

Article

Diagnosis of Nutrient Discharges and Management Alternatives in Developing Countries and the Use of Microalgae as a Potential Solution: A Case Study from Different Provinces in Antioquia, Colombia

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Abstract: This research aims to propose management strategies to mitigate eutrophication caused by inefficient wastewater treatment plants in Colombia. The information analyzed was provided by environmental authorities such as IDEAM, CORANTIOQUIA, and CORNARE in Antioquia, where the average concentrations of phosphorus in wastewater from municipal, livestock, and industrial activities are 5.1, 30.6, and 29.1 mg P/L. The total nitrogen concentrations are 77, 143, and 121 mg N/L, respectively, surpassing the limit concentrations stated by the European Union, the United States, and Mexico, among others, while Colombia has not established its own limits. Including limitations for nutrient concentrations will align Colombia with the 2050 Sustainable Development Goals (SDGs), where microalgae species like *Chlorella* or *Scenedesmus* could be used in wastewater treatment systems for municipalities and industries. These microalgae can capture organic matter, nutrients, and greenhouse emissions and reduce the concentrations observed in natural water. They could also be an alternative for capturing heavy metals and some pollutants of emerging concern. In addition to the ecological and social benefits, the algal biomass could be valorized by transforming it into biological products such as fuels, fertilizers, and pigments when micropollutants are not present, reducing operational costs for treatment systems.

Keywords: wastewater; microalgae; biofertilizers; eutrophication; nutrients



Citation: Pérez Mesa, A.; Saldarriaga Molina, J.C.; Ríos, L.A.; Ocampo Echeverri, E.; Ocampo Echeverri, D. Diagnosis of Nutrient Discharges and Management Alternatives in Developing Countries and the Use of Microalgae as a Potential Solution: A Case Study from Different Provinces in Antioquia, Colombia. *Water* **2024**, *16*, 2215. <https://doi.org/10.3390/w16162215>

Academic Editor: Alejandro Alvarado-Lassman, Carlos Velasco-Santos and Juan Manuel Méndez-Contreras

Received: 13 June 2024
Revised: 2 July 2024
Accepted: 8 July 2024
Published: 6 August 2024



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1. Introduction

Currently, there is a significant issue with increasing pollutants, such as carbon, nitrogen, phosphorus, heavy metals, pesticides, herbicides, drugs, and others, in natural water sources. These pollutants are primarily caused by untreated wastewater effluents, the composition of which varies based on domestic and industrial activities across different communities and territories [1]. Nitrogen and phosphorus promote eutrophication in natural water, while heavy metals, pesticides, and herbicides negatively affect cellular growth, metabolism, and DNA replication. Emerging contaminants, such as pharmaceuticals and polyfluoroalkyl substances (PFASs), pose threats that are yet to be fully understood, endangering both aquatic and terrestrial ecosystems and having profound impacts on human health [2] and economic systems, including an increase in the operational costs for water use [3].

Global efforts to mitigate these issues caused by untreated wastewater effluents have been substantial. Researchers and countries have developed novel treatment systems, such

as membrane bioreactors (MBRs), rotational biological disks, ultrafiltration, and photo-Fenton reactors, to improve nitrogen and phosphorus capture. Different configurations for secondary treatments, such as the BARDENPHO system, and practices like irrigating wastewater effluents onto croplands have also been explored [4,5]. Furthermore, there has been a push for policy implementations aimed at restricting the presence and concentration of pollutants, thereby encouraging improvements in wastewater treatment technologies.

In developing countries like Colombia, wastewater treatment plants (WWTPs) predominantly employ screening and decanting processes combined with anaerobic or aerobic biological treatments, with limited use of tertiary treatment systems beyond basic disinfection methods such as chlorination or UV treatment, as indicated in the National Water Study. The average efficiency for the removal of chemical and biochemical oxygen demand (COD, BOD) is 60%, while nutrients are 17% and 2% for municipal and industrial wastewater, respectively [6]. Recent efforts to control water pollution, such as Resolution 1256, promote wastewater reuse in industries, although implementation remains limited [7]. However, the regulations concerning nutrient concentrations are inadequately defined under Resolution 0631 from 2015, where no concentration limits are clearly established [8], and requirements for other pollutants such as PFASs and drugs are not included. This regulatory gap has contributed to eutrophication in lakes and reservoirs across Colombia, including La Fe, Rio Grande I and II, and Porce I and II in Antioquia [9], as well as El Quimbo in Huila [10], while the effects of other pollutants are yet to be determined.

The unregulated discharge of nutrients into water sources in Colombia, which has significant impacts on public health and the economy, underscores the urgent need to advance scientific knowledge in wastewater treatment systems. There is a particular interest in microalgae-based reactors, where research has yielded promising results at the laboratory, pilot plant, and industrial scales, not only for nutrient removal but also for capturing heavy metals, pharmaceuticals, and pesticides. For instance, countries like Mexico, Taiwan, and the United States have achieved nutrient removal rates approaching 90% [11]. This underscores their potential as sustainable solutions for mitigating nutrient pollution in water bodies and allows for leveraging wastewater effluents to replace microalgae's nutritional requirements, which currently represent significant operational costs in producing bioproducts such as biofuels or biofertilizers.

This study aims to introduce management alternatives using microalgae-based wastewater treatment systems to reduce nutrient concentrations and prevent the eutrophication of ecosystems. It details the concentrations of nitrogen and phosphorus in natural water and compares nutrient and organic matter concentrations in wastewater effluents in Antioquia against wastewater regulations from other countries. Finally, a projection for 2050 is performed based on historical removal efficiencies in WWTPs in Colombia and theoretical efficiencies for wastewater plants if they were adapted to nutrient removal using microalgae-based systems, incentivized by the inclusion of a regulatory framework for nutrients.

This effort aligns with global sustainability goals, particularly Sustainable Development Goals 6 (Clean Water and Sanitation) and 12 (Responsible Consumption and Production), as well as national policy directives like CONPES 4088 [12], thereby contributing to the preservation and improvement of water quality in Colombia and beyond.

2. Materials and Methods

This research is divided into three clear sections: first, the research and compilation of information associated with wastewater treatment systems that use microalgae as a tertiary treatment system; second, an analysis of secondary information provided by environmental corporations in Antioquia, including a comparison of nutrient concentrations in natural water and wastewater with norms from other countries; and finally, a future perspective for 2050.

2.1. Scope of Technologies

Bibliometric research related to microalgae-based wastewater treatment systems was conducted according to the topics described in Table 1, where records of publications were identified and analyzed to establish which countries and authors have conducted more research on the topic. From this information, the types of microalgae and wastewater employed, as well as the removal yields for the pollutants of interest, were extracted. This information enabled the identification of which microalgae could be used based on the type of wastewater and the pollutant of interest.

Table 1. Bibliographic search criteria.

Search Criteria	Limitations	Date Ranges
"Wastewater" + "Tertiary Treatment" + "Microalgae".	Matches: All/Publication status: Completed/Type of Document: Articles, Review, book chapters/Subject: Environmental sciences/All Open Access Scopus database.	2002–2022

Note: Cutoff date—31 December 2022.

From the collected information, at least the 10 most relevant countries, arranged by the number of research studies, were selected to compare their environmental regulations concerning nutrient concentrations in wastewater effluents with the pollutant concentrations in wastewater in Antioquia. This comparison helped visualize the actual status of wastewater effluents.

