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Can Lagoons Serve as a Quaternary Treatment for Micropollutants in Wastewater Treatment Plants? Recent Implications for Compliance with the New Urban Wastewater Treatment Directive

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Abstract: This study explores the potential of storage lagoons as a quaternary treatment step in wastewater treatment plants (WWTPs), focusing on compliance with the recent European Urban Wastewater Treatment Directive (UWWTD), which mandates an 80% reduction in specific micropollutants. While conventional treatments effectively remove residual nutrients and solids, the potential of storage lagoons as an additional treatment is not fully defined. This research aims to address this gap by assessing the efficacy of storage lagoons in refining the effluent quality at the Cabezo Beaza WWTP, considering recent UWWTD requirements. We conduct a comprehensive assessment of the water quality parameters and micropollutants, before and after the storage lagoon stage, at the Cabezo Beaza WWTP. The results indicate that this strategy of prolonged storage in lagoons manages to meet the reduction objectives established by the Directive, reaching elimination percentages greater than 80% for the majority of the analyzed micropollutants. Our findings suggest that lagoons significantly improve water quality and reduce contaminants beyond conventional treatments, offering environmental and economic benefits. This paper discusses the mechanisms behind these improvements, such as natural sedimentation, microbial activity, and potential phytoremediation. This study contributes to the research on advanced wastewater treatment and supports the integration of storage lagoons as a viable quaternary treatment solution that meets the UWWTD standards.

Keywords: wastewater treatment; micropollutants; UWWTD; 91/271/EEC; quaternary treatment; nature-based solutions

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1. Introduction

Water scarcity is a growing concern worldwide, especially in arid and semi-arid regions. In such areas, the reuse of treated wastewater for agricultural purposes represents a sustainable solution to mitigate water scarcity problems [1]. However, the reuse of reclaimed water requires compliance with stringent quality standards to ensure public health and environmental safety, highlighting the importance of advanced wastewater treatment processes in wastewater treatment plants (WWTPs).

Micropollutants, which are chemical compounds such as pharmaceuticals, personal care products and pesticides, can be detected in treated effluent from wastewater treatment plants. Environmental concerns encompass not only the presence of individual compounds but also their intricate interactions and the potential formation of new, occasionally more harmful by-products [2,3]. In the dynamic field of environmental research, the occurrence of micropollutants in water has become a major concern. Micropollutants are identified under Regulation (EC) 1907/2006 (REACH) as substances, together with their degradation products, that persist in the environment at minimal concentrations and are potentially harmful to human health or the environment [4]. This classification is based on the strict criteria set out in Regulation (EC) No. 1272/2008, Parts 3 (Health Hazards) and 4 (Environmental Hazards) of Annex I to Regulation (EC) 1272/2008 [5]. Known as the Classification, Labelling and Packaging (CLP) Regulation, this regulatory framework integrates the United Nations' Globally Harmonized System (GHS) to standardize the classification and labeling of chemical products across the European Union. In response to evolving scientific knowledge and environmental concerns, the European Chemicals Agency (ECHA) periodically reviews and updates the classification of chemical substances listed in Annex VI of the CLP Regulation to ensure that safety measures and regulatory compliance evolve with the latest research. Regulatory frameworks such as the Water Framework Directive (WFD, 2000/60/EC) and the Minimum Requirements for Water Reuse (Regulation (EU) 2020/741) establish specific guidelines for water quality, including the permissible levels of micropollutants, nutrients, organic matter, and pathogens [6]. These guidelines are crucial for ensuring that reclaimed water meets the rigorous standards of safety and quality for its intended uses. Simultaneously, the Urban Wastewater Treatment Directive (UWWTD) complements these water quality frameworks by mandating the elimination of micropollutants from wastewater and emphasizing the necessity of quaternary treatment processes.

Directive 91/271/EEC has played a fundamental role in improving the water quality and the environment in the European Union for more than 30 years, leading to significant reductions in organic pollution, nutrients, and pathogens. Despite these achievements, challenges persist, notably the presence of chemicals resistant to conventional urban wastewater treatment, which has led to the need for additional treatment [1,7]. In response to this ongoing issue, Directive 91/271/EEC was updated in 2024 (now known as the UWWTD) to align with European environmental initiatives, such as the European Green Deal, the Zero Pollution Action Plan, and the Circular Economy Plan [8]. Among the new regulations, the UWWTD mandates an 80% reduction in micropollutants and demands the implementation of quaternary treatment for all treated water, regardless of its intended reuse. These treatments will become mandatory for plants exceeding 150,000 h-e, as well as for facilities with a capacity surpassing 10,000 h-e, particularly in regions where micropollutants pose potential hazards to human health and the environment.

Compliance with this directive requires systematic monitoring of a selected group of representative micropollutants to ensure the effectiveness of the treatments in reducing micropollutant levels [9]. The Directive emphasizes the monitoring of 12 indicator substances, categorized to optimize their management and treatment processes. Category 1 comprises eight pharmaceuticals described as "very easy to treat", highlighting their relative ease of removal through standard wastewater treatment processes. Category 2 includes four substances referred to as "substances that can be easily disposed of", acknowledging their ease of elimination but emphasizing the importance of vigilance due to their increasing detection in wastewater. In accordance with these guidelines, the quantification of pollutant removal rates requires a calculation based on a minimum of six identified substances. If concentrations fall below measurable thresholds for fewer than six substances, regulators have the authority to designate additional substances for inclusion in the assessment. The assessment of compliance relies on calculating the average of the specific removal percentages for each individual substance analyzed. This average serves as the central metric for evaluating whether the mandated minimum removal threshold of 80% has been achieved [9].

In addition, given the stringent requirements of the Directive, there is growing recognition of the importance of natural attenuation mechanisms in reducing micropollutant levels in aquatic environments. Natural water bodies, including lagoons, lakes, and agricultural ponds, act as significant sinks for micropollutants. They facilitate a variety of physical, chemical, and biological processes that collectively diminish the concentrations and harmful effects of these compounds [10]. Understanding and harnessing these natural attenuation processes is essential for assessing the long-term environmental impact of micropollutants and for developing effective strategies to manage and mitigate their presence in ecosystems. Physical phenomena such as adsorption to sediments and photodegradation, along with dilution effects, play a key role in reducing micropollutant concentrations, especially in large water bodies like lakes [3,10,11]. However, microbial degradation is considered the most important process. It metabolizes a wide range of organic compounds and significantly reduces the presence and impact of micropollutants [12]. The efficiency of these processes varies depending on the nature of the compound, the environmental conditions, and the microbial community present. In some cases, micropollutants may be completely mineralized to carbon dioxide and water, while in others, they may be transformed into other compounds that could be less or more toxic than the original compound [12,13].

