuarine mangrove wetland. *Water*, 13(15), 2064. <https://doi.org/10.3390/w13152064>
- INEN. (1998). *Norma Técnica Ecuatoriana NTE INEN 2169:1998. Water. Water quality. Sampling. Handling and maintenance of samples*. Instituto Ecuatoriano de Normalización (1st ed.). Ecuador: Quito.
- INEN. (2013). *Norma Técnica Ecuatoriana NTE INEN 2176:2013. Water quality. Sampling. Guidance on sampling techniques*. Instituto Ecuatoriano de Normalización (1st ed.). Ecuador: Quito.
- Ke, L., Wong, T. W. Y., Wong, Y. S., & Tam, N. F. Y. (2002). Fate of polycyclic aromatic hydrocarbon (PAH) contamination in a mangrove swamp in Hong Kong following an oil spill. *Marine Pollution Bulletin*, 45(1-12), 339–347. [https://doi.org/10.1016/S0025-326X\(02\)00117-0](https://doi.org/10.1016/S0025-326X(02)00117-0)
- Koklu, R., Sengorur, B., & Topal, B. (2010). Water quality assessment using multivariate statistical methods-A case study: Melen River System (Turkey). *Water Resources Management*, 24, 959–978. <https://doi.org/10.1007/s11269-009-9481-7>
- Li, L., Shen, X., & Jiang, M. (2019). Characteristics of total petroleum hydrocarbon contamination in sediments in the Yangtze Estuary and adjacent sea areas. *Continental Shelf Research*, 175, 110–115. <https://doi.org/10.1016/j.csr.2019.02.003>
- Liu, X., & Wirtz, K. W. (2007). Decision making of oil spill contingency options with fuzzy comprehensive evaluation. *Water Resources Management*, 21, 663–676. <https://doi.org/10.1007/s11269-006-9031-5>
- Martínez-Hernández, I. A., Rivera-Cruz, M. C., Carballar-Hernández, S., Trujillo-Narcía, A., Ortíz-García, C. F., Hernández-Galvez, G., & Alarcón, A. (2021). Arbuscular mycorrhizal colonization in a mangrove forest exposed to weathering oil for half a century. *Water, Air, & Soil Pollution*, 232, 34. <https://doi.org/10.1007/s11270-021-04986-8>