2.2. Pollutant Analysis for Municipalities in Antioquia

During this stage of the study, we analyzed and selected information provided by autonomous environmental corporations in Antioquia, one of the most productive regions in Colombia, regarding water bodies and wastewater effluents. The parameters studied in water sources were selected to identify pollution associated with eutrophicated ecosystems. The chemical oxygen demand (COD), biochemical oxygen demand (BOD), and dissolved oxygen saturation (%OD) provide information about the presence of organic matter and the water quality references, whereas nitrates (NO_3^-), ammonia (NH_3^+), and phosphorus (P) are indicators of eutrophication. The statistical analysis performed for this information was organized by municipality to examine the current distribution of pollutant concentrations across municipalities, categorized by quantiles, and presented on the map of Antioquia for each variable.

Wastewater effluent reports were classified into four main groups based on economic activity: domestic users (Dom), livestock (LS), mining (MN), and various industrial users, where specific activity information that was unavailable was merged as non-classified non-domestic wastewater (ARnD_NC). Initially, statistical parameters such as minimum and maximum values, mean, median, and quantiles were calculated to show the distribution and variability of the information for each group. Finally, a Spearman correlation matrix was calculated to investigate the relationship and variability of pollutants among different activities and how they are related to nutrients.

2.3. Forecast for Current Pollutant Discharges in Antioquia

The mean pollutant concentrations for the category DOM calculated in 1.2 were compared with the environmental regulations for COD, BOD, total nitrogen, and total phosphorus from Colombia and the countries with the most scientific research found in 1.1. From this information, we expected to highlight the necessity of updated environmental norms for nitrogen and phosphorus effluents.

Finally, a projection for 2050 for theoretical removal efficiencies in Colombia for COD, BOD, total nitrogen, solids, and phosphorus, with the inclusion of a regulatory framework for nutrients, was realized. To achieve this, historical information was collected about the

use of wastewater technologies in Colombia, the coverage in the country, and pollutant removal yields reported from 2000 to 2022. In the end, assuming that microalgae-based technologies were implemented nationwide by 2050, as expected by IDEAM's wastewater treatment coverage goals, the maximum achievable efficiencies were contrasted with the assumption that the most efficient current technologies employed in Colombia were installed and fully operational nationwide. This comparison highlights the maximum efficiencies achievable by current technologies versus microalgae-based wastewater treatment systems.

3. Results and Analysis

3.1. Scope of Microalgae-Based Technologies

By applying the methodology described in Section 2.1, it was determined that research studies using microalgae in WWTPs have shown a significant increase in the last 10 years. Figure 1 illustrates that Spain (13.92%), the United States (8.58%), China (7.66%), and India (7.42%) are the countries with the highest research activity. Research on microalgae according to the search criteria has primarily been conducted in countries in Europe, Asia, and North America, with limited studies from South America. Brazil has been the main contributor with 16 publications, while Colombia has contributed only 3 out of a total of 431 publications.

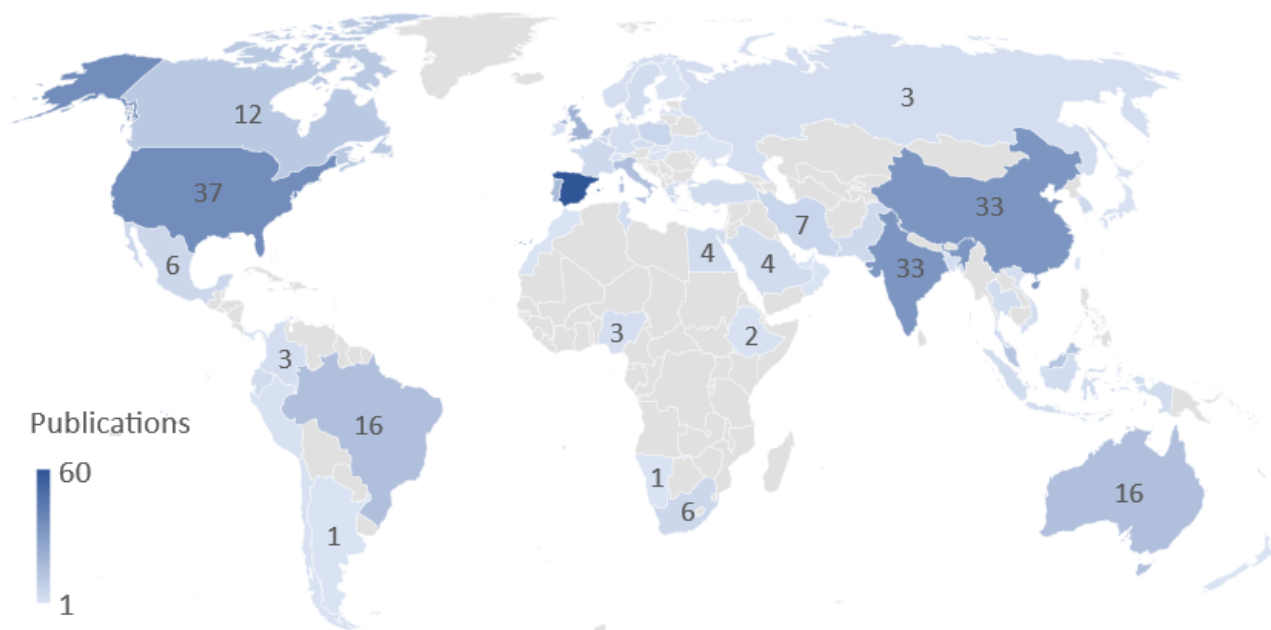


Figure 1. Map of publications by country using the Scopus database, created using Microsoft Excel 2019.

According to the information collected, different advances were developed in the laboratory, ranging from volume photobioreactors of 250 mL in Erlenmeyer flasks up to 4.5 L flat-panel reactors [13–15]. There were also pilot scale experiments conducted in 11.3 m³ horizontal tubular photobioreactors [16–18], and even in 22 m³ high-rate algal ponds [19]. Based on the pollutant removal yields described in Table 2, it can be inferred that the efficiency of these systems was determined by the microalgae culture metabolism, the type of wastewater employed (i.e., raw, anaerobic, or aerobic effluents), and environmental conditions such as temperature, solar radiation, and photoperiod. Temperature had a strong effect on kinetics and cell growth; for instance, growth rates varied significantly below 20 °C, with lower pollutant removal efficiencies observed at minimum temperatures of 10.7 °C in winter and maximum values at 20 °C in summer [20]. However, there were no significant differences observed in efficiencies between temperatures ranging from 30 to 36 °C [21].

Table 2. Microalgae used in WWTP technologies. SE = secondary effluent; WWTP = wastewater treatment plant.