This study evaluates the incorporation of storage lagoons at the Cabezo Beaza WWTP as a quaternary treatment to improve effluent quality and comply with the stringent criteria of the latest Directive. Although storage lagoons offer a cost-effective and energy-efficient alternative to conventional tertiary treatment, their effectiveness in removing residual pollutants remains insufficiently documented. The Cabezo Beaza WWTP, located in a water-stressed region, serves as an ideal case study due to its existing primary and secondary treatment stages, complemented by the incorporation of storage lagoons as a potential quaternary treatment for a wide range of micropollutants. Our goal is to comprehensively assess the impact of the lagoons on effluent quality, thereby contributing to the advancement of sustainable wastewater management practices within the framework of current environmental guidelines.

2. Materials and Methods

2.1. Description of the WWTP and Lagoons

The Cabezo Beaza WWTP is located in the municipality of Cartagena (coordinates ETRS89 UTMX: 680853 and UTMY: 4167004), southeast of the Region of Murcia, Spain (Figure 1). Operating as a full-scale facility, the plant has a treatment capacity of 12,775,000 m^3/year and serves a population of 176,921 inhabitants [14]. As shown in Figure 2, this WWTP has a secondary treatment system based on conventional activated sludge.

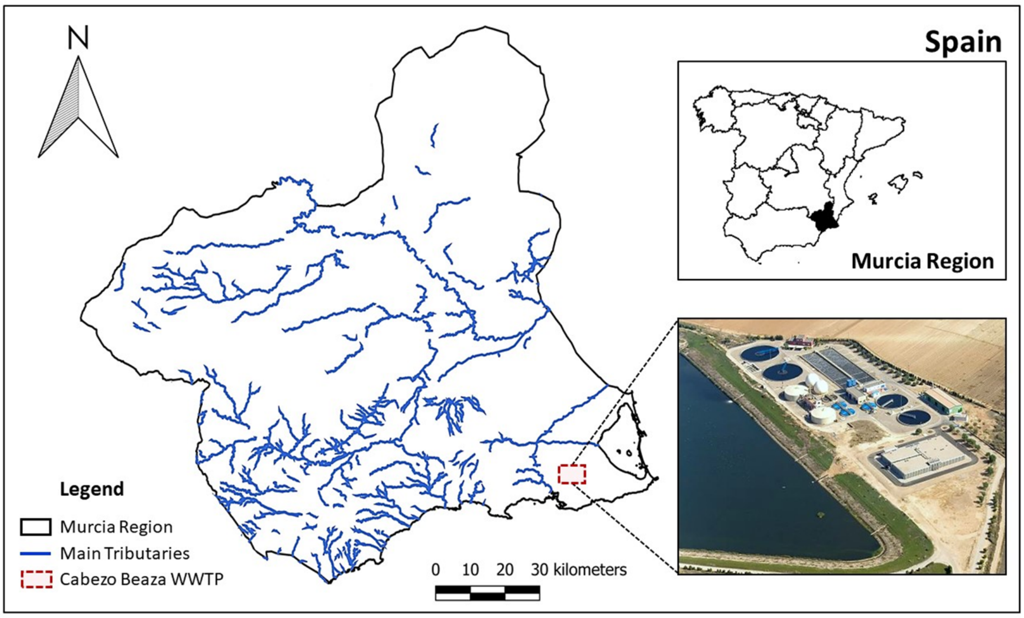

Figure 1. Location and image of the WWTP used in this study.

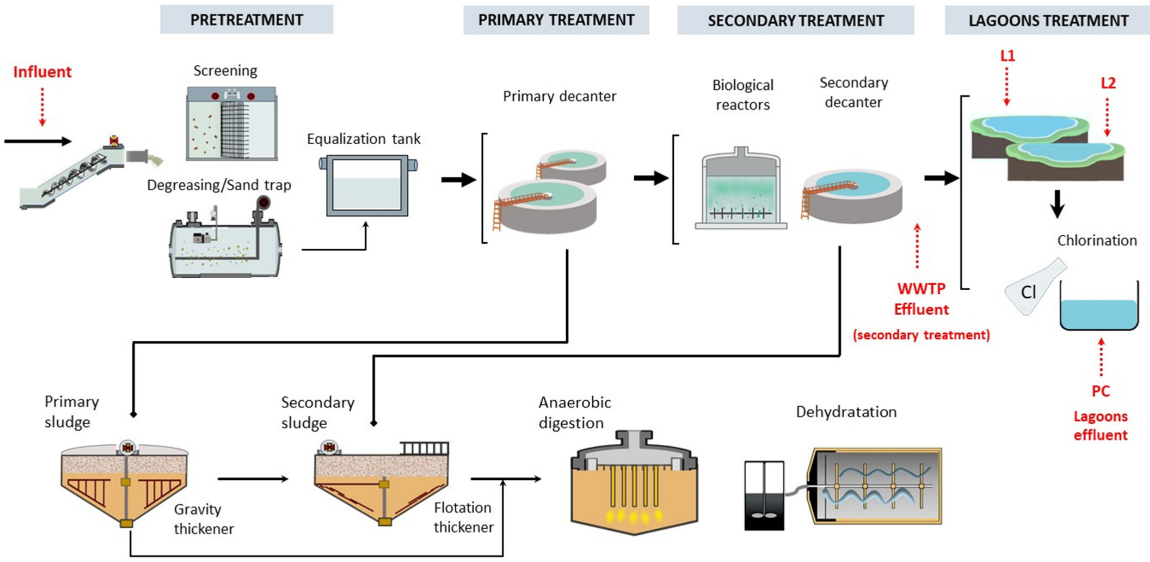

Figure 2. Graphical representation of the Cabezo Beaza WWTP's treatment stages and sampling sites.

This WWTP employs two plug flow biological reactors with anoxic and anaerobic zones at the inlet (A^2/O). These reactors maintain aerobic conditions through aeration facilitated by blowers and employ a suspended growth system to keep microorganisms in suspension. Engineered primarily for nitrification–denitrification, these reactors are geared toward the elimination of ammoniacal nitrogen and other nitrogenous compounds from the wastewater stream. Additionally, for the chemical precipitation of phosphorus, agents such as polyaluminum chloride and ferric chloride are dosed directly into the aeration tank. The sludge retention time is 10 days, while the hydraulic retention time of the WWTP up to the secondary treatment stage is 16 h.

