ESCUELA POLITÉCNICA NACIONAL

FACULTAD DE INGENIERÍA EN GEOLOGÍA Y PETRÓLEOS

SPATIAL PATTERNS VARIATION IN WATER QUALITY PARAMETERS UNDER THE INFLUENCE OF HYDROCARBON COMPOSITES EXPLOITATION IN A HYDROGRAPHIC UNIT OF THE NAPO RIVER BASIN

SPATIAL VARIABILITY OF PHYSICOCHEMICAL WATER PARAMETERS APPLYING RASTER CORRELATION ANALYSIS IN THE AGUARICO RIVER

TRABAJO DE INTEGRACIÓN CURRICULAR PRESENTADO COMO REQUISITO PARA LA OBTENCIÓN DEL TÍTULO EN INGENIERO EN PETRÓLEOS

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DMQ, febrero 2024

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I, WILMAN JOSEPH FLORES YEPEZ, declare that the curricular integration work described here is my authorship; who has not previously been submitted for any degree or professional qualification; and, that I have consulted the bibliographical references included in this document

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DEDICATORY

To my loving parents and supportive siblings, whose unwavering encouragement and understanding have been my guiding light throughout this journey. Your boundless love and belief in me have made this achievement possible.

ACKNOWLEDGEMENTS

I extend my gratitude to Ph.D José Luis Rivera for consistently upholding his unwavering faith in me throughout this period, demonstrating exceptional academic mentorship prowess.

We extend our sincere appreciation to the Ministerio del Ambiente, Agua y Transición Ecológica (MAATE) for their generous provision of the data crucial for the development of this research. Their invaluable contribution has significantly enriched our study.

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SUMMARY

Aguarico River, a prominent freshwater body stream in the in the Northeastern Ecuador, currently lacks of comprehensive understanding regarding the spatial and temporal variability in water parameters. The primary objectives in this study are characterize concentrations and heterogeneities of water quality parameters under the influence of oil resources exploitation over space and time, identifying which of those physicochemical attributes have most negatively impacted the water quality in the region.

In order to achieve this, the dataset employed to perform the predictions and interpolations comes from water samples collected at nine unique sites in 2013 and 2014, along with fourteen additional points in 2015. Sixteen water quality parameters were analyzed using layering tools and interpolation techniques. While most parameters fell within permissible ranges defined by Ecuadorian and international guidelines, Apparent Color (Pt-Co), Sulfur as Hydrogen Sulfide (H₂S), Temperature (°C), and Turbidity (NTU) exceeded allowed thresholds.

Upon statistical analysis, the average WQI value for the consecutive three-year timeframe was 59.67 points, ranking "medium" in the category of water quality status. This deterioration in water quality can be attributed to anthropogenic activities, most certainly those related to the oil industry. In fact, oilfields located within Block 56 and Block 57 are distinguished as primary sources of contamination due to their substantial production of formation water, characterized by their moderate to high concentrations of Salts and Barium (Ba)

This study highlights the potential risks of pollutant exposure to local settlements along the Aguarico River and its tributaries. Focused on the Napo River Basin, it compares datasets with current regulations, emphasizing the need for regulatory interventions to safeguard human health and environmental sustainability in the region.

KEY WORDS: Aguarico River, oil exploitation, water quality index, spatial and temporal variation, water quality parameters.

ABSTRACT

El río Aguarico, un importante cuerpo de agua dulce localizado al noreste de Ecuador, actualmente carece de una comprensión integral sobre las fluctuaciones espaciales y temporales en los parámetros de calidad del agua. Los objetivos principales de este estudio son caracterizar las concentraciones y heterogeneidades de los parámetros de calidad del agua a lo largo del tiempo y espacio bajo la influencia de actividades relacionadas con la explotación de hidrocarburos. Además, se identifican cuáles de esos atributos físico-químicos han impactado negativamente la calidad del agua en la región.

Para lograr esto, el conjunto de datos empleado para realizar este estudio proviene de muestras de agua recolectadas en nueve sitios únicos en 2013 y 2014, junto con catorce puntos adicionales en 2015. Se analizaron dieciséis parámetros de calidad del agua utilizando herramientas de creación de capas ráster. y técnicas de interpolación. Si bien la mayoría de los parámetros se encontraron dentro de los rangos permisibles definidos por las normativas ecuatorianas e internacionales, Color Aparente (Pt-Co), Sulfuro como Sulfuro de Hidrógeno (H2S), Temperatura (°C) y Turbidez (NTU) superaron los limites permisibles.

Tras análisis estadístico, el valor promedio del Índice de Calidad del Agua (WQI) durante el período de tres años consecutivos entre 2013 y 2015 fue de 59.67 puntos, clasificándose en la categoría "media" en términos del índice de calidad del agua. El deterioro puede atribuirse a actividades antropogénicas, más notablemente a aquellas relacionadas con la industria petrolera. De hecho, campos petroleros localizados dentro de los Bloques 56 y 57 se distinguen entre las fuentes principales de contaminación debido a su producción sustancial de agua de formación, caracterizada por sus concentraciones moderadas y altas de Sales y Bario (Ba).

Este estudio proporciona una valiosa perspectiva sobre el potencial riesgo a la exposición de contaminantes por parte de asentamientos y pueblos locales distribuidos a lo largo de los ríos principales y afluentes. Finalmente, este estudio se centrará únicamente en la Cuenca del Río Napo y en la validación de información entre los datos disponibles y las regulaciones nacionales e internacionales actualmente en rigor.

KEYWORDS: Río Aguarico, petróleo, índice de calidad del agua, variación espacial y temporal, parámetros de calidad del agua.

1 DEVELOPMENT COMPONENT OVERVIEW

The main purpose of this study is to analyze the spatial variability of water quality parameters associated with onshore hydrocarbon exploitation within the Aguarico River Basin. Geographic Information System (GIS) software was employed in order to produce maps of temporal and spatial trends. This approach offers a comprehensive visual representation of widely spread water quality data points within the dataset. Being a software equipped with a robust toolkit, it is intended to effectively manage and analyze all the available cluster of data (Kraak and Ormeling, 2003). Therefore, this research relies on ArcGIS analysis tools to further dissect a variety of indicators, all of them gathered across the years 2013, 2014 and 2015. The methodology emphasizes in the crafting of color-coded maps Data collection was accomplished through surveying and control campaigns carried out by MAATE (Ministerio de Ambiente, Agua y Transición Ecológica). Raster layer analysis and interpolation techniques were used in order to unveil and examinate distribution patterns prior to delving into the characterization of the river's welfare evolution. The use of imagery tolls and workflows integrated in the software will aid in comprehending the following aspects; 1) determine the relationship in differing magnitudes between the sampling location dataset containing concentration values for each water parameter, and the effective documented guidelines will be addressed; 2) determine which contaminating and polluting elements had the most critical impact over water quality. 3) analyze the extent of the vulnerability of aboriginal groups exposed to contaminants and pollutants dispersed along the streams network; and, 4) determine which populated zones could potentially be exposed to oil-related pollutants

1.1 Main Objective

The main purpose of this study is to analyze the spatial variability of water quality parameters associated with onshore hydrocarbon exploitation within the Aguarico River Basin. Geographic Information System (GIS) software was employed to design color coded maps depicting temporal and spatial distributions of water quality indicators. This approach provides a comprehensive visual representation of the widespread dataset on water quality along the flow course of main and secondary rivers.

1.2 Secondary Objectives

- Determine the relationship in differing magnitudes between the sampling location dataset containing concentration values for each water parameter, and the effective documented guidelines will be addressed
- 2. Determine which contaminating and polluting elements had the most critical impact over water quality
- 3. Analyze the extent of the vulnerability of aboriginal groups exposed to contaminants and pollutants dispersed along the network of streams.
- 4. Determine which populated zones could potentially be exposed to oil-related pollutants.

1.3 Scope

This study focuses on the spatial variation assessment of the Aguarico hydrographic unit, located within the Napo River Basin, applying GIS survey and interpretation techniques, particularly raster interpolation analysis developed through layer overlays. In addition, the potential risk of exposure to pollutants and contaminants by the local population will be estimated. This project will use previously collected and documented data; therefore, it will not be necessary to perform technical field trips for analysis and sampling purposes. Finally, this study will only focus on the Aguarico River Basin and the comparison between the already available dataset and the applicable regulations currently in force.

1.4 Literature Review

Over the years, humankind has severely modified the natural environment in order to keep up with his desire for industrialization throughout the development of science and technology. This pursuit to meet socioeconomical demands has led to devastating and irremediable impacts to the biosphere (Rivera-Parra et al., 2020). Undoubtedly, oilproducing zones within the Amazon rain forest in Ecuador have faced numerous environmental disasters related to the exploitation, production and transportation of hydrocarbon composites (Espinosa et al., 2021). These tragedies have inflicted severe damage upon the delicate ecosystem of the Amazon, resulting in widespread deforestation, soil contamination, water pollution, and habitat deterioration. Moreover, the use of polluted water near oil fields is also contributing to the spread of illness and diseases among human settlements in close proximity to rivers and streams (Castello et al., 2013). To address these issues, it becomes imperative to regularly monitor water quality. Essential parameters commonly subject to analysis include Temperature, pH, Turbidity, Salinity, Nitrates, and Phosphates, Dissolved Oxygen (D.O.), Biochemical Oxygen Demand (BOD), etc.

Freshwater environments are vital ecosystems that support a diverse range of life forms. from microscopic organisms to large species of flora and fauna. Despite all the numerous manifestations of water in the nature, chemically pure sources of water do not occur naturally in the real world. Therefore, body of water is considered to be practically pure when it is constituted by minimal dissolved or suspended solids, absence of undesirable gases, and limited biological activity (Gorde and Jadhav, 2013). Therefore, it is a crucial necessity for the progress and growth of both human and industrial developments to contribute to the preservation and sustainability of a nation's natural water resources. This statement is considered by many as a foundation for a country's social and economic advancement (Das and Tripathy, 2021). Unfortunately, insufficient funding destinated for infrastructure and research, the limited enforcement of the current legal instruments along with the lack of environmental education are only a few reasons of the detrimental current state of many freshwater ecosystems (Lawler, 2011). Moreover, the rapid growth of the oil and gas industry, along with the unconscious use of chemical additives intended for treatment of crude oil have overwhelmingly promoted the deterioration of our biosphere. All of these factors have led to the degradation of water quality, hindering the flourishing of aquatic life and human development (Sebastián and Hurtig, 2004).