Refs.	Microalgae	Type of Wastewater or Process	Pollutant Removal Yield
[22]	<i>Spirulina platensis</i> C. <i>vulgaris</i>	Biosorption process	$Al \approx 95\%$; $Ni \approx 87\%$; $Cu \approx 63\%$ $Al \approx 87\%$; $Ni \approx 79.1\%$; $Cu \approx 80\%$
[23]	<i>Scenedesmus</i> , <i>Pediastrum</i> , <i>Chlorella</i> mixture	Supernatant sludge sedimentation	$NTK \approx 88.7\%$; $P \approx 81\%$ $P \approx 81\%$; $P - PO_4^{3-} \& NH_3^+ - N \approx 100\%$ $Mn \approx 84.21\%$; $Zn \approx 80.92\%$; $Fe \approx 85.41\%$
[14]	<i>Chlorella</i> sp.	Filtered and sterilized agricultural runoff	$NTK \approx 98\%$; $P \approx 65\%$; $CIVatBlueI \approx 97.2\%$
[24]	<i>Scenedesmus</i> sp. <i>Chlorella</i> sp. <i>Hapalosyphon</i> sp.	Supernatant sludge sedimentation	$NO_3^- - N = 88\%$; $PO_4^{3-} = 82\%$; $Chlorpyrifos = 50\%$ $NO_3^- - N = 85\%$; $PO_4^{3-} = 82\%$; $Chlorpyrifos = 40\%$ $NO_3^- - N = 85\%$; $PO_4^{3-} = 82\%$; $Chlorpyrifos = 60\%$
[25]	<i>Scenedesmus obliquus</i>	SE-WWTP	$TN \approx 94.9\%$; $TP \approx 94.0\%$
[26]	<i>Chlorella vulgaris</i>	Filt-WW	$TN \approx 100\%$; $TP \approx 75.0\%$
[27]	<i>Chlorella</i> sp. and <i>Stigeoclonium</i> sp.	SE-WWTP	$NH_4^+ - N > 98\%$ Removal efficiency for most emerging pollutants $> 80\%$
[28]	<i>Scenedesmus</i> sp.	SE-WWTP	$NH_4^+ - N = 75.2\%$; $P = 77.9\%$
[29]	<i>Cyanobacteria</i> (cf. <i>Oscillatoria</i>) + Microalgae (<i>Chlorella</i> and <i>Stigeoclonium</i>)	SE-WWTP mixture	$N - NH_4^+ > 95\%$, $N - NO_3^-$, low, even negative with low inorganic carbon
[30]	<i>Cyanobacteria</i> (cf. <i>Aphanocapsa</i> sp.) + Microalgae (<i>Chlorella</i> and <i>Scenedesmus</i> sp.)	SE-WWTP mixture	$TN = 63\%$, $TOC = 84\%$
[5]	<i>Chlorella</i> sp., <i>Scenedesmus</i> sp., and <i>Stigeoclonium</i> sp.	SE-WWTP diluted	$COD = 70\%$; $N - NO_3^- = 58\%$, $NH_4^+ - N = 100\%$, $P = 100\%$

Table 2. Cont.

Refs.	Microalgae	Type of Wastewater or Process	Pollutant Removal Yield
[31]	<i>Scenedesmus</i> sp. and <i>Aphanocapsa</i> sp.	SE-WWTP mixture	TOC = 82.61%; TN = 80.05%; TP = 88.27%
[32]	<i>Chlorella</i> sp. among others	SE-WWTP	TOC = 60.53%; TN = 31.98%; TP = 17.94%; Other pollutants, varied removal efficiencies
[16,17]	<i>cyanobacteria</i> <i>Synechocystis</i> sp.	SE-WWTP diluted	$P - PO_4^{3-} = 100\%$; TN = 0%; COD = Negative. Other pollutants, varied removal efficiencies. Pesticides, herbicide mixtures, pharmaceuticals, personal care, flame retardants, and surfactants from negative to 100% removal
[20]	Non-specified microalgae consortia	SE-WWTP	In 4 different seasons: TTN = 18.8 to 64.2%; $NO_3^- = 32.7$ to 42.8%; $NH_4^+ = 65.7$ to 95.4%; TP = 33.4 to 84.8%
[33]	<i>Chlorella vulgaris</i> , <i>Nannochloropsis oculata</i> , <i>Scenedesmus acutus</i> , and <i>Scenedesmus obliquus</i>	Synthetic	Diclofenac from 59 to 91.1%
[34]	<i>Acutodesmus obliquus</i> , <i>Desmodesmus Maximus</i> , and <i>Chlorella vulgaris</i>	SE-WWTP sterilized	D. Maximus: TN= 91% $NH_3 - N = 78\%$ TP = 100%; A. obliquus: TN = 96%; $NH_3 - N = 100\%$; TP = 100%; C.Vulgaris: TN = 90%; $NH_3 - N = 78\%$; TP = 100%
[35]	<i>Scenedesmus</i> sp. DDVG I	SE-WWTP filtered and sterilized	COD = (75.6%); TN = 99.8%; $NH_3 - N$ & TP = 100%

Table 2. Cont.

Refs.	Microalgae	Type of Wastewater or Process	Pollutant Removal Yield
[36]	<i>Chroococcus turgidus</i>	SE-WWTP	$COD = 58.02\%$; $TN = 74.68\%$; $NH_3 - N = 82.78\%$; $P - PO_4^{3-} = 92.41\%$; $NO_2^- - N = 22.22\%$; $NO_3^- - N = 67.99\%$; $BOD_5 = 72.23\%$
[21]	<i>Chlorella sorokiniana</i>	Chicken and cow WW filtered	$N - NH_4^+ > 99\%$ at 3 different temperatures
[37]	<i>Chlorella vulgaris</i>	Fisheries WW	$NO_3^- = 98\%$; $TP = 20\%$

From the previous information, it is possible to infer that if these technologies were replicated in the Colombian context [38], the wide range of altitude differences in the territory and their effect on environmental temperature must be considered for locating these systems, particularly in higher mountain zones where temperatures below 20 °C are expected, which could lead to lower yields. It is also important to note that domestic or municipal secondary effluents have been widely studied, showing significant improvements not only in nutrient removal but also in COD, TOC, and metals such as aluminum, copper, nickel, zinc, iron, manganese, and even emerging pollutants such as colorants, herbicides, pesticides, personal care products, flame retardants, surfactants, and pharmaceuticals. This is particularly relevant for Colombia, where domestic activities contribute 46.13% and 92.07% of the nitrogen and total phosphorus loads introduced into water resources, respectively [6]. It is important to emphasize that the presence of pollutants such as heavy metals, pesticides, and other micropollutants described previously in wastewater varies according to the type of industry, which must be thoroughly considered and investigated to ensure optimal microalgae growth and the effectiveness of the technologies.

3.2. Pollutant Analysis for Municipalities in Antioquia

To identify the state of natural water quality in Antioquia, information was provided by the autonomous corporations CORANTIOQUIA and CORNARE, which are responsible for collecting samples and compiling information about natural water and wastewater effluents. The information was divided into two main categories: natural water and wastewater effluents.

3.2.1. Nutrient Concentrations in Natural Water

The data analyzed consisted of 1046 observations with dates from 2019 to 2022. This information was cleaned by considering only data with valid information for all variables of interest, omitting data with errors or empty results, and assigning lower limit values (<) to variables with results below the quantification limits. This process resulted in a total of 677 valid observations. To demonstrate the full variability and concentration ranges for all variables, an initial descriptive analysis was conducted, as shown in Table 3.

Table 3. Main statistical parameters for pollutants in natural rivers in Antioquia; n = 677 from 96 municipalities.