The secondary treatment effluent is stored in 2 lagoons with an average hydraulic retention time of 34 days (Figure 2). These lagoons, which operate in parallel, serve as an integral complementary treatment stage to the wastewater treatment of the WWTP. Lagoon 1 (L1) and Lagoon 2 (L2) have a maximum surface area of 175,000 m^2 and 143,000 m^2, respectively, with a maximum depth of 7.8 m and a regulation volume of 855,000 m^3. While the WWTP lacks a tertiary treatment, the potential for the lagoons to eliminate micropollutants elevates them to a quaternary treatment level. The lagoons were constructed with compacted clay slopes of 1:5 and waterproofed with a 1200 Gauge polyethylene membrane to block water seepage into the surrounding soil or groundwater. Additionally, a 15 cm protective layer covers the slopes to shield the membrane from damage and stabilize it against erosion or slippage. These design features ensure the lagoons are impermeable and securely sealed, preventing groundwater infiltration. Significantly, it is essential to highlight that these lagoons do not experience any dilution effect, as they exclusively receive effluent directly from the WWTP. Moreover, precipitation does not contribute to dilution, as the Region of Murcia experiences low rainfall, with an annual average of 300 mm (Spanish State Meteorological Agency, AEMET). Finally, the effluent from the lagoons undergoes chlorination disinfection (post-chlorination) specifically to safeguard the microbiological quality of the water before it is used for agricultural irrigation.

2.2. Collection of Samples

In this study, water samples from the influent and effluent were collected, processed, and analyzed according to the standards procedures [15]. To evaluate the quality of the influent water, a comprehensive sampling approach was adopted, with 24 h samples taken over a 24 h period to capture daily variations. The use of an automated sampler, calibrated to match the sample volume to the flow rate, further enhanced the accuracy and representativeness of the samples. For the effluents, spot sampling was utilized. The secondary treatment effluents were sampled at the outlet of the biological treatment stage. Similarly, the effluents from the lagoons were sampled at specific discharge points before (L1 and L2) and after chlorination (post-chlorination). All the samples taken, including the lagoon effluents (L1 and L2), were designated for physicochemical analysis. For the detection of micropollutants, representative samples were selected according to the focus of this study (influent, secondary treatment effluent, and lagoon effluent post-chlorination). The choice to adopt spot sampling was influenced by the treatment and storage processes, which ensure a uniform distribution of contaminants and other water quality parameters. This is supported by the function of the lamination tank in the WWTP, which homogenizes the water at the plant entrance, ensuring equalized input flows and uniform distribution of contaminants throughout the treatment. Moreover, the design of the WWTP's lagoons is engineered to prevent preferential currents, facilitating uniform mixing of water. With a hydraulic retention time exceeding one day, these processes guarantee the complete mixing and uniform distribution of contaminants. Evidence suggests that through adequate mixing and sufficient residence time, these processes effectively contribute to the homogenization of effluents. Consequently, the need for integrated sampling at these points was effectively minimized.

2.3. Physicochemical Characterization

The physicochemical parameters, namely the pH, Electrical Conductivity (EC), Suspended Solids (SS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD_5), Total Nitrogen (nitric nitrogen, nitrite nitrogen, ammoniacal nitrogen and organic nitrogen bound structures), and Total Phosphorous (orthophosphate, condensed phosphate, and organic phosphate), were analyzed according to ISO water quality standards and reference methods for monitoring the requirements for urban wastewater (Annex 1 of the UWWTD).

2.4. Micropollutants Analysis

2.4.1. Micropollutants Characterization

In this work, 12 chemical compounds described as micropollutants were evaluated in both the influent and effluent streams of the WWTP after secondary treatment, as well as in the lagoon treatment after chlorination (post-chlorination). These compounds, specified by the UWWTD, are utilized in Switzerland as indicators, totaling 12 substances (or 13 when considering methylbenzotriazole as a mixture of 2 substances), and are representative of the overall organic micropollutant load found in urban wastewater [16]. The most relevant characteristics of these compounds in terms of the chemical properties that influence the persistence and bioaccumulation of compounds in the environment are shown in Table 1. This table shows the variation in the hydrophobicity (logarithm of the octanol–water partition coefficient) and dissociation constants of the different compounds. Within the two categories, the compounds with the highest hydrophobicity are diclofenac, candesartan and irbesartan. In terms of the dissociation constants, within the typical pH range found in wastewater treatment plants (pH 5–9), the highest values are observed for compounds with neutral properties (such as carbamazepine and hydrochlorothiazide) and basic properties (such as metoprolol and benzotriazole), while the remaining compounds have lower values.

Table 1. Main characteristics of the 12 micropollutants. Chemical Abstract Service (CAS) registry number, logarithm of the octanol–water partition coefficient ($LogK_{ow}$) and dissociation constant (pKa).

Category	Micropollutants	CAS N°	$LogK_{ow}$ (25 °C)	pKa
Category 1 (substances that can be very easily treated)	Amisulpride	71675-85-9	–	9.37 [a]
	Carbamazepine	298-46-4	2.45 [b]	<1–13.9 [a]
	Citalopram	59729-33-8	1.39 [a]	9.38–9.78 [a]
	Clarithromycin	81103-11-9	3.16 [a]	8.99 [a]
	Diclofenac	15307-86-5	4.51 [a]	4.15–4.3 [a]
	Hydrochlorothiazide	58-93-5	-0.07 [a]	7.9–9.2 [a]
	Metoprolol	37350-58-6	1.88 [b]	9.5–10.09 [a]
	Venlafaxine	93413-69-5	3.20 [a]	9.56–9.7 [a]

Table 1. *Cont.*

Category	Micropollutants	CAS N°	$LogK_{ow}$ (25 °C)	pKa
Category 2 (substances that can be easily disposed of)	Benzotriazole	95-14-7	1.44 [a]	8.37 [a]
	Candesartan	139481-59-7	4.79 [a]	3.82–3.92 [c]
	Irbesartan	138402-11-6	5.31 [a]	4.08–4.29 [a]
	Methylbenzotriazole			
	(4-Methylbenzotriazole	29878-31-7	–	8.74 [b]
	5-Methylbenzotriazole)	136-85-6	–	8.74 [b]

[a] $LogK_{ow}$ (log octanol–water partition coefficient) and pK_a values were obtained from PubChem, accessed on 15 March 2024 (https://pubchem.ncbi.nlm.nih.gov/); [b] pK_a values were obtained from Chemical Book, accessed on 1 April 2024 (https://www.chemicalbook.com); [c] Jezko et al. (2015) [17].