Rivers represent the main water supply in land, mostly destinated for domestic, irrigation and industrial purposes. Due to its wide hydrochemistry spectrum, in terms of temporal and spatial differences, it is imperative and avoid any kind of pollution. Taking accountability for our actions is a key factor for the sake of gathering genuine and solid information about water quality (Gazzaz et al., 2013). Although long-term surveys and quality monitoring provide sufficient in-depth understanding of a river physical and chemical water composition, they also generate large amounts of raw data. This massive bulk of information demands the use of machines adequate for high computational power (Gazzaz et al., 2013). In order to address intricate variations of water, the term of water quality index, also known as WQI, is introduced. It represents a singular value that encompasses various water quality factors. It aims to offer a straightforward and compact approach in order to assess the overall quality of water (Gorde and Jadhav, 2013). This approach also highlights the significance of implementing protective measures in order to mitigate adverse effects over the population (Tandel et al., 2010).

Currently, the northern amazon territory in Ecuador is distributed into 83 oil blocks (Figure 1). Each of those chunks of land encloses no more than 200,000 hectares and are solely

intended for oil exploration, production and commercialization. All of these activities are currently being managed by both private and governmental agencies (Mayorga and Rivera, 2018). These endeavors are conducted within land portions proximate to the Aguarico and Napo watersheds, which constitute the primary freshwater source for Cofán, Waorani, Ai'cofan and many other indigenous communities extended all over the Amazon rainforest (Rivera-Parra et al., 2020).

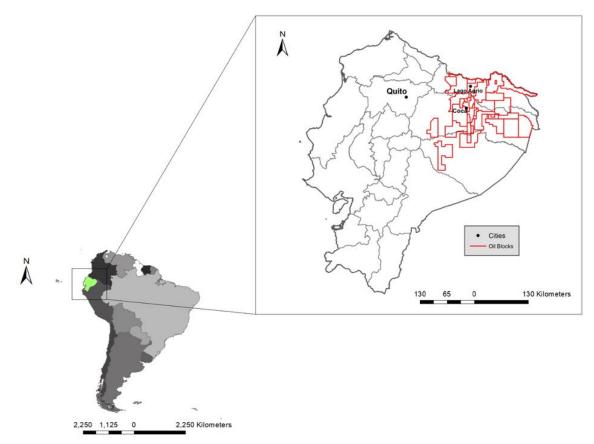


Figure 1. Oil block distribution in the northern region of the Napo River Basin

Elaborated by: Wilman Flores.

1.5 Water Quality Parameters

Water quality parameters involves chemical, physical and biological attributes which are essential for health and integrity appraisal of water bodies. Concentrations values of these quality indicators can vary greatly depending on the environmental conditions of the surrounding area. Their assessment allows to unveil the effects of natural phenomena and human activities on aquatic ecosystems. Consistent and systematical evaluation of these parameters helps to ensure that water resources are suitable for consumption, irrigation, and other purposes (Gholizadeh et at., 2016).

1.5.1 Classification of Water Quality Parameters

Chemical Parameters: Include a wide variety of chemical substances which originate from industrial discharges and urban wastes. These parameters are pH, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), nutrients (Nitrogen and Phosphorus), heavy metals (Lead, Mercury, Arsenic), and other dissolved solids (Omer, 2019). Chemical attributes of water bodies can significantly affect water's suitability for human consumption, land and aquatic development. Furthermore, an increase in nutrient levels can trigger eutrophication, potentially leading to high-risk diseases, such as cancer (Rivera-Parra, 2020; Ochoa and Rivera, 2021).

Physical Parameters: This category addresses factors such as temperature, turbidity, color, and total suspended solids. Such parameters are subject to influences from weather patterns, geographic location, and human activities, including deforestation and urban development. The physical properties of water, regarding visual and aesthetic attributes, significantly influence its suitability across a wide range of applications including recreational activities, industrial operations, and domestic uses (Omer 2019).

Biological Parameters: This classification encompass the presence and concentration of bacteria, viruses, algae, and other microorganisms. Their presence in water can indicate the level of nutrient pollution and the potential for algal blooms. Although microorganisms are naturally present in all freshwater sources, high concentrations of microbial pathogens impose a significant health concern (Omer, 2019; Marie and Lin, 2018).

1.6 Water Quality Index (WQI)

Different methodologies, including statistical methods, modeling techniques, and Water Quality Index (WQI), have been employed to assess water quality over the pasts several decades (Shrestha et al., 2023). However, WQI stands out as the most effective and reliable assessment tool for quality management. This is attributed to its straightforward and user-friendly approach dealing with large amounts of raw data (Shrestha et al., 2023). This statistical method is defined is a numerical value that portray the combined impact of various water quality attributes on the overall state of water body (Ramanarayan, 2018). This statistical tool has been employed to perform and overall quality assessment of water throughout the Aguarico River Basin and unveil its suitability for human consumption. Further considerations presented in this study adhere to the guidelines of INEN and WHO for drinking water quality.

1.6.1 Canadian Council of Ministers of the Environment Water Quality Index

Among all the available alternatives for water quality assessment, the CCME-WQI stands out for its adaptability for variegated water ecosystems and its straightforward application. This approach allows scientists to choose appropriate water quality guidelines based on their requirements (Xia et al., 2018). Due to these advantages, the CCME-WQI has amassed a significant number of positive acclaims by many agencies in charge of assessing water quality (Xia et al., 2018; Lee, 2006). The index is calculated as follows:

$$WQI = 100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732}\right)$$

Equation 1. CCME Water Quality Index equation.

Where:

 F_1 (scope): Percentage of the water quality parameters that do not meet the criteria. Failed water quality parameters.

 F_2 (frequency): Percentage of individual test measurements that do not meet the respective water quality guidelines in the period considered (failed tests).

 F_2 (amplitude): Amount by which the failed measurements do not meet the criteria.

The CCME-WQI has a scale from 0 to 100, where values near 0 represent very poor water quality, while those close to 100 indicate excellent water quality. Results are categorized into five groups: excellent (95–100), good (80–95), fair (65–79), marginal (45–64), and poor (0–44) (Lee, 2006).

1.7 Review of Current Regulatory Laws on Permissible Limits and Wastewater Management

In 2001, RAOHE (Reglamento Sustitutivo del Reglamento Ambiental para las Operaciones Hidrocarburíferas en el Ecuador) guidelines were published focused to tackle the inherent deficiencies of the Environmental Regulation Law of 1995. Many revisions and reconsiderations were conducted in order to enhance the former methodology. One of the main modifications involved a drastic overhaul concerning the number water quality parameters aiming to control and regulate wastes discharge into waterbodies (Castillo, 2018; RAOHE, 2001). RAOHE guidelines coalesce all the criteria pertaining permissible limits and concentrations in Chapter XII, Article 86. Tables 1 through 3 present the

permissible thresholds established in the RAOHE for effluent management. Values correspond to the allowed limits set for points of discharge. All limits listed are general, thus acknowledge for inherent variations of natural ecosystems is advised. This leads to the use of specific information oriented to craft suitable environmental quality guidelines tailored to each unique circumstance (Castillo, 2018).

Governmental entities in Ecuador such as MAATE (Ministerio de Ambiente, Agua y Transición Ecológica) and INAMI (Instituto Nacional de Meteorología e Hidrología) are responsible to conduct monitoring and surveying campaigns to assess the overall quality of waterbodies throughout the whole country. Despite all considerable efforts and extensive amount of gathered information regarding water quality, data is seldom subjected to largescale spatial and temporal trend analyses. Such statistical evaluations are extremely important and are destinated to unveil distribution patterns of any psychochemical indicator along the flow path of main and secondary rivers. Hence, their study aids to comprehend the dynamics of freshwater ecosystem in response to anthropogenic activities being executed in a specific area (Gazzaz et al., 2013; Park and Park, 2000).

Water Parameter	Abbreviation	Units
Temperature	-	°C
Potential of Hydrogen	рН	-
Electrical Conductivity	CE	µS/cm
Coliforms	Colonies	Col/100 ml
Dissolved Oxygen	OD	mg/l
Biochemical Oxygen Demand	DBO	mg/l
Chemical Oxygen Demand	DQO	mg/l
Ammonium	NH4	mg/l
Barium	Ва	mg/l
Cadmium	Cd	mg/l
Chrome	Cr	mg/l

Table 1. Most influential measured parameters of water as per RAOHE.

Nickel	Ni	mg/l
Lead	Pb	mg/l
Vanadium	V	mg/l
Surfactants (Methylene Blue)	MBAS	mg/l
Phenols	-	mg/l
Hydrocarbons	TPH	mg/l

Source: Ministerio de Energía y Minas, 2001.

Elaborated by: Wilman Flores

Parameter	Abbreviation	Units	Maximum allowed limit
Potential of Hydrogen	рН	-	5 <ph<9< td=""></ph<9<>
Electrical conductivity	CE	µS/cm	<2500
Hydrocarbons (Total)	TPH	mg/l	<20
Chemical Oxygen Demand	DQO	mg/l	<120
Solids (Total)	ST	mg/l	<1700
Barium	Ва	mg/l	<5
Chrome (Total)	Cr	mg/l	<0.5
Lead	Pb	mg/l	<0.5
Vanadium	v	mg/l	<1
Nitrogen (includes organic			
nitrogen, ammoniacal and oxides)	NI-4-N	mg/l	<20
Phenols		mg/l	<0.15

Table 2. Water parameters subject to evaluation at discharge points as per RAOHE.

Source: Ministerio de Energía y Minas, 2001.

Elaborated by: Wilman Flores

Parameter	Abbreviation	Units	Maximum allowed limit
Temperature		°C	+3°C
Potential of Hydrogen	рН		6.0 <ph<8.0< td=""></ph<8.0<>
Electrical Conductivity	CE	µS/cm	<170
Hydrocarbons (Total)	TPH	mg/l	<0.5
Chemical Oxygen Demand	DQO	mg/l	<30
Polycyclic Aromatic Hydrocarbons (PAH)	С	mg/l	<0.0003

Table 3. Water parameters subject to evaluation at a specific point of control within thewater body as per RAOHE.

Source: Ministerio de Energía y Minas, 2001.

Elaborated by: Wilman Flores

Moreover, guidelines concerning water quality for human consumption have been published by the Ecuadorian Institute of Standardization, INEN 1108. These guidelines include criteria for the physical, chemical, and microbiological qualities of water to ensure its safety and suitability for human consumption. Guidelines encompass a set of permissible thresholds for various substances, including arsenic, cadmium, chlorine, copper, and lead, as well as for microbial contaminants such as fecal coliforms, Cryptosporidium, and Giardia (Servicio Ecuatoriano de Normalización INEN, 2020). Table 4 below gathers the most influential parameters commonly studied in water quality assessments, alongside with their maximum permissible limit.

Parameter	Unit	Maximum allowed limit
рН	рН	6.5-8
Arsenic	mg/L	001
Cadmium	mg/L	0.003
Free residual chlorine	mg/L	0.3 a 1.5

Table 4. Physical and chemical properties of water as per INEN 1108, Sixth Edition.