Variable	$NO_3^- - N$	$NO_2^- - N$	$NH_3^+ - N$	NTU	ST	SST	Ssed	NTK	P	Alcal	DT
Units	mg N – NO_3^-/L	mg N – NO_2^-/L	mg N – NH_3^+/L	NTU	mg/L	mg/L	mL/L	mg N/L	mg/L	mg $CaCO_3/L$	mg $CaCO_3/L$
Min:	0.2259	0.02	2.5	0.531	3.37	7	0.1	2.5	0.05	2.84	2.65
Q1:	0.2485	0.02	5	6.768	82	7	0.1	5	0.1	17.62	19.1
Median:	0.2485	0.03	5	25.25	150	29	0.1	5	0.237	34.75	30.35
Mean:	1.545	0.0492	5.98	193.53	307.08	146.7	0.497	6.725	0.58	49.36	62.43
Q3:	0.7319	0.03	5	119.5	331.75	125.2	0.3	5	0.5108	60.5	60.4
Max.:	114.078	1.56	59	10,000	6510	5179	30	79.1	14.1	361	1008

Variable	H	Q	pH	Cond	Tw	Tamb	O ₂	COD	BOD	ColT *	OrtoP
Units	m.s.n.m	L/s	U pH	uS/cm	°C	°C	mg/L	mg O ₂ /L	mg O ₂ /L	NMP	mg P – PO_4/L
Min:	37	0	1.65	3.08	10.8	13	0.17	10	2	−0.3567	0.153
Q1:	171.2	31	6.82	51.05	19.1	21.8	6.082	12	2	9.5568	0.153
Median:	978.5	207	7.3	95.6	22.3	25.2	7	12.45	2	10.8563	0.5
Mean:	1043.4	127,604	7.248	195.29	22.81	25.45	6.411	37.61	11.154	11.196	0.9418
Q3:	1690	1991	7.71	194.57	26.8	29	7.49	28	3.933	12.7569	0.5
Max.:	2952	44,166,000	8.96	9501	37.7	50.3	10	1008	620	19.2105	39.2

Note: * Variable transformed as log10(ColT).

According to the results obtained, the samples were collected from rivers at different elevations, ranging from 37 to 2952 m.s.n.m. (H), with water temperatures (Tw) ranging from 10.8 to 37.7 °C and flows (Q) ranging from 0 to 44 m³/s. There was also significant variability in the chemical parameters: oxygen concentrations (O₂) ranged from 0.17 to 10 mg/L, with 25% of the samples showing concentrations below 6.08 mg/L, potentially indicating the presence of organic and inorganic matter. The chemical oxygen demand (COD) values ranged from 10 to 1008 mg O₂/L, with more than 25% of the samples having concentrations above 28 mg O₂/L. The biochemical oxygen demand (BOD) values ranged from 2 to 620 mg O₂/L, with 25% of the samples above 3.9 mg O₂/L. For nitrates, concentrations ranged from 0.023 to 114.078 mg N – NO₃⁻/L, with 25% of the samples above 0.732 mg N – NO₃⁻/L. Ammonia concentrations ranged from 2.5 to 59 mg N – NH₃⁺/L, with 25% of the samples above 5 mg N – NH₃⁺/L. Nitrite concentrations ranged from 0.002 to 1.56 mg N – NO₂⁻/L, with 25% of the samples above 0.030 mg N – NO₂⁻/L, while Kjeldahl nitrogen ranged from 2.5 to 79.1 mg N/L. In the case of total phosphorus, concentrations ranged from 0.05 to 14.10 mg P/L, with 25% of the data above 0.51 mg P/L.

Next, through principal component analysis (PCA), an explanation of the variability and relationships among the variables was obtained. According to results in Figure 2, using six latent variables or dimensions, up to 71.331% of the variability in the samples could be explained. Dimension 1 explained almost 25.8% of the variability, with significant contributions from NTK (14.50%), COD (13.55%), OrtoP (12.97%), total phosphorus (12.32%), and alkalinity (10.12%). This dimension could be interpreted as representing variability due to organic matter. Dimension 2 explained 15.8%, with significant contributions from total solids (24.46%), suspended solids (23.40%), settleable solids (16.39%), and turbidity (18.89%), which were related to climatological events or mining activities. Dimension 3 explained environmental parameters such as water temperature (Tw), air temperature (Tair), and altitude (H), contributing to 10.67% of the variability. Dimension 4 explained 8.378%, with contributions from variables such as hardness (21.73%), pH (19.29%), nitrites (16.93%), conductivity (11.45%), and dissolved oxygen (7.71%). It is important to note that the presence of organic matter (Dimension 1) had a negative correlation with variables such as oxygen, which is highly related to common problems associated with eutrophication in ecosystems.

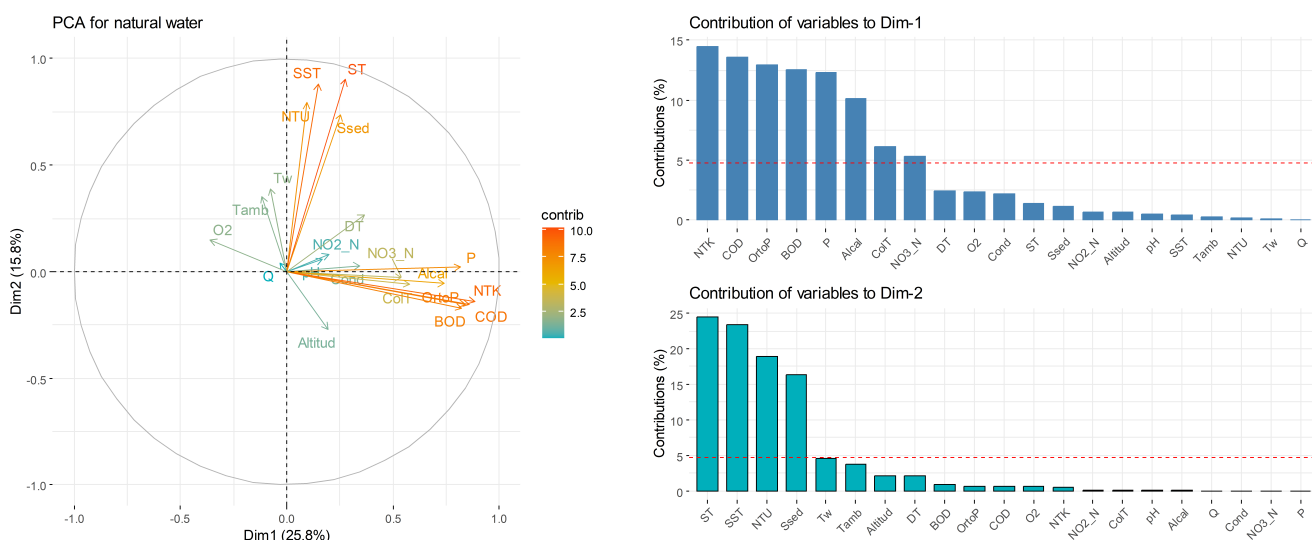


Figure 2. Principal components analysis (PCA) analysis of natural water and variable contributions; n = 677 for 20 variables.

From this information, it can be established that the increases in at least 25% of the samples for COD concentrations were strongly related to increases in BOD, NH₃, and P in rivers in the municipalities, which resulted in a reduction in the dissolved oxygen present

in water. To present the information more effectively, the average for each variable was calculated and arranged by municipality, and maps were plotted (see Figure 3a–c).