2.4.2. Quantitative Analysis

The pharmaceuticals and other organic substances were analyzed in accordance with the German standard methods [18] for the examination of water and wastewater, using high-performance liquid chromatography and mass spectrometric detection, HPLC-MS/MS or -HRMS, after direct injection.

2.5. Estimation of Removal Efficiency

The estimation of the removal efficiency (RE) in the WWTP can be calculated by comparing the concentration of the micropollutant in the influent and effluent waters. In this work, the RE for each analyte was estimated based on the average concentrations of the respective compound in the influents and effluents of the WWTP secondary treatment and lagoons (Equation (1)). This approach provides insights into the treatment effectiveness by quantifying the percentage of contaminant reduction achieved through the wastewater treatment process.

$$RE(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Here, Ci and Ce represent the average concentration in the influent wastewater and effluent samples, respectively. In cases where a compound was detected but could not be quantified (due to its concentration being below the limit of quantification, LQ), a concentration equivalent to half the quantification value was considered for the purpose of calculating the removal efficiency (Table S1 in Supplementary Materials). Murcia Region has an evaporation rate of 1.8 m^3/m^2 per year, which significantly impacts the water volume in lagoons, potentially affecting the flow dynamics [19]. However, when accounting for evaporation in contaminant removal efficiency calculations, the actual reductions in the contaminant concentrations are negligible. Consequently, there has been no adjustment made to the removal efficiency calculations to include the impact of evaporation.

To evaluate compliance with the mandatory minimum removal level of 80%, the analysis involved calculating the average of the specific removal percentages for each substance, in accordance with the methodology prescribed by the new UWWTD. This calculation was then extended to determine the average removal percentages for the six micropollutants with the most significant removal efficiencies in both categories after secondary treatment at the WWTP and treatment in the lagoons. In calculating the average, negative removal values were treated as zero.

2.6. Statistical Analysis and Data Treatment

The mean concentrations of micropollutants in both the influent and effluent of the WWTP secondary treatment and lagoon treatments were used for statistical comparisons. Since most of the data were not normally distributed, the Kruskal–Wallis one-way ANOVA test ($p < 0.05$) was applied, and post hoc multiple comparisons were performed using Dunn's test, with the confidence intervals set at $p < 0.05$ and $p < 0.01$. These statistical procedures were used to identify significant differences in micropollutants between the two studied treatments. In addition, a correlation test was performed to evaluate the possible associations between micropollutants and physicochemical indicators. Therefore, considering the number of samples (<20) and the fact that most of the data failed the normality test (Shapiro–Wilk), Spearman's rank coefficients were used to evaluate the correlations between the parameters. The statistical significance of these correlations was determined using Spearman's coefficient, with a confidence level of $p < 0.05$. Graphs of the results and descriptive statistics were generated in Excel, and all the additional statistical analyses were performed using GraphPad Prism 9.4.1 software.

3. Results and Discussion

3.1. Physicochemical Parameters

The physicochemical characteristics of the Cabezo Beaza WWTP are shown in Table 2. The pH values registered a variation between 7 and 8.5 at all the sampling points studied, remaining within the threshold required for effluent discharge into receiving waters. A significant reduction in the concentration of suspended solids was observed at all the treatment stages of the WWTP. Both the WWTP secondary treatment and lagoons treatment (L1 + L2 + PC) demonstrated compliance with the Urban Wastewater Treatment Directive (UWWTD) concerning suspended solids. The UWWTD stipulates a maximum suspended solids limit of 35 mg/L and a minimum elimination efficiency of 90%. The treatments showed suspended solids concentrations of 9.2 mg/L and 9.3 mg/L, respectively, achieving an elimination efficiency of 98% in both cases. The effective reduction of suspended solids (SSs) is critical because their accumulation can lead to sedimentation in receiving waters and contribute to oxygen depletion [20]. However, a slight increase in SSs was observed between the secondary treatment effluent and lagoon effluents. Specifically, in the lagoon treatment, the presence of biological activities can lead to the production of biological suspended solids, resulting in elevated SSs concentrations. This includes the growth of microalgae and other living organisms.

Table 2. Physicochemical properties of the Cabezo Beaza WWTP at the different stages of wastewater treatment.

	WWTP		Lagoons				
Parameters	**Influent**	**Effluent**	**Lagoon 1 (L1)**	**Lagoon 2 (L2)**	**Post Chlorination (PC)**	**Removal Rate WWTP (%)**	**Removal Rate PC (%)**
pH	7.45	7.17	7.84	8.10	8.09	NA	NA
Electrical Conductivity (EC)	2467.23	2132.52	2141.33	2209.14	2148.98	NA	NA
Oxidation–Reduction Potential (ORP)	−236.18	106.18	89.08	50.80	149.14	NA	NA
Suspended Solids (SS)	388.10	9.22	10.00	10.00	9.28	97.63	97.61
Chemical Oxygen Demand (COD)	725.28	35.06	33.00	31.00	25.00	95.17	96.55
Biochemical Oxygen Demand (BOD_5)	364.09	6.83	5.00	5.00	7.96	98.13	97.81
Ammoniacal nitrogen (NH_4-N)	65.17	19.23	20.80	17.80	9.67	70.49	85.16
Nitrate nitrogen (NO_3-N)	2.50	31.69	3.50	2.53	12.75	NA	NA
Total Nitrogen	76.82	27.99	26.00	22.00	10.35	63.56	86.53
Total Phosphorous	10.67	1.18	1.35	2.10	1.15	88.94	89.22

Note: All parameters are shown in mg/L, except for pH (pH on a scale), EC (µS/cm) and ORP (mV); NA, not applicable.

Electrical conductivity, another important indicator of water quality, showed no significant changes between the influent (2467 µS/cm) and the effluents of both the WWTP secondary treatment (2132 µS/cm) and the lagoons after chlorination (2149 µS/cm). The stability of these values indicates consistent electrical conductivity throughout the treatment stages. While elevated electrical conductivity often indicates an increase in certain pollutants, especially organic compounds, the stability of these values suggests minimal alterations in the chemical composition of the treated water as it undergoes the different treatment phases [21]. From an agronomic perspective, maintaining consistent electrical conductivity levels is imperative. It suggests that the treatment processes are not introducing additional contaminants that could endanger crop health or soil quality. This stability is imperative, given the adverse effects sudden changes in electrical conductivity can impose on agricultural productivity, such as soil salinization, which can hinder plant growth and yield [22]. Although the consistency in electrical conductivity serves as a positive indicator of steady water quality, it also prompts further exploration. The need for additional investigation arises from the potential interactions and associated risks between elevated electrical conductivity levels and the presence of other contaminants.