Copper	mg/L	20
Apparent color	Pt-Co	15
Chromium	mg/L	005
Fluoride	mg/L	15
Mercury	mg/L	0.006
Nitrates	mg/L	500
Nitrites	mg/L	30
Lead	mg/L	001
Turbidity	NTU	5
Antimony	mg/L	2.2
Barium	mg/L	1.3
Boron	mg/L	2.4
Nickel	mg/L	0.07
Selenium	mg/L	0.04

Source: Servicio Ecuatoriano de Normalización INEN, 2020.

Elaborated by: Wilman Flores

1.8 Inverse Distance Weighted (IDW) Method

A wide variety of statistical methods can be used for predicting or estimating water quality data, such as the Inverse Distance Weighted (IDW) technique, Kriging, Minimum Curvature, Natural Neighbor, and Nearest Neighbor (Lateef et al., 2020). The IDW method is a deterministic interpolation approach that creates surface representations based on the proximity and similarity of data points. Essentially, it operates on the assumption that points located near each other are more similar than those further away (Johnston et al., 2001). This method emphasizes in the principle that the relevance of a measured point reduces as its distance increases. Consequently, giving more weight to points closer to area being exanimated.

The IDW method was selected in this study because it provided a suitable technique that can used to determinate concentration values of any given parameter along river segments where no direct measurements exist. In consequence, points in closer proximity to the target area have a greater impact than those points situated farther away (Lateef et al., 2020; Johnston et al., 2001). The method is defined by the following formula:

$$Z \ S_o \ = \sum_{i=1}^N \lambda_i Z \ S_i$$

Equation 2. Radial basis function for interpolation.

Where:

 $Z S_o$: Value to be predicted for location S_o .

N: Number of measured sample points surrounding the prediction location.

 λ_i : Weights assigned to each measured point. These weights will decrease with distance.

 $Z S_i$: Observed value at the location S_i .

Equations to determine the weights is the following:

$$\lambda_i = \frac{d_{i0}^{-p}}{\sum_{i=1}^N d_{i0}^{-p}}, \sum_{i=1}^N \lambda_i = 1$$

Equation 3. Weight assigned to each individual point.

Where d_{i0} is the distance between the prediction location S_0 and each of the measured locations S_i .

2 METHODOLOGY

2.1 Description of the Study Area and Site Selection

Napo Basin, located within the Ecuadorian Amazon (Figure 2), is acclaimed worldwide as a biodiversity hotspot and one of the most studied ecosystems nowadays. The Napo River is a main tributary located alongside the upper eastern Ecuadorian rainforest (Ibarra and Stewart, 1989). It compromises several streams and rivers which emerge from the Andes, at over 5000 m of altitude. The climate varies from hot to humid throughout the year, with temperatures ranging the 20 and 25 °C and annual precipitation between 200 and 400 cm (Ibarra and Stewart, 1989).

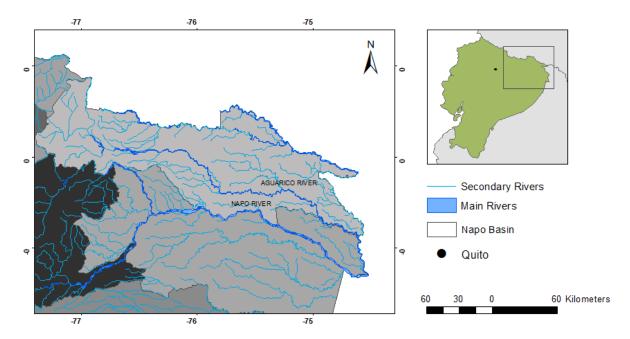
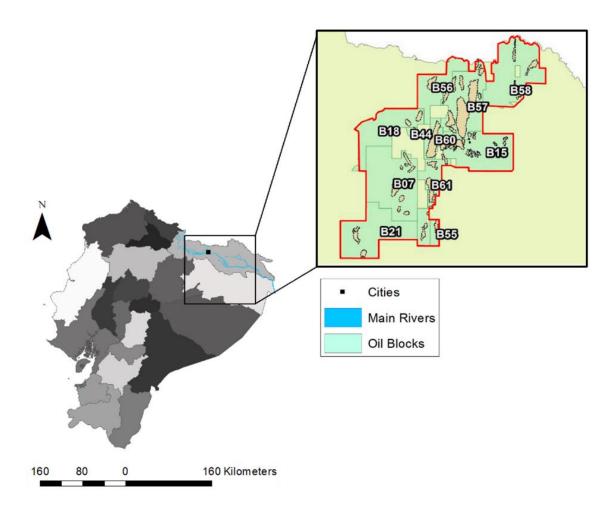


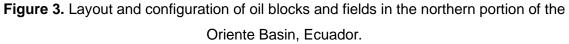
Figure 2. Ecuadorean Amazon Basin, showing the main and tributary rivers.

Elaborated by: Wilman Flores

The Aguarico River (10,290 km²), part of the Ecuadorian Amazon basin, is located in the northeastern region of Ecuador. Its course crosses a massive northern portion of the Amazon region. PETROECUADOR as the main national operator company is in charge of 11 oil blocks within the zone (Figure 3). Oil production of these blocks represent at least 73% of the daily oil production of Ecuador (PETROECUADOR EP, 2024). The climate here is categorized by its tropical rainforest, with an abundant rainfall year-round. The average annual precipitation ranges between 3500 mm with approximately 19 rainy days per month. The river stream originates in the highlands of the Pimampiro mountain range, located to the west of Sucumbíos. It's altitude ranges 3746 meters approximately, above sea level.

The river itself stretches for roughly 390 km until it reaches the border with Perú (Cabrera et al., 2021).





Elaborated by: Wilman Flores

According to official records, the Napo River basin is estimated to harbor more than 45,000 kichwa indigenous settlements along with many other communities and tribes such as Waorani, Cofán, Secoyas; The majority of whom still remains uncontacted, willing to live in isolation (Alexiades et al., 2019). Therefore, the main concerns lay upon the endeavor to define the extent of the vulnerability of aboriginal groups. These human settlements are prone to develop critical health related issues as a consequence of the extensively exposure to pollutants dispersed along the streams network (Espinosa et al., 2021). Currently, oil related activities rest among the primary sources of revenue income in Ecuador and has been the main driving force for the nation's social and economic growth since the 1970s. Prior the oil price boom era, Ecuador was ranked among the least prosperous nations of

the whole Latin America region (Sebastián and Hurtig, 2004). This crude oil deposits underly the Amazon basin, one of the most biodiverse regions around the globe, characterized by its tropical rain forest with a substantial rainfall of more than 6 m each year (Ibarra and Stewart, 1989). Unfortunately, oil companies settled down along the northeastern Amazon territory have neglected in adopting proper strategies and practices regarding risk mitigation in compliance with environmental regulations (Ochoa and Rivera, 2021). Despite extensive pollution sources and process related to the industry, large scale evaluations of river basins behavior, as well as human and ecological welfare studies, were lacking at the time. Moreover, the rapidly anthropogenic advancement related to road building, hydroelectric projects, oil extraction and mining, have resulted in major threats to this pristine fresh water ecosystem. Therefore, compromising physicochemical water parameters such as dissolved oxygen and minerals, pH, turbidity, conductivities, etc. (Alexiades et al., 2019).

To tackle this major issue, a water quality assessment is conducted in order to address biological, chemical and physical irregularities in water. Thus, ensuring both human welfare and environmental conservation. This process is accomplished through statistical correlations between the collected data and the current legislation standards (Gazzaz et al., 2013). Through the use of geoprocessing tools for mapping and analysis, the aim of this research relays in the use of ArcGIS, a geographic information system software developed by Esri, used for manipulating and analyzing geographic data. Raster analysis in ArcGIS is widely used in fields such as environmental science, land management, agriculture, hydrology, remote sensing, and urban planning. The software supports various techniques such as zonal analysis, focal statistics, distance analysis, density calculations, interpolation among others. The layered data is then represented as a grid of cells or pixels, therefore allowing for a more accurate spatial analysis (Johnston et al., 2001). These techniques help to further understand patterns, trends, and relationships within the raster dataset.

2.2 Data Collection

Within the study area, sixteen points along the Aguarico River course were chosen for sampling purposes. The data was gathered and gently provided by MAATE (Ministerio de Ambiente, Agua y Transición Ecológica). Field sampling campaigns were carried out in 2013, 2014 and 2015. These locations are depicted throughout Figures 6 and 7. These surveys took place along the Napo River and Aguarico River within the Oriente basin. MAATE's (Ministerio de Ambiente, Agua y Transición Ecológica) technicians and engineers gathered water samples along these main rivers and their tributaries. Further laboratory

analysis was conducted at GRUENTEC Environmental Services and Laboratories. Table 5 provides an overview of the testing methods associated to each individual water parameter. Samples were gathered in sterile plastic containers and ensured they were properly sealed. To maintain sample integrity and avoid environmental degradation, analysis was conducted within 24 hours after collection. Standardized procedures were meticulously followed for collecting, transporting, and storing all water samples in order to ensure accurate data analysis. Additionally, GPS equipment was employed to determine elevation data for each sampling point. Moreover, handheld probes measured stream velocity multiple times at strategic points. Measurements of river depth and width were taken to explore correlations between variables. However, these values are not taken into consideration.

This study focuses in assessing water quality parameters of both domestic (organic) and industrial pollutants, as these two sources are major contributors to water contamination. Although the concentration values in water parameters do not coincide with the current development timeframe of this research, it is assumed that study area retained its fundamental pattern layout since the late 2015. It should be pointed out that the results may not accurately reflect the current water quality status in the northern portion of the Napo River Basin. However, they still provide a valid representation at a regional level of the general trends and patterns throughout this ten-year period. Annual average values accounting for years 2013, 2014 and 2015 are employed for statistical analyses.

Parameter	Units	Testing Method
Barium	mg/L	EPA 6020 A
Boron	mg/L	EPA 6020 A
Copper	mg/L	EPA 6020 A
Coliforms	NMP/100ml	SM 9293 A, B
Apparent Color	Pt-Co	SM 2120 C
Conductivity	μS/cm	EPA 9050 A
Chromium	mg/L	EPA 6020 A
Chemical Oxygen Demand	mg/L	SM 5220 D

Table 5. Water quality parameters subjected to analysis, along with their units andassociated testing method.

Nitrates	mg/L	EPA 300.1
рН		SM 4500 H
Lead	mg/L	EPA 6020 A
Total Dissolved Solids	mg/L	SM 2510 A
Sulfates	mg/L	EPA 300.1
Hydrogen Sulfide as H2S	mg/L	EPA 376.2
Temperature	°C	SM 2550
Turbidity	NTU	HACH 8237

Elaborated by: Wilman Flores

Table 6 shows a compilation of water parameters that consistently appear over the span of the three-year timeframe, between 2013 and 2015. By sorting and filtrating the original database, table below briefly highlights the main parameters influencing the water quality of the Aguarico River Basin. Similarly, this compiled list of physicochemical indicators also aids to identify all the parameters that are present throughout the three years.