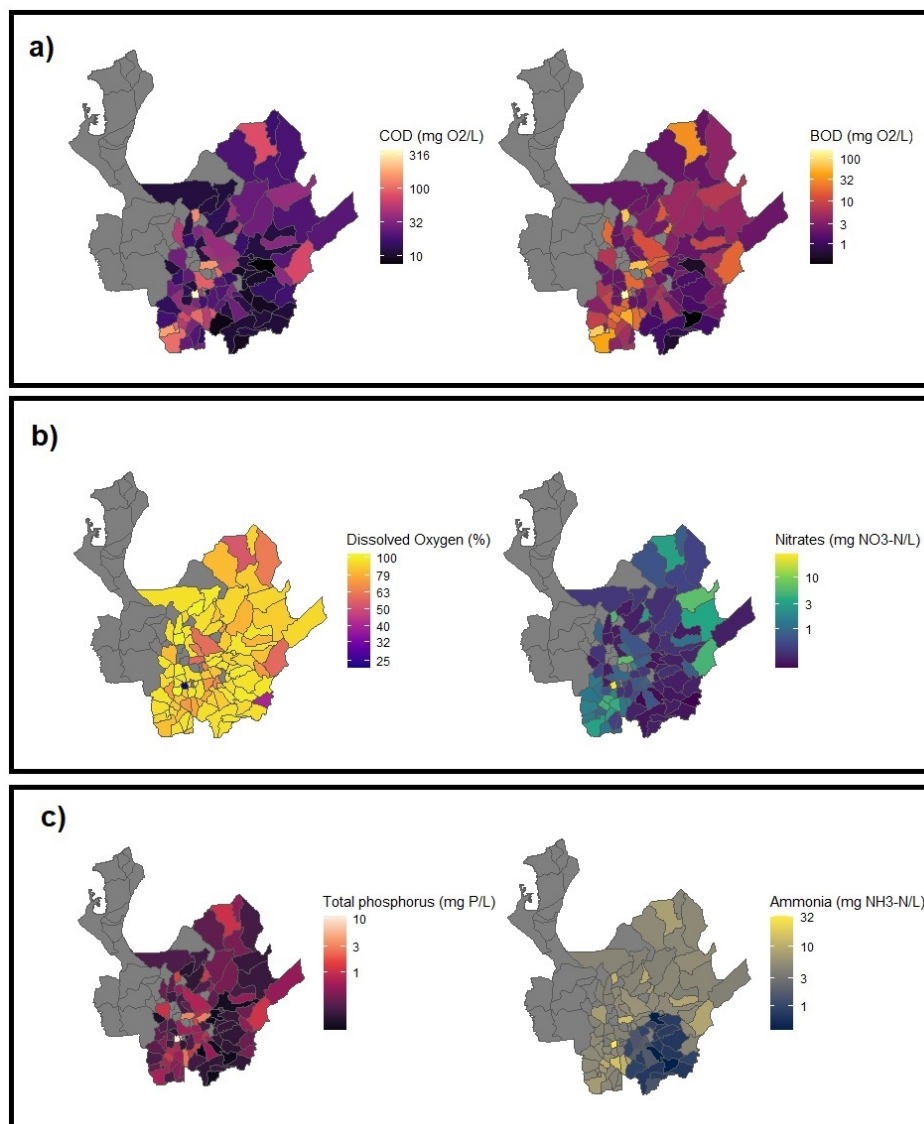


Figure 3. Average pollutant concentrations in water sources from municipalities in Antioquia for (a) COD and BOD, (b) oxygen saturation (%) and nitrates, (c) total phosphorus and ammonia.

According to the results, out of a total of 98 municipalities, those with the highest presence of contaminants in descending order were Angelópolis, La Estrella, San Pedro de los Milagros, Betania, Toledo, Fredonia, Puerto Berrío, Caucasia, Girardota, and Andes, highlighting that Angelópolis had nearly three times higher contamination levels compared to La Estrella. The results suggest that these municipalities exhibit significantly elevated concentrations of pollutants, nutrients, and organic matter compared to others, providing valuable information to prioritize efforts in identifying their sources and reducing their presence in these areas.

It is important to note that the data represent means obtained from 2019 to 2022 and may not account for possible effects caused by recent developments realized in these municipalities aimed at reducing the presence of organic matter in the sampled zones, such as the installation or enhancement of wastewater treatment plants, improvement of water resources and soil use management, and collective creation and implementation of river basin management and development plans (POMCA), such as those for Rio Negro and Aburrá Valley [39,40].

3.2.2. Pollutant Concentrations in Wastewater

Now, information on wastewater effluents was analyzed. The database consisted of 645 observations from different municipalities, with 13 variables in total. Only samples with complete data, without any errors or empty results for all 13 variables, were analyzed, resulting in a total of 497 complete observations. In Table 4, the correlation matrix for the variables is shown, where it can be observed that the data variability, such as COD, BOD, and surfactants (SAAM), has significant positive relationships with nutrients and nitrogen species like ammonia ($COD : N - NH_3^+ = 0.52$) and Kjeldahl nitrogen ($COD : NTK = 0.59$). Regarding total and reactive phosphorus, the correlation factor was 0.61 (> 0.5), while variables such as pH, nitrites, nitrates, and solids showed weak correlations for the entire dataset analyzed.

From this information, it can be concluded that in similar contexts for regions or municipalities with secondary treatment systems and without segregating the information by the type of users, the presence of COD and BOD (usually monitored by users and autonomous corporations) also implies the presence of nutrients such as ammonia, Kjeldahl nitrogen, phosphorus, oils, and surfactants. However, nitrite, nitrates, pH, and solids are not directly related to these variables. Furthermore, even if COD and BOD are highly removed in WWTPs, this is not the case for nutrients, which remain in wastewater and are subsequently incorporated into rivers and lakes.

According to the literature review in Section 3.1, microalgae grow in environments with a high presence of organic matter and nutrients such as nitrogen and phosphorus species. In the previous correlation matrix, it was observed that these variables were also correlated with other variables, except for pH, which showed no significant relationships. Additionally, since pH can be controlled in WWTPs, it was excluded from the subsequent analysis. The wastewater information was classified by averaging data across municipalities in the dataset, and four main groups of activities were identified. This included a total of 342 observations for domestic or service users (Dom) across 50 municipalities, 50 observations for all kinds of livestock users (LS) distributed across 16 municipalities, 122 observations for mining activities (MN) distributed across 11 municipalities, and finally, all other types of activities where specific information was not available, grouped as non-classified non-domestic wastewater (ARnD_NC), totaling 146 observations across 14 municipalities.

Table 4. Main statistical parameters for pollutants in wastewater in Antioquia; n = 497 from 96 municipalities.

Cor.Matrix	pH	DQO	DBO	G&A	SAAM	$P - PO_4^{3-}$	$NO_3^- - N$	$NO_2^- - N$	SST	SSED	NTK	$NH_3 - N$	P
pH	1.00												
DQO	0.15	1.00											
DBO	0.13	0.92	1.00										
G&A	0.10	0.50	0.54	1.00									
SAAM	0.10	0.57	0.63	0.59	1.00								
OrtoP	0.18	0.61	0.62	0.47	0.50	1.00							
$NO_3^- - N$	0.26	0.36	0.36	0.19	0.19	0.43	1.00						
$NO_2^- - N$	-0.04	-0.10	-0.09	-0.19	-0.17	-0.07	0.00	1.00					
SST	0.16	0.45	0.40	0.28	0.07	0.19	0.36	-0.18	1.00				
SSED	0.14	0.45	0.42	0.30	0.20	0.34	0.36	-0.13	0.63	1.00			
NTK	0.14	0.59	0.60	0.39	0.59	0.63	0.22	-0.10	0.02	0.13	1.00		
$NH_3 - N$	0.19	0.52	0.52	0.40	0.52	0.62	0.18	-0.14	0.05	0.15	0.86	1.00	
P	0.16	0.61	0.62	0.48	0.54	0.76	0.20	-0.11	0.15	0.25	0.71	0.69	1.00

Note: Correlation matrix for identified variables in wastewater effluents reported in Antioquia.