The ORP values during the wastewater treatment highlight the role of oxidation in enhancing water quality. The negative value in the influent (−236 mV) indicates reducing conditions. This is common in raw wastewater, where the presence of organic matter and other contaminants can consume oxygen, creating an anaerobic or anoxic environment [23]. The transition to a positive value after secondary treatment (106 mV) suggests a shift toward more oxidizing conditions. Secondary treatment based on aerobic biological processes increases the redox potential by reducing the organic load through biological oxidation [23,24]. Although the ORP values decreased in the lagoon effluents, a subsequent increase to 149 mV post-chlorination indicates a further improvement in the oxidative conditions of the water. The decrease in the ORP values within the lagoons could be attributed to the accumulation of reduced substances resulting from incomplete biological processes. A higher ORP value at this stage demonstrates a greater oxidation capacity, which is favorable for the final elimination of pathogenic microorganisms, persistent organic compounds, and other contaminants [23,25].

The concentration of NH_4-N in the raw wastewater was relatively high (65.17 mg/L), suggesting a significant loading of ammoniacal nitrogen from the wastewater in the influent. During the secondary treatment, the concentration of NH_4-N decreased considerably to 19.23 mg/L. This indicates effective ammonium removal through biological processes such as nitrification. In the lagoons, the ammonium concentrations did not show significant changes compared to the secondary treatment; however, these concentrations remained relatively low compared to the influent. The concentration of NH_4-N in the final effluent after chlorination was 9.67 mg/L, indicating a further decrease in the ammonium concentration. Chlorination can contribute to the oxidation of residual ammonium and the formation of more stable nitrogen compounds [26].

In relation to NO_3-N, its concentration in the influent was relatively low (2.50 mg/L), suggesting that nitrate is a less predominant form of nitrogen compared to ammonium. However, during the secondary treatment, the concentration of NO_3-N significantly increased to 31.69 mg/L, and it subsequently decreased in the treatment lagoons (3.50 mg/L in L1 and 2.53 mg/L in L2). These fluctuations suggest active nitrification and denitrification processes occurring within this phase of the wastewater treatment. In the post-chlorination effluent, the concentration of NO_3-N increased to 12.75 mg/L. This elevation suggests that additional degradation of nitrogenous compounds occurred during chlorination; it is likely that chlorine oxidized the residual ammonium into nitrate, thus increasing the nitrate concentration [26]. While the calculation of the nitrate removal efficiency was not applicable due to the low concentration in the influent, it is notable that the nitrate concentrations formed during the secondary treatment decreased in the lagoon stages, and although they increased during chlorination, they remained lower than in the secondary treatment.

Regarding the remaining physicochemical parameters, including the COD, BOD_5, Total Nitrogen and Total Phosphorus, their concentrations decreased significantly with similar removal percentages throughout the WWTP process. After chlorination, the lagoon effluent resulted in final concentrations of COD, BOD_5, Total Nitrogen, and Total Phosphorus of 25 mg/L, 8 mg/L, 10 mg/L, and 1 mg/L, respectively, achieving elimination rates exceeding 86%. This analysis shows that the evaluated physicochemical parameters in the lagoon treatment, combined with chlorination, complied with the minimum quality requirements established in the UWWTD. However, a slight increase in some parameters, such as the Total Phosphorous and BOD_5, was observed between the secondary treatment effluent and lagoon effluents or after chlorination. The release of phosphorus from decomposing organic matter in sediments, especially under hypoxic conditions, alongside the metabolic activities of microorganisms, can contribute to an increase in the phosphorus levels in the lagoons [27]. Chlorination, although primarily used for disinfection, can also partially oxidize organic matter present in the effluent. This oxidation process may temporarily increase the BOD_5 levels. Lastly, the occasional release of microalgae or organic matter from lagoon sediment also further complicates the consistency of the BOD_5 measurements, highlighting the dynamic interactions within the treatment stages.

3.2. Micropollutants Results

The results of this study present a visual narrative that accentuates the concentration and elimination dynamics of 12 substances at the Cabezo Beaza WWTP, placing particular emphasis on the efficiency of removal after of the secondary treatment and maturation lagoon treatments. The compounds categorized under category 1, identified as pharmaceutical products, predominantly include antihypertensives, antidepressants, anti-inflammatory/analgesics, and an antibiotic, among others (Figure 3). The micropollutants with the highest influent concentrations were hydrochlorothiazide (3.00 µg/L), diclofenac (0.87 µg/L), and venlafaxine (0.75 µg/L). Following the removal treatment in the WWTP after the secondary treatment, they showed removal percentages of less than 67% (Figure 3a). Conversely, when treating these micropollutants with maturation lagoons (L1 + L2 + PC), their concentrations were significantly reduced ($p < 0.01$), achieving elimination rates exceeding 80%, except for venlafaxine, which showed reduction percentages around 50% in the lagoon treatment. The average concentration values of these micropollutants at the end of the lagoon treatment were 0.38 µg/L, 0.16 µg/L, and 0.36 µg/L, respectively (Figure 3b).

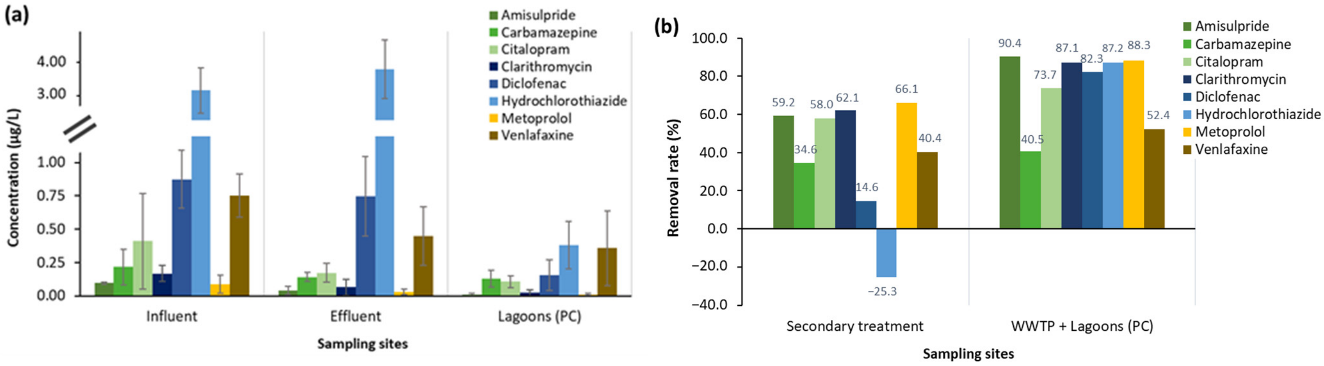

Figure 3. (**a**) Mean concentrations and (**b**) elimination percentages of micropollutants in category 1 from influent and effluent samples for both the WWTP secondary treatment and lagoon treatment, ($n \geq 5$).