Table 6. Physical and che	emical elements encountere	d across vears 2013	. 2014 and 2015.
		a abiobo youro 2010	, 2011 and 2010.

Parameter	Units	Abbreviation
Barium	mg/L	Ва
Boron	mg/L	В
Copper	mg/L	Cu
Coliforms	NMP/100ml	
Apparent Color	Pt-Co	
Conductivity	µS/cm	
Chromium	mg/L	Cr
Chemical Oxygen Demand	mg/L	COD
Nitrates	mg/L	NO3
рН		

Lead	mg/L	Pb
Total Dissolved Solids	mg/L	TDS
Sulfates	mg/L	SO4
Hydrogen Sulfide as H2S	mg/L	
Temperature	°C	
Turbidity	NTU	

Elaborated by: Wilman Flores

In order to evaluate the overall quality of the Aguarico River, water quality index studies were carried out. The WQI classification status used follows the ranking approach found on the KnowYourH2O[™] website, featuring two sections. The "Indoor" section focuses on drinking water for the general public, while the "Outdoor" which focuses on surface water (KnowYourH2O Water Research Center, n.d.). WQI score ranges from 0 to 100 and are classified into three categories: "Good" (70–100), "Medium" (50-69), and "Bad" for scores below 50. This method assigns a higher score to indicate a more desirable status regarding water quality. Table 7 summarize the fifteen parameters considered for subsequent calculations.

Table 7. Parameters considered for the WQI analysis, along with their units and associated abbreviation.

Parameter	Units	Abbreviation
Oxygen Saturation	%	
Fecal Coliforms	NMP/100ml	
рН		
Temperature	°C	
Nitrate	mg/L	NO3
Turbidity	NTU	
Total Dissolved Solids	mg/L	TDS

Alkalinity	mg as CaCO3/L	
Aluminum	mg/L	AI
Dissolved Oxygen	mg/L	DO
Hardness	mg as CaCO3/L	
Iron	mg/L	Fe
Sulfate	mg/L	SO4
Manganese	mg/L	Mn
Total Coliforms	NMP/100ml	

Elaborated by: Wilman Flores

2.3 Data Pretreatment and Screening

The analysis and assessment of water quality parameters in this study involved several stages, starting with data collection and preparation. During this initial phase, some challenges were encountered, such as irregular monitoring campaigns and limited or inconsistent data at some survey locations. Therefore, comprehensive analyses were conducted to address these inaccuracies and verify the authenticity of collected data against regulatory entities. This methodology was anchored in a detailed understanding of water quality, guided by the framework of Ecuadorian regulations and international benchmarks. Specifically, the research involved the comparison of collected water quality data with the standards established by the Servicio Ecuatoriano de Normalización (INEN) for water consumption, the Reglamento Ambiental para las Operaciones Hidrocarburíferas en el Ecuador (RAOHE), and the World Health Organization (WHO) guidelines for drinking water. The aim was to authenticate the collected data against these regulatory guidelines, a process directed to uncovering and rectifying inaccuracies within the dataset. This meticulous verification and correlation process was essential, laying a solid foundation for a thorough comprehension of water quality within both the Ecuadorian and global contexts. Ultimately, this approach enabled an in-depth assessment of the potential health and environmental impacts of water quality, ensuring the study's findings were both reliable and meaningful.

2.4 Data Processing

Upon prior evaluation and sorting process of the dataset supplied by MAATE (Ministerio del Ambiente, Agua y Transición Ecológica), information was arranged into separate Excel spreadsheets files. This technique allowed the creation of matrices and tables containing all the necessary information required to perform an accurate data analysis. These tables encompassed the following fields: sampling date, coordinates and codes for each surveying point, and parameter concentrations. Map crafting and interpolated raster surfaces were possible using ArcMap 10.8, focusing on interpolation techniques over raster layers derived from shape files. First of all, this file format is used on many other GIS software in the intended to store location coordinates and other essential attributes needed for mapping (Ormsby and Feaster, 2004). Similarly, raster surfaces are a type of raster data used to represent continuous phenomena or features across a geographic area. Consists of group of cells or pixels arranged in a grid. Each cell in a raster surface holds a value representing a particular attribute or measurement for that specific location (Johnston et al., 2001). All this information in conjunction provides a highly accurate spatial representation of the river's structure and flow path. Finally, in order to estimate concentration values and distribution for each water parameter along the Aguarico River, deterministic interpolation tools were used.

In this case study, the Inverse Distance Weighted (IDW) technique was employed to estimate concentration values in areas of sparse or insufficient data. As a result, an array of detailed maps was meticulously crafted. Each map offers a comprehensive analysis of the spatial and temporal variability of every parameter encompassed in this study. Concentration levels were then compared to maximum permissible limits, providing an insightful view of the overall health of the Aguarico River. The results are presented into color-coded maps. Red symbolizes parameters that exceeded established limits, thereby indicating potential concern over population and. Green denotes parameter concentrations within acceptable ranges. Finally. white dots represent zones where data was limited or not available at all, requiring further research.

2.5 Map Crafting

Mapping the spatial variability of water parameters in the Aguarico River required the use of Microsoft Excel and GIS ArcMap 10.8 (Esri, Redlands, CA, USA). Each sampling point's global coordinates and location were easily obtained within the dataset upon data validation endeavors. Microsoft Excel played a key role in filtering essential input data regarding concertation values for each physicochemical parameter, which was crucial before running the statistical GIS model. Integration of sampling site locations with water quality data made it possible to render spatial distribution maps. In order to facilitate the layering process in ArcGIS, a diverse range of assets were sourced from multiple digital and governmental platforms. The layers depicting territory extension and boundaries of Ecuador were sourced from Diva GIS repository. Meanwhile, human settlements, natural reserves, primary and secondary rivers layers were obtained from the Sistema National de Información (SNI) webpage. Lastly, layers depicting the layout and distribution of oil blocks and fields in the northern portion of the Amazon basin were rendered using information presented in a scientific article published by Ochoa-Caballero 2021.

All maps presented in this study are intended to provide meaningful insights about the potential risks to human settlements arising from oil and gas exploitation activities. Mapping process involved spatial analysis tools and the creation of buffer zones and interpolated raster surfaces. While the IDW technique was the statistical tool chosen for mapping spatial quality patterns due to personal preferences, Kriging is often used for performing water quality assessments and year-to-year analytical comparisons (Tsihrintzis et al., 1996; Lateef et al., 2020). Finally, to accurately assess potential threats and vulnerabilities of rural communities within the study area, it was necessary to compare permissible limits and concentrations thresholds. This endeavor was accomplished using Ecuador's water quality guidelines, specifically those outlined by RAOHE and INEN. Additionally, comparisons were made with the World Health Organization's general recommendations for water consumption (WHO, 2022).

2.6 Pollution Sources

Household and oil-related activities rest among the primary sources of pollution in the Napo River Basin. Key pollutants, including organic matter, salts, and carcinogenic elements, are discharged directly into freshwater ecosystems, thereby posing a risk to public health and impairing the development of aquatic life (Rivera-Parra et al., 2020; Espinosa et al., 2021). Discharge of household waste into watersheds increases salt concentrations, promoting the proliferation of phytoplankton. This type of algae consumes significant amounts of dissolved oxygen, consequently exerting a detrimental effect over other aquatic organisms (Lateef et al., 2020). Furthermore, oil spills and the widespread use of pesticides and fertilizers in large crop areas are also significant contributors to this phenomenon. The use of both chemical and organic fertilizers over agricultural lands tend to reduce the levels of dissolved oxygen. A situation further exacerbated by the rapid increase of algae populations along the river's flow path (Espinosa et al., 2021; Mayorga and Rivera, 2018). Additionally, hot water discharges can also reduce dissolved oxygen levels in water, adversely affecting freshwater environments (Lateef et al., 2020). Therefore, the lack of adequate treatment for wastewater effluents discharged into rivers in the northern part of the Napo basin constitutes a significant threat to public health and the environment.

2.7 Vulnerability Mapping Assessment

An assessment was conducted to evaluate the vulnerability of human settlements, correlating the distribution of populated areas with the courses of main and secondary rivers. Thus, the spatial association between these rivers, as well as oil fields, was also examined. Recorded data for each water quality parameter served as indicators of land use activities taking place in the nearby areas, comprising practices from adjacent communities, towns, and local oil fields operations. In fact, this study assumes that the interactions between surface waters and both domestic and industrial wastewater assist in the dispersion and mixing of pollutants within the downstream paths of main rivers and tributaries. Furthermore, when analyzing population distribution at key locations, a distinction was made between cities, which typically have higher population densities, and smaller rural villages with fewer inhabitants.

To investigate the relationship between land use and water quality within a specific area, buffer zones encompassing a 200-meter radius are established along the main river and its tributaries. Subsequently, these zones are systematically overlaid onto geographical layers that represent the northern portion of the Napo River Basin. Particular attention was given to certain areas designated for oil production activities. In addition, a layer delineating population distribution at a subdistrict level was employed to further analyze the potential correlation between the average population density and the extent of contamination. For spatial and statistical analysis endeavors, ArcGIS 10.8 was used to ensure precise and accurate map crafting. Although spatial analysis approaches are often a common practice to address risk exposure, metrics based primarily on distance carry inherent limitations. For instance, assuming a uniform dispersion of contamination from the source and neglecting properties of the medium through which it spreads can lead to significant errors regarding pattern distribution. Moreover, establishing buffer distances frequently lacks objectivity and tends to be arbitrary (Espinosa et al., 2021; Maroko, 2012).

3 RESULTS, CONCLUSIONS AND RECOMMENDATIONS

3.1 Water Quality Status of the Aguarico River

Figure 4 shows all the sampled points as well as their corresponding minimum and maximum WQI score for each year in sequence. Scores ranged from 36 to 74. Both the spatial and temporal analysis showed that the water quality values remained relatively steady across the years. However, the vast majority of the surveyed locations exceed the 50 mark, most of them falling within the "medium" category range in terms of water quality. An exception to this pattern occurs at point 6 in 2013 and points 10 and 11 in 2015, where the WQI falls below the 50 mark, denoting a poor water quality. Point 6 exhibits diminished concentrations of oxygen saturation and dissolved oxygen, being 67.5 % and 5.4 mg/l respectively. These levels can be attributed more likely to the relatively high temperatures of the Amazon rain forest. Temperature values peaked at 24.8 °C, potentially decreasing the solubility of oxygen in water bodies (Rajwa-Kuligiewicz et al., 2015). The same effect is present for points 10 and 11 in 2015, with both samples registering oxygen saturation values of 30.3%, dissolved oxygen of 2.4 mg/l and temperature of 25.3 °C.