- Maurice, L., López, F., Becerra, S., Jamhoury, H., Le Menach, K., Dévier, M. H., Budzinski, H., Prunier, J., Juteau-Martineau, G., Ochoa-Herrera, V., Quiroga, D., & Schreck, E. (2019). Drinking water quality in areas impacted by oil activities in Ecuador: Associated health risks and social perception of human exposure. *Science of the Total Environment*, 690, 1203–1217. <https://doi.org/10.1016/j.scitotenv.2019.07.089>
- Ministry of Production, Foreign Trade, Investments and Fisheries (MPCEIP) of Ecuador. (2021). *Informe de Gestión 2020*, Ecuador.
- Ministry of the Environment of Ecuador. (2009). *Reserva de producción faunística marino costera Puntilla de Santa Elena*. Plan de Manejo.
- Ministry of the Environment of Ecuador. (2010). *Informe técnico: MAEDPSE-2010*. Dirección Provincial de Santa Elena.
- Ministry of the Environment of Ecuador. (2015). Ministerial Agreement 097-A. *Standard for environmental quality and discharge of effluents to water resources*. Annex I of Book VI of the Unified Text of Secondary Legislation of the Ministry of the Environment. *Special Edition of the Official Gazette*, 387, 11–12.
- Molina, E. (2015). Evaluación de niveles de Cd, Pb y Hg en raíces de *Rhizophora Mangle L.* en cuatro localidades de muestreo del perfil costanero de la provincia de El Oro en épocas de sequía y lluvia, 2014. In *Tesis de Grado en Ingeniería Química*. Universidad Técnica de Machala.
- Monroy-Torres, M., Flores-Verdugo, F., & Flores-de-Santiago, F. (2014). Growth of three subtropical mangrove species in response to varying hydroperiod in an experimental tank. *Ciencias Marinas*, 40(4), 263–275. <https://doi.org/10.7773/cm.v40i4.2455>
- Moreira, I. T. A., Oliveira, O. M. C., Triguís, J. A., Dos Santos, A. M. P., Queiroz, A. F. S., Martins, C. M. S., Silva, C. S., & Jesus, R. S. (2011). Phytoremediation using *Rizophora mangle L.* in mangrove sediments contaminated by persistent total petroleum hydrocarbons (TPH's). *Microchemical Journal*, 99(2), 376–382. <https://doi.org/10.1016/j.microc.2011.06.011>
- Olgún, E. J., Hernández, M. E., & Sánchez-Galván, G. (2007). Contaminación de manglares por hidrocarburos y estrategias de biorremediación, fitorremediación y restauración. *Revista Internacional de Contaminación Ambiental*, 23(3), 139–154.
- Pernía, B., Mero, M., Cornejo, X., & Zambrano, J. (2019). *Impactos de la contaminación sobre los manglares de Ecuador* (pp. 424–466). Universidad Espíritu Santo, Samborondón, Ecuador.
- Phulpoto, I. A., Hu, B., Wang, Y., Ndayisenga, F., Li, J., & Yu, Z. (2020). Effect of natural microbiome and culturable biosurfactants-producing bacterial consortia of freshwater lake on petroleum-hydrocarbon degradation. *Science of the Total Environment*, 751, 141720. <https://doi.org/10.1016/j.scitotenv.2020.141720>
- Pinto, A. B., Pagnocca, F. C., Pinheiro, M. A. A., Fontes, R. F. C., & de Oliveira, A. J. F. C. (2015). Heavy metals and TPH effects on microbial abundance and diversity in two estuarine areas of the southern-central coast of São Paulo State, Brazil. *Marine Pollution Bulletin*, 96(1-2), 410–417. <https://doi.org/10.1016/j.marpolbul.2015.04.014>
- Revilla, M., Solaun, O., Menchaca, I., Zorita, I., Franco, J., Borja, A., Valencia, V., & Bald, J. (2017). *Estudio de la sensibilidad a la eutrofización de los estuarios del País Vasco. Informe 2017*. In *Azti-Tecnalia*. Agencia Vasca del Agua del Gobierno Vasco.
- Samara, F., Solovieva, N., Ghalayini, T., Nasrallah, Z., & Saburova, M. (2020). Assessment of the environmental status of the mangrove ecosystem in the United Arab Emirates. *Water*, 12(6), 1623. <https://doi.org/10.3390/w12061623>
- Sanches-Filho, P. J., Böhm, E. M., Böhm, G. M. B., Montenegro, G. O., Silveira, L. A., & Betemps, G. R. (2017). Determination of hydrocarbons transported by urban runoff in sediments of São Gonçalo Channel (Pelotas – RS, Brazil). *Marine Pollution Bulletin*, 114(2), 1088–1095. <https://doi.org/10.1016/j.marpolbul.2016.10.024>
- Sun, Y., Ma, J., Yue, G., Liu, S., Liu, H., Song, Q., & Wu, B. (2021). Comparisons of four methods for measuring total petroleum hydrocarbons and short-term weathering effect in soils contaminated by crude oil and fuel oils. *Water, Air, & Soil Pollution*, 232, 381. <https://doi.org/10.1007/s11270-021-05341-7>
- Suprayogi, B., & Murray, F. (1999). A field experiment of the physical and chemical effects of two oils on mangroves. *Environmental and Experimental Botany*, 42(3), 221–229. [https://doi.org/10.1016/S0098-8472\(99\)00037-4](https://doi.org/10.1016/S0098-8472(99)00037-4)
- Taketani, R. G., Franco, N. O., Rosado, A. S., & Van Elsas, J. D. (2010). Microbial community response to a simulated hydrocarbon spill in mangrove sediments. *Journal of Microbiology*, 48(1), 7–15. <https://doi.org/10.1007/s12275-009-0147-1>
- Tran, H. T., Lin, C., Bui, X. T., Ngo, H. H., Cheruiyot, N. K., Hoang, H. G., & Vu, C. T. (2021). Aerobic composting remediation of petroleum hydrocarbon-contaminated soil. Current and future perspectives. *Science of The Total Environment*, 753, 142250. <https://doi.org/10.1016/j.scitotenv.2020.142250>
- Vane, C. H., Kim, A. W., Moss-Hayes, V., Turner, G., Mills, K., Chenery, S. R., Barlow, T. S., Kemp, A. C., Engelhart, S. E., Hill, T. D., Horton, B. P., & Brain, M. (2020). Organic pollutants, heavy metals and toxicity in oil spill impacted salt marsh sediment cores, Staten Island, New York City, USA. *Marine Pollution Bulletin*, 151, 110721. <https://doi.org/10.1016/j.marpolbul.2019.110721>
- Veloz, E. (2013). *Afloramiento de hidrocarburos en el sector Valparaíso del cantón Salinas, provincia de Santa Elena-Ecuador*. Master Cientiae en Ciencias Ambientales, Universidad Nacional Agraria La Molina
- Veloz, E. (2015). Afloramiento de hidrocarburos en el sector Valparaíso del Cantón Salinas, provincia de Santa Elena-Ecuador. *Revista Técnica "energía"*, 11, 68–76. <https://doi.org/10.37116/revistaenergia.v11.n1.2015.73>
- Villate-Daza, D. A., Sánchez-Moreno, H., Portz, L., Portantolo-Manzollí, R., Bolívar-Anillo, H. J., & Anfuso, G. (2020). Mangrove forests evolution and threats in the Caribbean Sea of Colombia. *Water*, 12(4), 1113. <https://doi.org/10.3390/w12041113>
- Wang, L., Lu, X., Li, L. Y., Ren, C., Luo, D., & Chen, J. (2015). Content, speciation and pollution assessment of Cu, Pb and Zn in soil around the lead-zinc smelting plant of Baoji, NW China. *Environmental Earth Sciences*, 73, 5281–5288. <https://doi.org/10.1007/s12665-014-3777-5>

- Wang, Z., Yang, C., Yang, Z., Hollebone, B., Brown, C. E., Landriault, M., Sun, J., Mudge, S. M., Kelly-Hooper, F., & Dixon, D. G. (2012). Fingerprinting of petroleum hydrocarbons (PHC) and other biogenic organic compounds (BOC) in oil-contaminated and background soil samples. *Journal of Environmental Monitoring*, *14*, 2367–2381. <https://doi.org/10.1039/C2EM30339F>
- Zhang, J., Cai, L., Yuan, D., & Chen, M. (2004). Distribution and sources of polynuclear aromatic hydrocarbons in mangrove superficial sediments of Deep Bay, China. *Marine Pollution Bulletin*, *49*(5-6), 479–486. <https://doi.org/10.1016/j.marpolbul.2004.02.030>
- Zhou, R., Qin, X., Peng, S., & Deng, S. (2014). Total petroleum hydrocarbons and heavy metals in the surface sediments of Bohai Bay, China: Long-term variations in pollution status and adverse biological risk. *Marine Pollution Bulletin*, *83*(1), 290–297. <https://doi.org/10.1016/j.marpolbul.2014.03.003>

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