The lowest concentrations in the influent correspond to the antihypertensive metoprolol (0.09 µg/L), the antipsychotic amisulpride (0.10 µg/L), and the antibiotic clarithromycin (0.41 µg/L). However, their removal percentages were around 60% in the WWTP secondary treatment and greater than 85% in the treatment with the lagoons. The final concentrations of these micropollutants in the lagoon effluent after chlorination were 0.01 µg/L, 0.02 µg/L, and 0.01 µg/L, respectively. Finally, the antidepressant pharmaceuticals, carbamazepine, and citalopram, exhibited concentrations of 0.22 µg/L and 0.41 µg/L in the influent, respectively (Figure 3a). In the secondary treatment of the WWTP, both substances showed low removal efficiencies, with percentages of around 50%. However, in the lagoon treatment after chlorination, the removal efficiency for citalopram was significantly higher, achieving values greater than 70% (Figure 3b).

Within category 2, the classification encompasses two pharmaceuticals, specifically the antihypertensive pharmaceuticals candesartan and irbesartan, in addition to two chemicals intended for industrial use, the anticorrosive compounds benzotriazole and methylbenzotriazole (Figure 4). Benzotriazole and irbesartan exhibited the highest concentrations in the WWTP influent, recorded at 5.94 µg/L and 3.22 µg/L, respectively (Figure 4a). Notably, these compounds also achieved the most significant ($p < 0.01$) removal efficiencies during the lagoon treatment (post-chlorination), reaching elimination rates of 70%. This contrasts with the outcomes from the secondary treatment ($p < 0.05$), where benzotriazole showed a 50% removal rate and irbesartan exhibited negative removal percentages. Conversely, the lowest initial concentrations were observed for methylbenzotriazole and irbesartan, at 0.34 µg/L and 1.54 µg/L, respectively. Despite these lower concentrations, their removal efficiencies were notably poor, not surpassing a 7% elimination rate and predominantly resulting in negative removal percentages (Figure 4b).

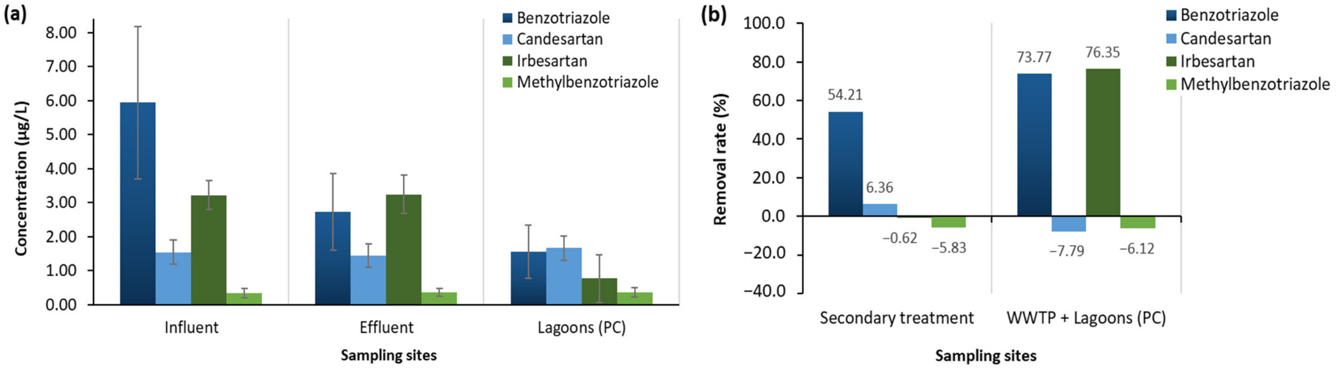

Figure 4. (**a**) Mean concentrations and (**b**) elimination percentages of micropollutants in category 2 from influent and effluent samples for both the WWTP secondary treatment and lagoon treatment ($n \geq 5$).

In essence, the antihypertensives hydrochlorothiazide, candesartan and irbesartan, along with the anticorrosive agent methylbenzotriazole, exhibited unusual behavior by demonstrating negative removal percentages. This behavior is primarily attributed to their higher concentrations observed in the effluent compared to the influent. This unusual phenomenon introduces significant uncertainties into the data analysis, exacerbated by the prevalence of values falling below the detection limit (limit of quantification, LQ). Moreover, the complexity of the influent matrix, often referred to as "matrix dirt", amplifies the LQ, potentially leading to the recording of negative removal efficiencies. These discrepancies are likely rooted in an underestimation of the interactions between the micropollutants and the wastewater matrix, particularly the solubility and sorption–desorption processes involving the wastewater solids and activated sludge [28]. Moreover, negative removal efficiencies in WWTPs could be attributed to the reversion of certain human or microbiological metabolites, such as conjugated pharmaceuticals (e.g., hydrochlorothiazide), back to their parent compounds. This can happen due to the presence of these metabolites in the influent or their formation within the collection system or biological process. This phenomenon is supported by the decrease in the metabolite concentrations in the influent and the reappearance of their original compounds in the effluent [29]. Such dynamics suggest that the observed negative removal rates may not accurately reflect the true behavior of these substances within the wastewater treatment system, underscoring the need for refined analytical methods to better understand and quantify these complex interactions [28].

In general, amisulpride and benzotriazole stand out as the best-performing compounds in categories 1 and 2, respectively. However, the substances in category 2 consistently showed predominantly negative elimination percentages, failing in every case to reach the desired 80% elimination threshold. This group, which includes benzotriazole, candesartan, irbesartan and methylbenzotriazole, presents a significant challenge due to their recalcitrant nature. The resistance of these compounds to removal in treatment processes is demonstrated by their consistently low elimination percentages, regardless of the treatment method used. This persistence can be attributed to the intrinsic physicochemical properties of the compounds, which hinder their degradability and/or their ability to adsorb on solid phases, thus impeding their removal in conventional treatment processes.

By conducting a correlation test with the initial quality indicators of the influent, which encompassed the physicochemical parameters, it was determined that the concentrations and elimination percentages of certain analgesics might be linked to specific conventional parameters in the influent. This study showed positive correlations for carbamazepine and diclofenac, and negative correlations for amisulpride and candesartan, with the concentrations of these pharmaceuticals and influent characterization parameters such as the suspended solids, BOD_5, and Total Phosphorus. This finding corroborates prior research conducted by references [30,31], which also observed similar correlations for diclofenac and carbamazepine. For other quality parameters, no statistically significant correlations were found with the initial influent concentrations.