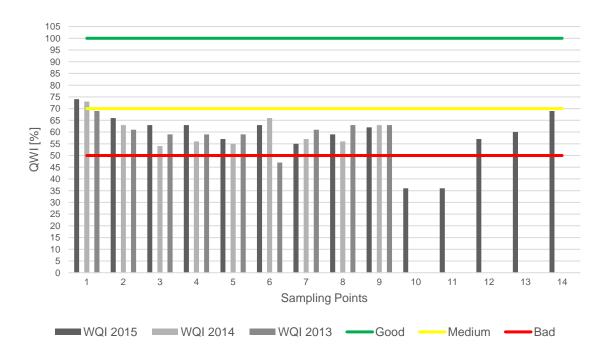


Figure 4. QWI statistics chart of the Aguarico River and its tributaries. Elaborated by: Wilman Flores

Moreover, these points lay within the lower downstream portion de of the river, as shown in the spatial and temporal distribution maps in Figure 5. Substantial sediment accumulation and deposition within the river are key factors influencing the overall quality of freshwater ecosystems. This issue is often linked to the discharge of polluting effluents into water bodies (Shrestha et al., 2023). Buildup of industrial and household waste from nearby areas is likely to worsen the region's existing contamination problem. Furthermore, operations in oil fields and the expansive oil pipeline network across Ecuador contribute to this issue, as pollutants can be carried over and transported downstream the Napo River Basin. Therefore, such average WQI score can be effectively attributed to heavy metals and organic matter runoff as well as a substantial sediment accumulation along the trajectory of main rivers and tributaries (Cabrera et al., 2021; Espinosa et al., 2021; Lateef et al., 2020).

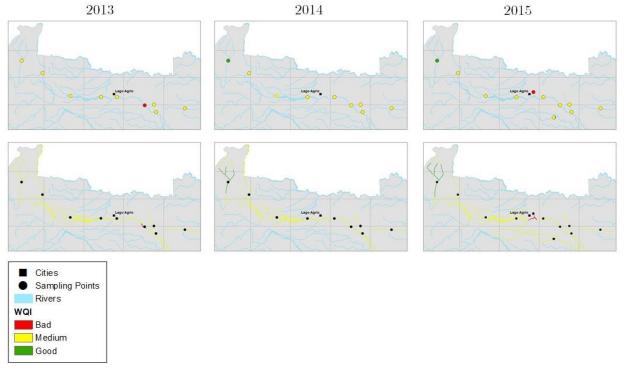


Figure 5. Spatial and temporal distribution of WQI. Elaborated by: Wilman Flores

3.2 Spatial and Temporal Variation in the Concentration of Water Quality Paraments

Generally, results indicate that most of the analyzed parameters fall within the permissible thresholds established by regulatory standards in Ecuador. However, several water quality indicators significantly exceed the maximum recommended limits at every surveying location. Parameters deteriorating the overall water quality include Apparent Color (APHA PtCo), Temperature (°C), Hydrogen Sulfide (mg/l), and Turbidity (NTU). Various characteristics were observed across the three years, along with the dispersion trends of each parameter as shown in Figure 6.

Table 8. Concentrations of the water quality parameters that failed to meet the stablishedquality standards, along with the average during the period of 2013-2015.

Parameter	2013	2014	2015	Average
Apparent Color	179.333	144.222	84.643	136.066
Sulfur as H ₂ S	0.005	0.011	0.007	0.008
Temperature	23.267	21.678	23.264	22.736
Turbidity	96.600	107.333	31.071	78.335

Elaborated by: Wilman Flores

Turbidity levels fluctuated from a minimum of 2 NTU in 2015 to a peak of 338 NTU in 2014, with an average of 78.33 NTU over the three years. High turbidity significantly reduces light penetration in rivers and streams and is associated with a decrease in plant material and fish food organisms, ultimately leading to a decline in fish populations (Lloyd, 1987; Al-Badaii et al., 2013). Additionally, established relationships exist between turbidity and the concentration of suspended solids, often influenced by surface and sediment runoff (Huey and Meyer, 2010; Lloyd et al., 1987). High turbidity levels can be attributed to waste discharges taking place in the nearby area.

Table 9. Minimum recorded concentration values of water quality trends that exceededpermissible limits (2013–2015) in the Aguarico River basin.

Parameter	2013	2014	2015	Average
Apparent Color	97	12	5	136.066

Sulfur as H2S	0.005	0.005	0.006	0.005
Temperature	13.9	13.5	15.9	14.433
Turbidity	15	10	2	9

Elaborated	by:	Wilman	Flores
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In 2013, temperature peaked at 26.7 °C, but dropped significantly to 13.5°C in 2014 averaging 22.7 °C among all three years. Although water temperature itself may not indicate potential pollution, it directly correlates with levels of Dissolved Oxygen (DO), which are indicative of biochemical pollution. Furthermore, lower temperatures inhibit aquatic life activity, resulting in reduced oxygen consumption (Xia et al., 2018; U.S. Geological Survey, 2018).

Table 10. Maximum recorded concentration values of water quality trends that exceededpermissible limits (2013–2015) in the Aguarico River basin.

Parameter	2013	2014	2015	Average
Apparent Color	336	584	171	136.066
Sulfur as H ₂ S	0.005	0.023	0.012	0.013
Temperature	26.7	26.2	25.7	26.200
Turbidity	256	338	73	222.333

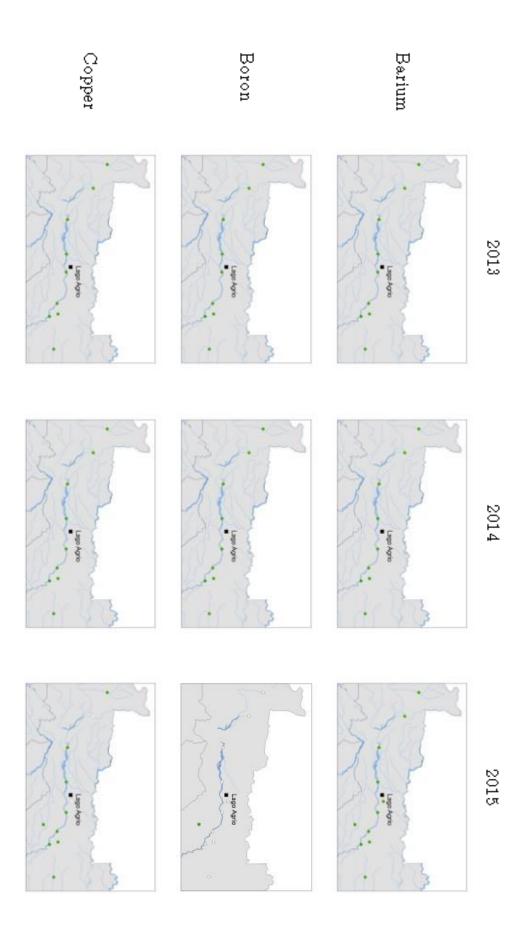
Elaborated by: Wilman Flores

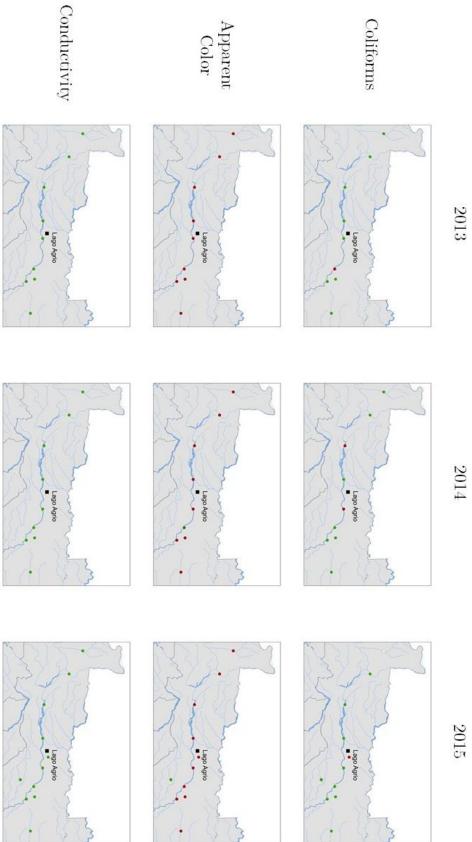
Sulfur as Hydrogen Sulfide (H₂S) concentrations peaked at 0.023 mg/l in 2014, with a lower historical level of 0.005 mg/l observed during 2013 and 2014. This compound is naturally present in crude oil and natural gas and is expected to be found at various stages of oil recovery operations, including drilling locations, producing wells, storage tanks, production facilities, gas plants, sweetening plants, and pipelines (Tarver and Dasgupta, 1997). Furthermore, a significant portion of the emissions appears to end up in the soil, which can then be displaced into nearby rivers and streams. Moreover, strong fluctuations in sulfur levels can also be attributed to seasonal variations in precipitation and sediment discharges (Zaiss, 1996; Tarver and Dasgupta, 1997).

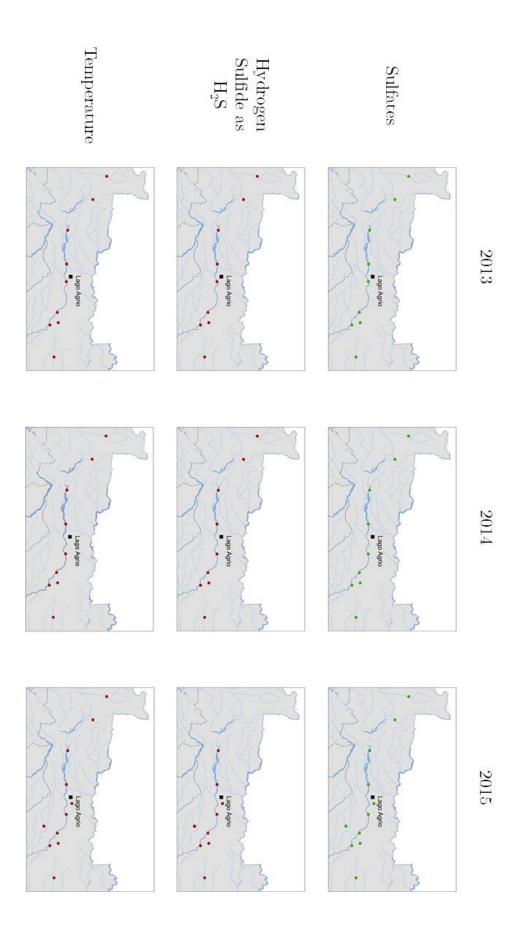
Organic matter decomposition coming from household waste can increase the overall levels of Sulfur in water bodies. This process is carried out by anaerobic bacteria are capable of using sulfate as a terminal electron acceptor during anaerobic respiration, leading to the reduction of Sulfur to Hydrogen Sulfide. This process occurs in environments devoid of oxygen. Additionally, pesticides and fertilizers being used in farmland soils also contribute to this phenomenon (Apriliana et al., 2014; Hernandi et al., 2019).