The data, summarized in Table 5, describe the minimum, maximum, mean, and median values for each variable, along with the Q1 and Q3 quartiles, to comprehend the data distribution across the average number of observations for activities present in the

municipalities. From this information, it can be recognized which activity has the presence of certain pollutants of interest. Domestic users and livestock are highlighted by NTK, ammonia, and phosphorus concentrations, while mining activities contribute significantly to SST loads. Industrial effluents exhibit a wide range of values for all variables.

Table 5. Statistical distributions of pollutants.

<i>Dom</i> ^a	<i>COD</i>	<i>BOD</i>	<i>G&A</i>	<i>SAAM</i>	<i>P</i> <i>PO</i> ₄ ³⁻	<i>NO</i> ₃ ⁻ <i>N</i>	<i>NO</i> ₂ ⁻ <i>N</i>	<i>SST</i>	<i>SS</i> <i>ED</i>	<i>NTK</i>	<i>NH</i> ₃ ⁻ <i>N</i>	<i>P</i>
Min	10.0	2.0	0.5	0.0	0.0	0.0	0.0012	3.4	0.1	2.4	0.1	0.0
Q1	98.0	27.7	10.0	0.7	0.6	1.0	0.0200	17.2	0.1	21.8	11.1	1.8
Median	209.0	71.6	15.0	3.5	2.9	5.0	0.0200	37.0	0.2	43.6	26.5	3.9
Mean	316.7	131.5	34.6	5.3	6.1	39.1	0.2849	82.9	1.2	62.4	37.9	5.1
Q3	447.2	195.0	40.0	7.8	8.8	44.6	0.0800	102.1	1.0	69.9	45.3	7.0
Max	2290.0	968.0	311.0	27.6	46.3	464.0	10.8000	643.0	50.0	1198.0	374.3	83.6
<i>LS</i> ^b	<i>COD</i>	<i>BOD</i>	<i>G&A</i>	<i>SAAM</i>	<i>P</i> <i>PO</i> ₄ ³⁻	<i>NO</i> ₃ ⁻ <i>N</i>	<i>NO</i> ₂ ⁻ <i>N</i>	<i>SST</i>	<i>SS</i> <i>ED</i>	<i>NTK</i>	<i>NH</i> ₃ ⁻ <i>N</i>	<i>P</i>
Min	12.0	2.0	1.1	0.1	0.0	0.0	0.0150	3.0	0.1	3.6	0.0	0.1
Q1	29.5	14.6	5.0	0.3	0.6	11.2	0.0200	15.0	0.1	52.6	32.6	1.1
Median	354.0	162.0	10.5	1.1	14.5	40.3	0.0200	46.0	0.2	102.4	67.2	7.4
Mean	655.3	303.7	25.9	3.2	27.0	63.6	4.4140	119.6	1.5	118.6	79.8	30.6
Q3	629.0	343.0	29.3	3.4	44.6	93.0	0.0200	131.0	1.7	177.5	115.8	19.1
Max	3545.0	1769.0	120.4	41.1	98.7	299.0	139.0	635.0	15.0	350.3	229.0	643.0
<i>MN</i> ^c	<i>COD</i>	<i>BOD</i>	<i>G&A</i>	<i>SAAM</i>	<i>P</i> <i>PO</i> ₄ ³⁻	<i>NO</i> ₃ ⁻ <i>N</i>	<i>NO</i> ₂ ⁻ <i>N</i>	<i>SST</i>	<i>SS</i> <i>ED</i>	<i>NTK</i>	<i>NH</i> ₃ ⁻ <i>N</i>	<i>P</i>
Min	10.0	2.0	1.2	0.1	0.0	0.1	0.02	3.0	0.1	2.5	2.5	0.1
Q1	12.0	2.0	5.0	0.1	0.2	4.8	0.02	34.0	0.1	5.0	5.0	0.1
Median	24.8	3.6	5.0	0.1	0.2	11.7	0.027	88.5	0.1	5.0	5.0	0.2
Mean	166.0	46.8	8.4	0.2	0.3	30.4	0.276	1290.0	5.9	6.7	5.4	0.6
Q3	171.2	38.4	10.0	0.1	0.2	25.6	0.118	248.2	1.0	5.0	5.0	0.4
Max	2312.0	968.0	48.0	3.8	16.0	318.0	5.400	74202.0	400.0	48.8	43.8	7.4
<i>RnD_NC</i> ^d	<i>COD</i>	<i>BOD</i>	<i>G&A</i>	<i>SAAM</i>	<i>P</i> <i>PO</i> ₄ ³⁻	<i>NO</i> ₃ ⁻ <i>N</i>	<i>NO</i> ₂ ⁻ <i>N</i>	<i>SST</i>	<i>SS</i> <i>ED</i>	<i>NTK</i>	<i>NH</i> ₃ ⁻ <i>N</i>	<i>P</i>
Min	10.0	1.0	0.1	0.1	0.0	0.1	0.002	6.0	0.1	0.4	0.3	0.1
Q1	25.0	3.4	6.3	0.1	0.0	1.2	0.020	18.6	0.1	5.0	5.0	0.3
Median	167.0	38.0	10.0	0.3	0.2	5.0	0.020	51.7	0.1	10.7	5.0	1.2
Mean	840.5	366.7	31.8	3.8	9.9	50.8	1.558	293.7	1.4	81.6	70.6	29.1
Q3	723.0	240.8	15.0	1.4	2.3	30.5	0.117	209.3	0.7	73.7	27.8	6.4
Max	9975.0	4028.0	882.0	250.0	194.0	519.0	60.90	6079.0	22.5	1000.0	1000.0	2973.0

Note: (a–d) Type of wastewater classification: a = Domestic/Municipal, b = Livestock industry, c = Mining industry, d = Industries residual wastewater without classification. According to their classification group in municipalities of Antioquia.

For the purposes of this investigation, it is recognized that domestic and livestock effluents have the potential to support microalgae-based tertiary wastewater treatment systems because they contain the nutrients used by microalgae to grow [13]. The mining industry has low concentrations of nutrients, making the technology impractical for this sector. In the case of non-classified industrial effluents, their wide variability implies that more information must be analyzed to categorize them into sub-groups, such as the food industry, textiles, metal mechanics, etc., to establish where there could be potential applications. It is important to note that even if an industry or domestic user has appropriate nutrient concentrations in their effluent for microalgae use, the presence of heavy metals or other micropollutants must be considered, and research must be conducted to ensure the technical feasibility of using microalgae in these treatment systems.

3.3. Opportunities for Current Pollutant Discharges in Antioquia

The results obtained previously for domestic users were compared with environmental legislation from countries identified in Section 2.1 as having conducted significant research using microalgae-based WWTPs. The pollutants compared were COD, BOD, and SST because they currently define the efficiency of WWTPs in Colombia. NT and P were also included because they are the main precursors of eutrophication in ecosystems and have not been properly regulated in Colombia. The data refer to the concentration limits

established by each country for discharges from municipal wastewater treatment facilities into natural water bodies. Initially, when comparing Colombian regulations with those from other countries, it was found that Colombia does not have stipulated limits for nutrient discharges such as total nitrogen (mg N/L) and phosphorus (mg P/L), not only for municipal facilities but for individual and industrial water users. The exception is mining activities, where the max NT concentration is 10 mg/L, which, according to Table 4, aligns with average observations for these activities as per internal norms for NT concentrations.