Extending the analysis to the effectiveness of the Cabezo Beaza WWTP, particularly with the lagoon treatment, the pharmaceuticals characterized by high $LogK_{ow}$ values, such as diclofenac, irbesartan, and clarithromycin (as listed in Table 1), demonstrated effective removal. The specific physicochemical properties of these compounds (hydrophobicity and volatility), along with variations in the WWTP system (sludge retention time, hydraulic retention time, redox conditions, and pH), play a fundamental role in the efficiency of elimination processes [32,33]. This comprehensive approach, integrating the analysis of the pharmaceutical removal efficiency with the influent quality and treatment system variations, offers valuable insights into optimizing wastewater treatment processes for the effective elimination of micropollutants.

Furthermore, it is noteworthy that of the twelve substances identified in the recent directive, three were previously on the European Union's Watch List. Clarithromycin and diclofenac were listed according to the criteria set out in Implementing Decision established in 2015 [34]. However, the landscape changed in 2018 with the adoption of a new Implementing Decision [35], which determined that robust monitoring data existed for both substances, resulting in their removal from the Watch List [30]. In contrast, venlafaxine, with an acceptable upper limit of quantification set at 0.006 μg/L, remains under review, as evidenced by its inclusion in the most recent Implementing Decision Normative [36].

As shown in Figure 5, the removal efficiencies for the six micropollutants were significantly improved in both treatment methods. In particular, the lagoon treatment after chlorination successfully met the 80% removal target set by the UWWTD, in stark contrast to the WWTP secondary treatment process, which failed to meet this threshold. When the analysis was extended to include the average removal rates of 12 micropollutants, none of the treatment approaches assessed in this study achieved the 80% benchmark. It is also worth noting that the six micropollutants with the highest removal rates vary between different WWTPs, highlighting the variability in treatment efficiency between plants.

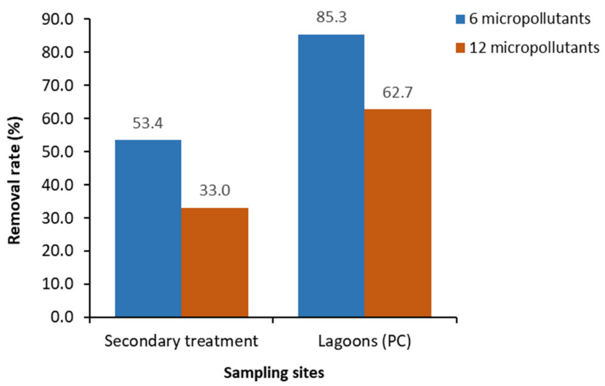

Figure 5. Average removal percentages of six and twelve micropollutants.

An essential aspect of this scheme is the detection of all 12 micropollutants in this WWTP, confirming their effectiveness as indicators. This highlights the advantage of analyzing a relatively small group of substances to ensure compliance with the Directive and to monitor the elimination of chemical pollutants. However, relying on a fixed set of six micropollutants as a standard for assessing the efficiency of wastewater treatment has significant limitations. Firstly, this approach assumes uniform removal behavior and characteristics for all the pollutants, which oversimplifies the complexity of wastewater matrices and the diversity of chemicals present. In addition, it may not adequately account for the variable occurrence of these contaminants in different geographical and operational settings. Finally, the effectiveness of treatment processes can vary significantly depending on the specific characteristics of each WWTP, such as the system design, treatment technologies applied and operating conditions. These variations suggest that a fixed set of micropollutants may not accurately represent the overall removal efficiency of a particular plant.

Alternatively, the inclusion of the Directive's maximum concentration limits for micropollutants in the effluent, together with the removal percentage, could provide a more comprehensive assessment of the quality of the treated water. This dual-criterion approach would consider both the absolute concentration of residual contaminants and the relative efficiency of their removal, providing a more thorough understanding of the environmental impact and potential risks to human health. In summary, while the detection of all the evaluated micropollutants in the WWTP underlines their value as indicators, it is important to recognize the limitations of relying solely on a fixed set of substances to assess the treatment efficiency. By integrating both the removal efficiency and the concentration limits of micropollutants in the effluent, stakeholders can obtain a more nuanced assessment of the treatment performance. This facilitates informed decision-making for environmental protection and public health preservation.

The evolution of wastewater treatment regulations, exemplified by the transition from Directive 91/271 to newer standards, underscores the need for more advanced treatment methods to tackle emerging challenges, particularly in relation to micropollutant removal. While secondary and tertiary treatments have historically sufficed, they fall short of meeting the stringent requirements of the new Directive. Consequently, quaternary treatments, such as membrane filtration, advanced oxidation, and adsorption techniques, are becoming imperative. However, all the mentioned treatments require the optimal functioning of the previous biological treatments, including tertiary treatments for the elimination of solids and nutrients [7,37]. Despite their efficacy, quaternary treatments pose significant limitations, including high operating costs, limited scalability, and potential environmental concerns. For instance, advanced oxidation processes, particularly ozone treatment, exhibit notable energy consumption and the formation of harmful by-products like N-Nitrosodimethylamine and bromates (BrO_3^-). These by-products, with their associated toxicity and carcinogenicity, necessitate additional measures to the mitigate risks [38].

This study highlights the potential of lagooning as a key advancement in the field of water treatment. Artificial wetlands emerge as exemplars of environmental stewardship. They delineate a treatment modality that effectively combines efficiency with environmental sustainability. Their ability to significantly reduce the presence of micropollutants in aquatic environments, coupled with their operation under the principles of reduced energy consumption and minimalistic waste generation, signals a new epoch in the pursuit of sustainable water management strategies. The observed micropollutant removal efficiency, exceeding the 80% threshold, represents a significant milestone and indicates a substantial advance in improving water quality. This quaternary treatment option is not solely focused on large-capacity WWTPs. For smaller WWTPs, which typically handle capacities under 10,000 h-e, implementing advanced quaternary treatments may not be necessary. Lagoons could be especially suitable for rural areas because they require less mechanical infrastructure and are more adaptable to the varying flow and load conditions typical of these regions. This makes them a cost-effective solution for managing pollutants in areas where advanced technologies might be impractical.