The minimum recorded Apparent Color value was 5 Pt-Co in 2015, while the maximum reached was 584 Pt-Co in 2014. Mean value was calculated at 136.06 Pt-Co across all three years, which exceeds the maximum allowable threshold for water quality standards. The increasing values are commonly associated to elevated concentrations of suspended particles (> 1.2μ m), which are closely associated with turbidity. Additionally, the presence of humic acids and biofilm can contribute to changes in water color (Santana et al., 2021).

Spatial and temporal variations in water quality parameters are also influenced by the geographical position of the sampling locations. For instance, concentration values are generally higher in areas within oil blocks and near oil fields. Moreover, higher elevation sites tend to show lower contamination levels, while downstream areas characterized by greater depth tend to exhibit a slight decrease in these values (Zhou et al., 2020).









Cities

Secondary rivers Main rivers 0

Exceeds the limit

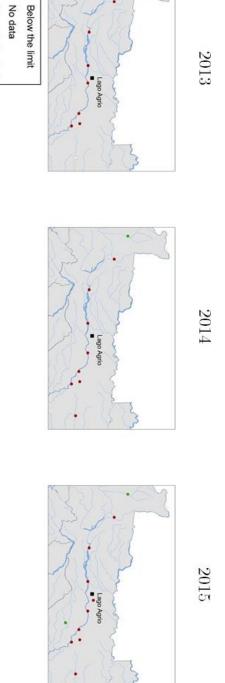


Figure 6. Spatial and temporal distribution of sampled points along the Aguarico River that exceed or fall below the regulatory criteria. Elaborated by: Wilman Flores

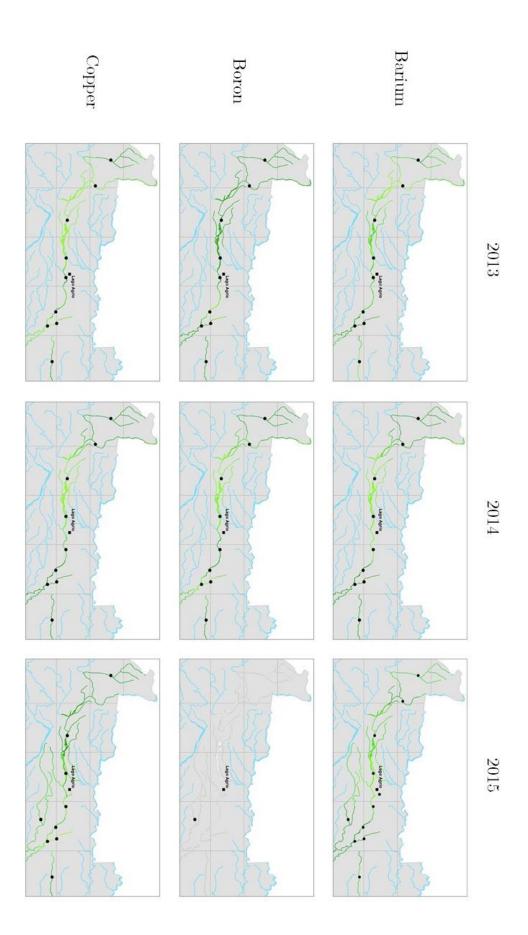
3.3 Toxicity assessment of water quality parameters

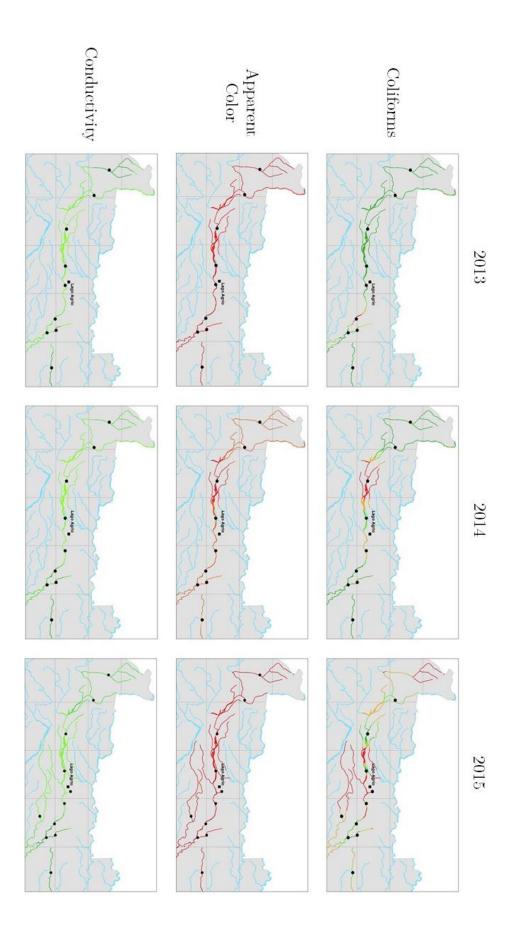
While assessing the potential health impacts of water paraments and their concentrations, only Chromium (Cr) have been identified as a carcinogen source accordingly to the World Health Organization in 2022 (WHO, 2022). Chemical elements such as Magnesium (Mg), Calcium (Ca) or Chloride (Cl) were not taken into consideration while assessing the overall water quality of the river due to insufficient information and data necessary for accurate calculations. Salts derived from presence of these chemical elements is not considered as a potential carcinogen source. Although, high concentrations have detrimental effects on biological processes of plants, algae and some bacteria. These effects primarily manifest as disruptions to cellular osmotic balance, interference with ion regulation mechanisms, and perturbations in metabolic pathways (Parida and Das, 2005). Furthermore, low values in water salinity are directly associated with high concentrations of Hydrogen Sulfide (H₂S), jeopardizing the growth of living organisms in freshwater ecosystems (Neff, 2002). This trend is reflected in Figure 6 and Figure 7. Sulfur as Hydrogen Sulfide (H₂S) concentrations of have consistently surpassed prescribed during the three-year timeframe, exceeding threshold values established by RAOHE and WHO (WHO, 2022; RAOHE, 2001.

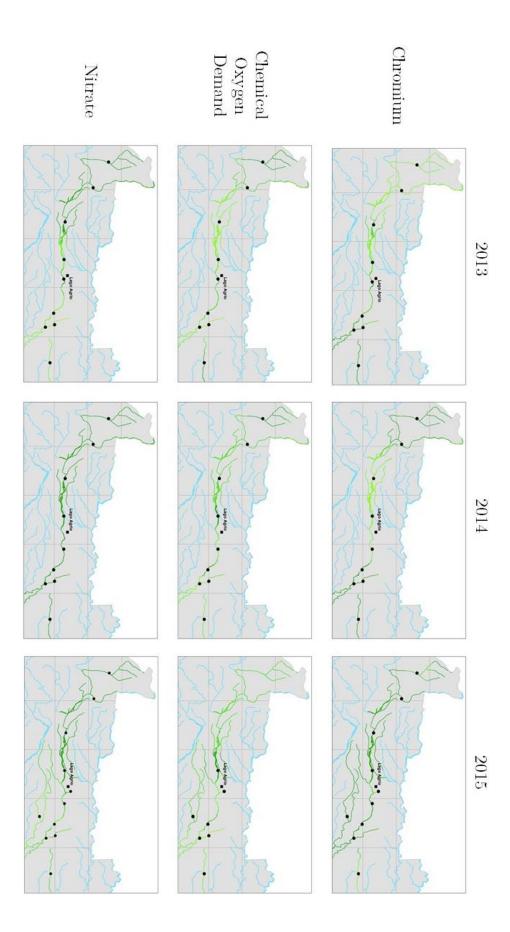
Distribution maps in Figures 6 and Figure 7 shown that Apparent Color does not meet the desirable standards according to INEN (Servicio Ecuatoriano de Normalización INEN, 2020). High values in this particular parameter are linked to decomposed organic matter such as vegetation and inorganic substances, raising aesthetic concerns, rather than health related issues. Although high Apparent Color (Pt-Co) concentrations not necessarily indicate health concerns, it influences visual and taste appeal of water (Santana et al., 2021; Omer, 2019).

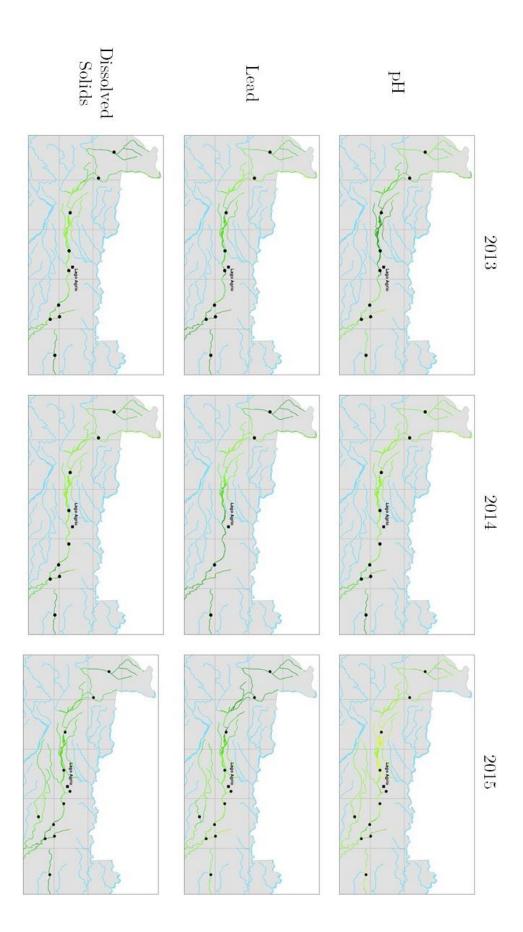
Regarding Temperature, results for shown a similar behavior, with values averaging 22.73 ^oC throughout the three-year period, way above the regulatory baseline (RAOHE, 2001; INEN, 2020). High temperatures significantly modify water chemistry, influencing biological activity and growth in aquatic ecosystems. In higher temperatures, water tends to dissolve more minerals from rocks, which results in greater electrical conductivity. Furthermore, low temperature water is more capable of retaining dissolved gases, such as oxygen. This is a crucial aspect since warmer water has a lower capacity for dissolved oxygen compared to cooler water, potentially leading to insufficient oxygen levels for the survival of aquatic species (U.S. Geological Survey, 2018; Xia et al., 2018; Santana et al., 2021).