From Figure 4, it is remarkable that while not all nitrogen and phosphorus species have limits established in countries like Brazil [41], Peru [42], and Colombia [8], there are varied limits for nitrogen (mg N/L) and phosphorus (mg P/L) in other countries. For instance, Australia, the country with the highest total nitrogen and phosphorus concentrations, has limits of 50 mg N/L and 12 mg P/L, respectively. In contrast, European Union (EU) countries, such as Ireland, have established limits of 10 mg N/L and 1 mg P/L [43]. Colorado in the United States has limits of 7.0 mg N/L and 0.7 mg P/L [44], India has limits of 10 mg NTK/L [45], and China also has specific limits [46]. It is important to note that the average concentrations observed for domestic users have exceeded not only the regulatory limits of Colombia (Col) but also those of all other countries for COD, BOD, SST, and NT, with the exception of Spain [47], which relates to discharges into sewage treatment systems rather than water bodies. Only total phosphorus levels remain below the regulatory limits of some countries, such as Venezuela [48], Mexico [49], and Ecuador [50].

According to the information, the countries with the most research on this topic have included restrictions for nitrogen and phosphorus concentrations in their legal frameworks, whereas Colombia has not. The concentrations found in this research, not only for domestic users but also for livestock and some industrial non-classified wastewater (ARnD_NC), exceed the legal frameworks established by other countries. This situation must be considered in Colombia to properly take action to mitigate the climate crisis, avoid the eutrophication of ecosystems, and address related problems.

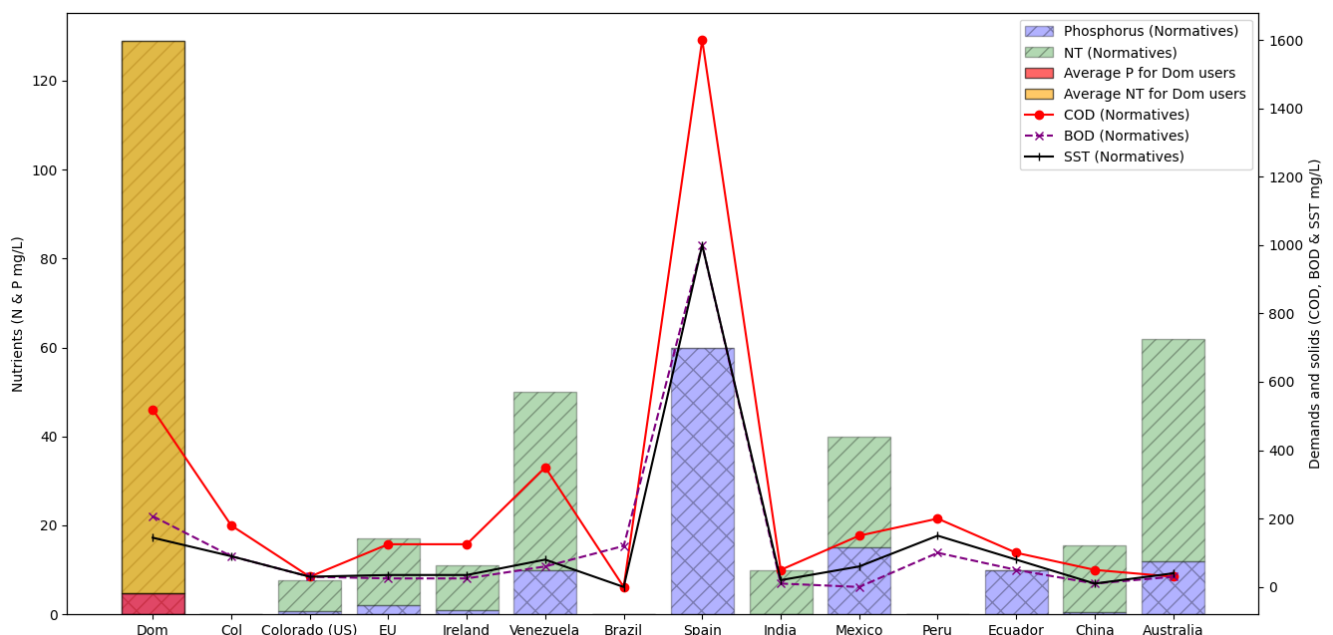


Figure 4. Domestic effluent pollutant concentrations compared with local and international environmental norms.

According to the national plan for wastewater management (2020–2050), the goal is to achieve 80% municipal wastewater treatment coverage by 2050. Significant progress has been made in installing new wastewater plants, increasing from 237 in 2004 to 712 in 2019 [51]. This increase accelerated after the implementation of Normative 0631 in 2015,

although the effects of Resolution 1256 are not yet observable [7]. However, many of the existing treatment plants need improvement or do not operate efficiently. It is important to note that there are no specific goals for removal efficiency in municipal wastewater plants, which could serve as an index to evaluate the effectiveness of political efforts in expanding wastewater treatment coverage.

These wastewater treatment facilities use primary sedimentation (17.3%) biological digesters such as UASB reactors, oxidation lagoons, natural wetlands, oil traps, and septic tanks (82%). However, these systems are not specialized in nutrient removal, as can be observed from the efficiencies reported in Table 6.

Figure 5 summarizes the evolution in coverage and overall efficiencies of domestic wastewater processes. The data were collected from national water studies from 2010 to 2022 [6,52–54] and include future perspectives for accomplishing the ODS goals in two scenarios. In scenario one, the projection is based on the assumption of not implementing nutrient regulations, which would delay the adoption of tertiary treatments specialized in nutrient removal. If we assume the use of conventional sludge treatments throughout the covered territory by 2050, there will be a technical limitation in improving the quality of wastewater effluents using only secondary treatments, as can be observed in Table 6. Even if COD and BOD were removed up to 90%, nutrient removal remains challenging, resulting in continued discharge into water sources through 2050.

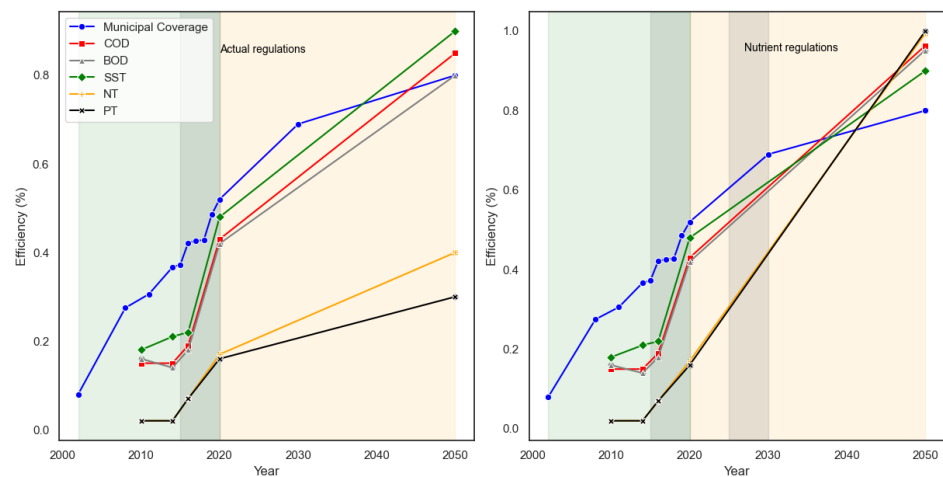


Figure 5. Historical trends and future projections for municipal wastewater treatment facilities from 2020 to 2050. (Left): without nutrient regulations. (Right): with nutrient regulations.