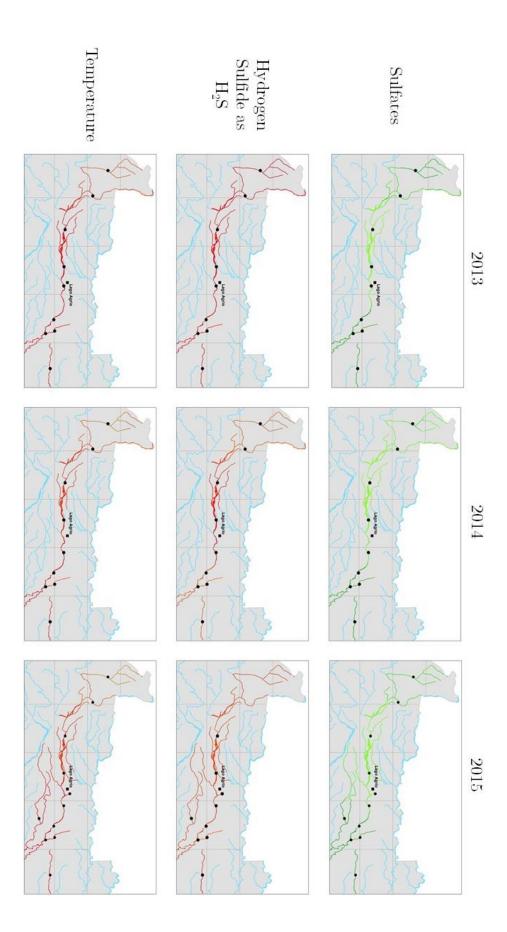
Lastly, Turbidity (NTU) concentrations in this study were higher than the permissible limit throughout the three years averaging 78.33 NTU. Comparing the data to governmental guidelines, almost all points assessed have consternations higher than the 5 NTU (Servicio Ecuatoriano de Normalización INEN, 2020). Elevated levels of turbidity can indicate the presence of contaminants and pollutants in the water, which may pose health risks to both humans and aquatic life. High values are particularly attributed to the presentence of suspended solids such as silt, plankton, clay, organic materials and a wide range of microorganism. Although Turbidity itself is not necessarily harmful, it can serve as an indicator of potential water quality issues and associated health risks in rivers and streams (Meyer, 2010; Lloyd et al., 1987; Al-Badaii et al., 2013).









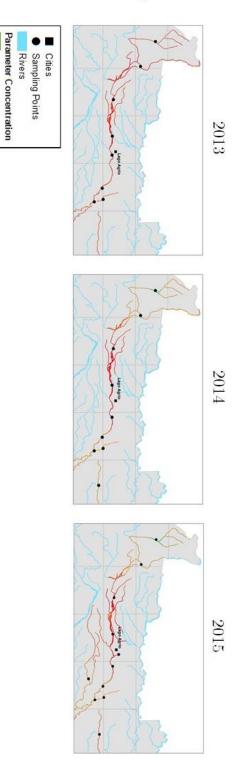


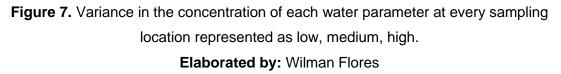


Low Medium High

None

Very High





Numerous chemical elements are recognized for their tendency to bioaccumulate, including Mercury (Hg), Lead (Pb), Cadmium (Cd), Arsenic (As), Dioxins, among the others (Mackay and Fraser, 2000). In this regard, bioaccumulation is defined as the process in which certain chemical elements or compounds are absorbed and accumulated by an organism faster than they can be metabolized or eliminated. Lead (Pb) is the only chemical element identified in this study able to bioaccumulate through food chains, however its concentrations remain below the permissible limit to be regarded as a potential threat to human health (Ochoa and Rivera, 2021). Despite the presence of other elements such as Sulfates and Sulfur as Hydrogen Sulfide (H₂S) covered in this study, there is a lack of substantial evidence to corroborate their magnification within natural ecosystems. Furthermore, there is still a scarcity of epidemiological data regarding the adverse effects of prolonged exposure to H₂S. Prior the 1990s, the prevailing belief was that prolonged exposure to H₂S did not pose a significant health risk unless it led to death (Ochoa and Rivera, 2021; Kennesary, 2017; Rivera-Parra, 2020).

3.4 Vulnerability of Human Populations

One of the main concerns regarding oil operation activities in the Amazon Region is the immense amount of biodiversity vulnerable to environmental threats and hazards. A sizeable portion of the study area is located within natural reserves and protected zones, which harbor a wide variety of species as well as indigenous communities and towns. Unfortunately, as indicated in Figure 8, flow course of the Aguarico River revelas that numerous towns and rural communities could be impacted by the aggressive expansion of the Ecuadorean oil industry. Consequently, any toxic or industrial waste directly discharged into rivers can significantly compromise a large portion of freshwater ecosystems located within the Amazon rainforest (Lessmann et al., 2016). Furthermore, the absence of essential infrastructure and financial resources exacerbates the challenges regarding wastewater management as well as and oil spills and leaks (Ochoa and Rivera, 2021; Mayorga and Rivera, 2018). Addressing these deficiencies is imperative to preserve the ecological integrity these aquatic environments against the detrimental effects of oil related pollution. Only Infrastructure investments as well as the adequate allocation of financial resources can prevent environmental catastrophes ensuring the ecological welfare of the Aguarico River Basin (Espinosa et al., 2021; Lessmann et al., 2016).



Figure 8. WQI distribution patterns show overlapping with several populated areas and towns all distributed along the course of the Aguarico River. Elaborated by: Wilman Flores

The Aguarico River passes through Blocks 56 and 57 before reaching the Cuyabeno Natural Reserve. This reserve harbors many aboriginal settlements from various indigenous tribes, including the Siona, Ai Cofan, Secoya, Shuar, and Quichua (Rivera-Parra et al., 2020). Moreover, Aguarico River mainstream crosses Lago Agrio, the principal city of Sucumbios province. Therefore, a significant concern arises regarding formation water being discharged by nearby oil fields, which are known for their production of formation water with relatively high concentrations of dissolved salts (Ochoa and Rivera, 2021). Thus, potentially jeopardizing a substantial portion of the surrounding communities and natural reserves. Another river that could have a detrimental impact to human settlements is the one that crosses Block 61, known for producing formation water with moderate salinity concentrations (Ochoa and Rivera, 2021). This river then flows into Yasuni National Park. Characterized for its rich natural biodiversity. Yasuni National Park harbors the Waorani indigenous people and so many others isolated groups, predominantly the Tagaeri and Taromenane (Lessmann et al., 2016). Findings reveal that numerous river networks, which extend across the entire Amazon rainforest, are likely contaminated to some degree. This interconnection results in potential risks extending far beyond operational zones, affecting vast areas throughout the region.

Although current policies declared by national authorities regarding the cease of all operational activities in Block 43 ITT, it is anticipated that significant advancement and expansion will occur in the near future (France24, 2023). Therefore, it is further advised to implement management strategies specifically designed to effectively address any potential environmental risks in the region. Studies should encompass oil blocks extending beyond the current study area by conducting comprehensive regional studies in a regular basis. This may have a positive overall impact, especially on the whole Napo River basin.

3.5 Discussion and Final Thoughts

Results presented in this study clearly indicate that some of the water quality parameters have highly elevated concentrations. Parameters such as Apparent Color (Pt-Co), Temperature (°C), Hydrogen Sulfide (mg/l) and Turbidity (NTU) are regarded as the main water quality indicators negatively impacting the overall quality of water within the Aguarico River Basin. Fortunately, the health risks associated to high levels of carcinogenic agents are insignificant compared to the risks associated with non-carcinogenic elements. Also, results also align with those reported on previous researches, showing that higher elevation sites tend to have lower concentration values. Similarly, points downstream with greater quality conditions compromise a significant portion of communities and settlements located along the Aguarico River Basin to a moderate risk of contamination. Based on the overall water quality of the Aguarico River, it is not advisable to consider it as a freshwater source intended for consumption, as several water quality indicators exceed permissible limits.

Moreover, regarding the information provided by governmental entities, the dataset used for statistical analysis contains certain locations lacking reliable information. Therefore, employing data filling methods to address the lack metrics is not advisable. Trying to standardize the information to a single value could lead distorted results, thus resulting in a misrepresentation of the authentic behavior and patterns in water quality (Mina, 2019). This situation makes it more challenging to address the lack of essential data required to perform interpolations, particularly the deficiency in data related to Boron concentrations in the year 2015. Such type of anthropogenic-induced stressor is most certainly linked to industrial activities rather than wastewater effluents coming from small towns or isolated homes in the middle of the jungle.

3.6 Conclusions

A comprehensive spatial analysis was performed on a segment of the Napo River basin, specifically the Aguarico River and its tributaries. In addition, spatial distribution maps using the IDW technique were meticulously crafted to analyze concertation levels for each parameter along river's path, thus aiding in the evaluation of potential health impacts over downstream towns and villages. This analysis involved the assessment of sixteen water parameters at fixed survey locations. Main conclusions were as follows:

- 1) In the Aguarico River basin, both temporal and spatial trends in water quality parameters and their concentration levels are primarily influenced by anthropogenic factors, including industrial, farmland, and domestic activities, as well as the varying geomorphological altitudes along main and secondary streams which originate from the Pimampiro mountain range. Notable differences in water quality and pollution types were observed between the main river and its tributaries. Generally, concentration values for any physicochemical indicator exhibit a slight decrease as the distance between sampling points increases. Almost all analyzed parameters stayed within the regulatory standard limits established for the discharge of effluents.
- 2) The expansion of oil-related infrastructure in the Amazon rainforest has led to oil activities becoming the predominant source of pollution affecting water quality in the region. This impact is reflected by high concentrations levels of Apparent Color (Pt-Co), Temperature (°C), Sulfur as Hydrogen Sulfide (mg/I), and Turbidity (NTU).
- 3) Results from the Water Quality Index (WQI) show that while the overall water quality index value was relatively low across the three-year period, it remained within the medium range. Although, some individual locations typically fluctuated between marginal and fair, with slight variations. Therefore, sampling points in areas with more industrial development particularly require further investigation regarding wastewater discharges into the environment. As a matter of fact, oil blocks 56 and 57 generate substantial volumes of formation water characterized by elevated concentrations of Salts and Barium (Ba).
- 4) The Aguarico River, coursing through the Cuyabeno Natural Reserve, serves as a predominant freshwater source for indigenous communities and a wide variety of species. Therefore, direct discharge of waste water resulting from oil exploitation and household affairs have significantly impacted riverine villages and towns. Such stressors had led to alterations in water quality and disruptions to local ecosystems.

This highlights the urgent need for comprehensive strategies to mitigate adverse effects of industrial activities over freshwater ecosystems.

Overall water quality of the Aguarico River Basin has been categorized as "medium" according to the Water Quality Index (WQI) ranking. Additionally, the majority of measured parameters exhibited a normal trend in terms of spatial variability, indicating consistent water quality across different locations. Among all water parameters subjected to the analysis, Barium (mg/l), Boron (mg/l), Copper (mg/l), Conductivity (µs/cm), Chromium (mg/l), COD (mg/l), Nitrate (mg/l), pH, Lead (mg/l), Dissolved Solids (mg/l) and Sulfates (mg/l) meet the water quality criteria across the three years span in all sampling locations. However, the parameters that did not exhibit this normal tendency and therefore do not meet the water quality target after further examination were Apparent Color (Pt-Co), Temperature (°C), Hydrogen Sulfide (mg/l) and Turbidity (NTU). Such parameters exhibit high variation in their concentration ranges, ranking way above the permissible limits established by RAOHE and INEN guidelines. In the case of Coliforms, its behavior can be attributed to the fact that the river flows through main rural areas and villages. The average score stands at 59.67 points across the three-year span period. According to this assessment, the water quality in the study area is categorized as 'medium,' indicating a certain level of pollution stemming from both domestic and industrial sources throughout the river and its tributaries.

3.7 Recommendations

Over the past several decades, the Ecuadorian Amazon Basin has withstood numerous drawbacks due extensive activities involving oil resources exploitation. In fact, the Aguarico River Basin has been affected by numerous oil spill incidents, thereby leaving a large portion of the population vulnerable to health-related issues. This situation renders these water sources vulnerable to the ongoing environmental degradation, condition further exacerbated by inadequate monitoring and a lack of management capacity.

While water bodies might remain suitable for irrigation purposes and wildlife development, extensive treatment prior domestic use as well as a revamped legal framework is advised. Therefore, in order to further improve management of freshwater ecosystems within the Aguarico River basin, several recommendations are proposed such as.

 Implementation of a more comprehensive law, as well as the reinforcement of the already existing water legislation encompassed in the Ecuadorean constitution.
 While the regulatory guidelines cited in this study offer valuable insights into the current criteria regarding wastewater discharge management, it is recommended that RAOHE procedures should be redesigned in order to better align with current international standards. This would ensure a more robust and consistent approach regarding environmental conservation and human welfare.

- 2) Frequency of survey campaigns intended to acquire accurate insights into water quality status should be increased. This endeavor is imperative to gain a comprehensive understanding and differentiation of the Napo River Basin as a whole. In fact, this study involved the analysis of water samples that were collected only once in a year for each surveying point, thus limiting the ability to conduct thorough examination of the Aguarico River basin.
- 3) Governmental entities should be advised to establish a validated and up to date water quality database for proper information management and accessibility. This will further improve decision-making and problem-solving decisions. Moreover, public administrations responsible of conducting water quality analysis should perform periodic surveying campaigns across the country.

These recommendations aim to mitigate the adverse effects of oil industry activities on water quality and promote sustainable management of freshwater ecosystems in the Amazon rainforest. Finally, findings published in this study can further assist governmental authorities into identifying areas prone to pollution hazards, thereby promoting the development of pollution prevention initiatives.

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5 APPENDIXES

2

6

7

0.00034

0.00041

0.00052

7.2E-05

0.0132

0.0132

0.1

0.022

0.036

0.0132

0.00013

0.00013

рН	Сог	nductividad us/cm	Solide disuel mg/	tos	Col apare API PtC	ente HA		bidez TU	Fluorur mg/l	D	Nitrato mg/l	Niti m			atos g/l	sul hid	ulfuro como lfuro de Irógeno mg/l	Coliformes Fecales NMP/100ml
7.2		19.97	10		97	7	3	35	0.1		0.15	0.0	03	0.	76	(0.005	40
7.4		42.1	21		28	6	2	56	0.12		0.16	0.0	02	1	.8	(0.005	230
7.8		77	42		15	9	1	14	0.07		0.23	0.0	02		.5	(0.005	150
8.1		80	44		33			71	0.06		0.62	0.0	02		.8	(0.005	90
7.8		78.4	41.9		10			4.8	0.13		0.22	0.0			.6	(0.005	230
6.6		40.3	20.1		21	9	8	38	0.13		0.62	0.0	02	0.	19	(0.005	4600
6.6		13.55	7.1		16	8		/D	0.11		0.7	0.0	02	0.	21	(0.005	230
6.6		21	12		12			15	0.04		0.77	0.0		0.	49	(0.005	230
7.5		50	27		11	8	1	9	0.05		0.76	0.0	02	0.	52	(0.005	750
Deman Quimica Oxigeno	de	Arsénico mg/l	Bario mg/l		oro ng/l	Cad m	mio g/l	Cobr mg/			Mercu mg/		Niq mg		Plon mg/		Vanadic mg/l	°C
2		0.00063	0.042	0.0	0132	0.00	0006	0.006	61 0.0 ⁻	12	0.000	06	0.00	055	0.00	18	0.004	13.9
5		0.0021	0.13	0.0	0132	0.00	0006	0.01	7 0.0	12	0.000	06	0.00	068	0.00)4	0.027	17.9
8		0.0012	0.067	0.0	0132	0.00	0006	0.01	6 0.00	62	0.000	06	0.00	017	0.002	21	0.014	26.3
7		0.0014	0.082	0.0	0132	0.00	0006	0.01	6 0.00	79	0.000	06	0.00	016	0.002	24	0.019	25.2
4		0.0012	0.054	0.0	0132	0.00	013	0.007	7 0.00	33	0.000	06	0.00	066	0.00	15	0.0099	25.3
4		0.0013	0.066	0.	095	0.00	015	0.00	8 0.00	54	0.000	15	0.00	165	0.002	24	0.016	24.8

APPENDIX I. Water quality parameters in 2013

0.0066

0.012

0.015

0.0021

0.0038

0.00098

0.00006

0.00006

0.00007

0.0016

0.0044

0.00066

0.00075

0.00086

0.00085

0.0038

0.0033

0.0036

25

24.3

26.7

рН	Conductividad us/cm	Temperatura °C	Solidos disueltos mg/l	Color aparente APHA PtCo	Turbidez NTU	Nitrato mg/l	Nitrito mg/l	Sulfatos mg/l	Sulfuro como sulfuro de hidrogeno mg/l
7.8	34	15.4	18	32	1	0.18	0.02	2.1	0.005
7.8	50	20	27	74	51	0.33	0.02	2.5	0.007
8.1	73	22	40	584	260	0.4	0.02	4.1	0.017
7.9	71	22.6	39	189	263	0.41	0.02	4.1	0.023
8	71	24.3	39	274	338	0.36	0.02	3.1	0.021
7.2	23	25.2	13	12	10	0.68	0.08	0.24	0.005
6.1	8.5	25.9	4.7	15	14	0.72	0.08	0.33	0.005
6.4	14	13.5	7.4	64	11	0.4	0.02	0.83	0.007
6.8	34	26.2	19	54	18	0.46	0.02	0.41	0.009

Coliformes Fecales NMP/100ml	Demanda Quimica de Oxigeno mg/l	Bario mg/l	Boro mg/l	Cadmio mg/l	Cobre mg/l	Cromo mg/l	Mercurio mg/l	Niquel mg/l	Plomo mg/l	Selenio mg/l
40	5	0.021	0.0066	0.0002	0.0016	0.00007	0.00003	<0,00033	<0,00017	<0,00033
230	8	0.052	0.081	0.00015	0.013	0.0041	0.00015	<0,00165	0.0025	<0,00165
2400	9	0.15	0.28	0.00018	0.055	0.018	0.00015	0.009	N/D	0.007
930	5	0.15	0.18	0.00015	0.046	0.019	0.00015	0.0099	N/D	0.0069
1500	11	0.18	0.033	0.00017	0.023	0.02	<0,00015	0.0094	N/D	0.0071
230	3	0.016	0.0066	0.00003	0.0016	0.00007	<0,0003	<0,00033	<0,00017	<0,00033
230	11	0.016	0.0066	0.00013	0.0016	0.00013	<0,00003	0.00052	<0,00017	<0,00033
150	8	0.021	0.21	0.00015	0.014	0.00068	<0,00015	<0,00165	N/D	0.00088
90	15	0.031	0.17	0.00015	0.014	0.001	<0,00015	<0,00165	N/D	0.0027

рН	Conductividad us/cm	Temperatura °C	Solidos disueltos mg/l	Color aparente APHA PtCo	Turbidez NTU	Nitrato mg/l	Sulfatos mg/l	Sulfuro como sulfuro de hidrogeno mg/l
7.6	44	15.9	24	20	3	0.1	2.8	N/D
7.8	68	20.6	38	41	7	0.23	3.2	N/D
8.1	82	22.5	45	68	56	0.42	6.1	0.006
8.1	85	20.5	47	104	58	0.33	4.2	0.007
8.3	88	21.1	48	103	73	0.49	3.8	0.006
7.4	25	25.4	14	83	16	1.1	0.37	0.007
8.1	10	24.4	5.8	171	46	1	0.32	0.012
7.1	15	24.1	8.3	113	15	0.39	0.36	0.007
7.8	25	25.7	14	110	20	0.56	0.4	0.007
7.4	144	25.3	79	85	52	0.47	6.3	0.007
7.4	144	25.3	79	85	52	0.47	6.3	0.007
8	87	24.9	115	118	21	1.9	0.8	N/D
7.9	88	24.9	77	79	14	1.7	0.69	0.007
7.9	103	25.1	57	5	2	1.8	0.7	N/D

APPENDIX III. Water quality parameters in 2015

Coliformes Fecales NMP/100ml	Demanda Quimica de Oxigeno mg/l	Bario mg/l	Boro mg/l	Cobre mg/l	Cromo mg/l	Plomo mg/l
N/D	N/D	0.026	N/D	0.01	0.0005	0.00064
750	N/D	0.023	N/D	N/D	0.00042	0.00035
40	N/D	0.031	N/D	0.0029	0.00016	0.00069
40	5	0.04	N/D	0.04	0.00032	0.0012
430	N/D	0.039	N/D	0.064	0.0003	0.0013
230	7	0.02	N/D	0.054	0.00019	0.0015
930	13	0.027	N/D	0.0069	0.0016	0.0014
230	15	0.021	N/D	0.11	N/D	0.0017
430	14	0.023	N/D	0.06	0.0001	0.0018
24000	17	0.056	N/D	N/D	0.00081	0.0016
24000	17	0.056	N/D	N/D	0.00081	0.0016
1500	11	0.025	N/D	0.04	0.00021	0.00058
930	14	0.019	0.009	0.052	0.00015	0.0015
N/D	4	0.014	N/D	0.0039	N/D	0.00051