In the second scenario, the implementation of tertiary treatments is promoted by including regulations for nutrient discharges, following the same approach observed in 2015 with Resolution 0631. The updated regulations are expected to improve the quality of wastewater effluents. Final removal efficiencies were assumed using microalgae-based tertiary systems as an adaptation to conventional sludge wastewater treatment facilities. This approach is expected to enhance the efficiency of removing not only nitrogen and phosphorus but also COD, BOD, and solids beyond the theoretical efficiencies achievable by conventional sludge wastewater treatment facilities.

Table 6. Secondary wastewater treatment efficiencies.

Removal Efficiency (%)	COD	BOD	SST	$NH_3^+ - N$	NT	PT	Refs.
Conventional sludge treatment	85–95	85–90	85–95	85–95	25–30	25–30	[55], p. 26
Extended sludge treatment	93–98	90–95	85–95	90–95	15–25	10–20	[55], p. 26
UASB-activated sludge	85–95	83–90	85–95	75–90	15–25	10–20	[55], p. 26
Septic tank (48HRT)	50–60	50–60	58.3–75	–5.2	20.8	26.9	[56,57]
Mesh rotating biological reactor (MRBR)	48–63	77–90	ND	ND	10–38	ND	[58,59]
UASB	52	66	60	62.4	< 1%	< 1%	[60]

Note: For pollutants of interest using commonly used processes in Colombia.

4. Discussion

The data presented highlight significant variability in nutrient concentrations across water sources in municipalities in Antioquia, largely driven by organic matter introduced through wastewater effluents from anthropogenic activities. This variability suggests that at least 25% of river samples from 89 municipalities exhibit higher nutrient concentrations, underscoring the need for comprehensive data collection campaigns to provide clearer and more current information.

It is crucial to note that the average values presented are aggregated over different years and may not fully reflect recent efforts by local communities and environmental agencies to manage water sources and land use impacts. Subsequent sampling campaigns conducted by autonomous corporations will be instrumental in assessing these ongoing impacts.

One of the primary reasons behind the current status of wastewater effluents and rivers is the regulatory gap outlined in Resolution 0631 of 2015, which lacks specific concentration limits for nutrients. This gap has hindered technological advancements in the effective operation of actual systems and the development of tertiary wastewater treatment technologies. Despite improvements in coverage and removal efficiencies over the past decade, significant challenges remain.

Initiatives like CONPES 4004 and Resolution 0631 have aimed to enhance removal efficiencies since 2015 to align with the 2050 Sustainable Development Goals (SDGs). However, achieving these goals requires not only expanding service coverage and sewerage but also improving pollutant removal efficiencies in wastewater treatment processes. Political support is essential for implementing policies that promote higher removal of nutrients and emerging pollutants, particularly in secondary wastewater treatment facilities commonly used in Colombia.

Considering microalgae-based tertiary wastewater treatment systems as a viable technology for capturing nutrients and micropollutants from domestic and livestock wastewater effluents opens up potential economic opportunities. Recent research highlights various uses for microalgae biomass, including energy production such as biodiesel and bioethanol, animal feed, biofertilizers [5,34,57], and bio-crude using hydrothermal liquefaction processes [61]. The main limitation consists of obtaining nutrient sources to feed microalgae, and wastewater could be used as an alternative, reducing operational costs.

There are also uses in animal feed for chickens and fish, as well as in agro-industrial products such as biofertilizers [21,35,37,62]. This creates novel market opportunities for developing countries. For example, livestock users studied in Antioquia could develop new technologies to recycle the nutrients present in their wastewater systems and transform the biomass into feed for their animals.

Furthermore, there remains a critical knowledge gap concerning how microalgae cultures respond to a wide range of pollutants, including emerging contaminants like PFASs, pesticides, herbicides, and flame retardants. Future investigations should focus on understanding the behavior of microalgae in tertiary treatment facilities and assessing the toxicity of pollutants to microalgae cultures. This research is essential for advancing sustainable wastewater management practices and safeguarding ecosystem health.

5. Conclusions

Based on the findings presented in this document, several significant conclusions can be drawn that are essential for establishing effective water resource management strategies in Antioquia.

It is crucial to note that the discharge of wastewater into water sources has sparked global efforts to mitigate eutrophication and its adverse effects on ecosystems and human health. Therefore, it is imperative for Colombia to promptly establish maximum nutrient concentrations to align with international standards set by the European Union, the United States, and Brazil.

This study serves as a valuable resource for researchers and environmental organizations, providing statistical distributions of pollutants in rivers and wastewater treatment facilities. Such data can inform similar studies in other regions and support the development of robust environmental policies through collaboration with the Environmental Ministry. It is evident that Colombia should prioritize controlling nutrient levels in water sources. By benchmarking against average municipal water quality results, specific limits for phosphorus and nitrogen can be set to curb these pollutants and facilitate the adoption of advanced treatment technologies aimed at effectively reducing nutrient concentrations.

Furthermore, microalgae species such as *Chlorella* sp. and *Scenedesmus* sp. are identified as promising alternatives for capturing and utilizing excess nutrients discharged from domestic, municipal, and industrial wastewater treatment plants. Integrating these microalgae into treatment systems can significantly reduce nitrogen and phosphorus levels in natural water bodies, thereby enhancing water quality and supporting ecosystem stability. This approach aligns with national policies outlined by the Consejo Nacional de Política Económica y Social (CONPES), 2022.

Moreover, employing microalgae in treatment systems not only enhances water resource management but also initiates a transformative approach within the water–energy–food nexus [21]. By converting wastewater nutrients into biofertilizers and biofuels, microalgae can contribute to a circular economy that mitigates CO₂ emissions, cleans water, supports sustainable food production, and reduces the operational costs associated with these technologies. Nonetheless, the adoption of these technologies should be preceded by a rigorous assessment of their limitations, particularly concerning the capacity of microalgae to mitigate micropollutants such as heavy metals, pesticides, herbicides, and emerging contaminants, ensuring ecological integrity and preventing cross-species pollution transfer.

Author Contributions: The authors' contributions to this project were as follows: L.A.R. conceptualized this study and provided supervision, ensuring its overall direction and integrity. A.P.M. curated the data, meticulously organizing and managing the dataset. Formal analysis was conducted collectively by all authors, ensuring a comprehensive examination and interpretation of the results. D.O.E. acquired the funding and administered this project, securing the necessary resources and overseeing the day-to-day operations. J.C.S.M. provided essential resources for this study's execution, such as the microalgae. Finally, visualization, writing—original draft, and writing—review and editing were collaborative efforts among all authors (A.P.M., J.C.S.M., L.A.R., E.O.E., and D.O.E.). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Minciencias (Colombia) and Universidad de Antioquia.

Data Availability Statement: Data are available upon request.

Acknowledgments: The authors gratefully acknowledge the financial support provided by University of Antioquia ("Comité para el desarrollo de la Investigación-CODI") and by the Ministry of Science, Technology, and Innovation of Colombia (Minciencias) within the call No. 914-2022 (contract No. 80740-098-2022). Additionally, this research was carried out with the support of different entities: 1. Corporación autónoma regional de las cuencas de los ríos Negro y Nare (CORNARE). 2. Corporación Autónoma Regional del Centro de Antioquia (CORANTIOQUIA).

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations were used in this manuscript:

MDPI	Multidisciplinary Digital Publishing Institute
DOAJ	Directory of open-access journals
TLA	Three-letter acronym
LD	Linear dichroism

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