While these results are promising, enthusiasm must be tempered. They serve as a preliminary endorsement of lagooning as a viable quaternary treatment method but also highlight the need for further empirical investigation. The quest for formal recognition of lagooning as a valid quaternary treatment method is still in its infancy. It is imperative that subsequent research efforts are directed toward confirming these initial findings. Such efforts are essential not only to validate the efficacy of lagooning as a treatment process but also to ensure its adaptability and scalability in different ecological and geographical contexts.

3.3. Lagoons as a Quaternary Treatment

This study has shown a decrease in micropollutants in the effluents from the lagoons (post-chlorination), underscoring the efficacy of this treatment step. Moreover, the influence of chlorine on the degradation of certain contaminants is notable, particularly affecting the physicochemical parameters and their final concentrations. At the same time, other studies corroborate the effect of chlorination on micropollutants, as evidenced by the by-products that form in chlorinated water [39]. However, these studies report minimal concentrations of such by-products and suggest that factors beyond chlorination alone may contribute to their formation [39,40]. In this context, this study directly evaluated the effluents used for irrigation, specifically the lagoon effluents after chlorination. However, this research did not strictly focus on the effects of chlorination on micropollutants.

Building on these findings, according to the results of this study and the external literature, it becomes apparent that lagoons harbor a complex interplay of physical, chemical, and biological processes that contribute to the removal of micropollutants. The capacity of lagoons to serve as a quaternary treatment stems from their ability to offer supplementary ecosystem services such as nutrient retention and the establishment of a conducive environment for natural processes. [12]. Specific enzymes play an important role in catalyzing the transformation of polluting compounds into less harmful substances or intermediate products [13], which can either be assimilated by other aquatic organisms or mineralized in the environment [12,41]. Notably, autotrophic ammonium-oxidizing bacteria play a significant role in the degradation of various micropollutants, such as trimethoprim, ibuprofen, and diclofenac, among others. The biodegradation rate of these substances is directly related to the concentration of the ammonium substrates in the water, underscoring the critical influence of these bacteria on the efficacy of the decomposition process [42,43]. The inherent ability of microorganisms to degrade such pollutants underlines their importance in improving water quality in lagoons and emphasizes the need to cultivate robust microbial communities for efficient pollutant degradation.

Algae and microalgae can play a pivotal role in the phytoremediation of micropollutants, heavy metals, and other organic compounds by absorbing and accumulating these substances through biosorption and bioaccumulation processes [44]. These organisms release organic exudates that serve as a substrate for microbial activity, thereby promoting the decomposition of contaminants through biodegradation processes. Certain algae species can secrete specific enzymes, facilitating the degradation of polluting compounds, while others contribute to nutrient fixation, thereby limiting the availability of these elements. The photosynthesis conducted by algae and microalgae can also indirectly influence the decomposition of micropollutants by affecting the redox conditions of the water, creating an environment conducive to chemical transformation processes [44,45]. In general terms, biodegradation processes, principally orchestrated by a consortium of bacteria, algae, and other aquatic organisms, transform complex chemical compounds into less toxic molecules through catalytic metabolic deterioration [46,47]. These processes represent an effective and efficient method for the removal of micropollutants. While biodegradation stands as a significant mechanism, it is fundamental to acknowledge that elevated concentrations of micropollutants, particularly pharmaceuticals, in conjunction with organic contaminants and their interactions with microbiological contaminants, may exert an influence on the growth and functionality of the involved organisms [47,48].

According to external studies, the degradation of contaminants in water bodies is influenced not only by biological processes but also significantly by abiotic mechanisms in the aquatic environment. Various abiotic factors, such as solar radiation, water temperature, and the presence of oxygen, play key roles in the chemical and physical decomposition of contaminants [43]. Solar radiation emerges as a determining factor since exposure to ultraviolet light can initiate photochemical reactions capable of decomposing specific organic pollutants. Sunlight exposure in lagoons is influenced by factors such as the water depth and clarity, seasonal variations, and environmental conditions [11]. However, the samples in this study were taken from a few meters deep, which corresponds to the upper photic zone, which suggests that solar light could have a direct, significant impact [49]. Additionally, the absence of preferential currents promotes uniform mixing, enhancing the exposure of suspended particles and microcontaminants to intense solar radiation in the lagoon's upper layer.

The water temperature significantly influences chemical reactions, with acceleration observed at higher temperatures, thus promoting the decomposition of contaminants [50]. In the context of Spain, the Murcia Region exhibits a Mediterranean climate, with hot summers and mild winters, where temperatures frequently surpass 30 degrees Celsius in summer [51]. In contrast to regions with milder climates, this climatic feature has notable implications for both natural and non-natural processes in contaminant treatment within water bodies [50]. Lastly, oxygen availability plays an important role in abiotic decomposition, with processes like chemical oxidation being capable of degrading organic compounds in the absence of living organisms [43,50]. Understanding these climate-induced variations is essential for optimizing water treatment approaches, especially in regions like the Murcia Region, where climatic and weather variations can significantly impact the treatment process efficiency.

Based on external studies, among other abiotic processes that occur in aquatic environments, natural sedimentation stands out as a fundamental mechanism when evaluating contaminant removal processes. This efficient system captures and precipitates undesirable particles as water gradually flows through lagoons at a reduced rate, creating a natural filtration system [10,52]. Moreover, sedimentation enhances the adsorption of chemical contaminants onto suspended particles, contributing to a higher efficiency in contaminant removal [10]. The interaction between settled particles and dissolved contaminants encourages the formation of larger aggregates, which eventually settle to the bottom of the water bodies, simplifying their subsequent removal [53].

Considering these abiotic mechanisms is essential to understand the full dynamics of contaminant degradation in natural waters. However, it is crucial to recognize that the interaction between abiotic and biotic mechanisms is complex and synergistic. Biological activities, such as photosynthesis by microorganisms and even the possible existence of aquatic plants, have the potential to alter abiotic conditions by influencing oxygen concentrations and nutrient availability [54,55].

Given these abiotic and biotic interactions and the results reported in this study, the use of lagoons as a treatment method appears to be an alternative to recently developed quaternary approaches, which have shown limited effectiveness in removing pollutants from wastewater. For example, certain advanced oxidation treatments, such as ozonation, may render certain pollutants more hazardous when in contact with ozone or lead to the formation of by-products with more pronounced toxic properties than the original pollutant [38,56]. It is important to note that in this study, chlorination was used as the final step in the treatment of the lagoon effluents. However, it is also recognized that chlorine can generate disinfection by-products. Therefore, future research aims to include a final treatment step that is less invasive and ensures compliance with appropriate microbiological and water quality standards for irrigation. While chlorination by-products are extensively studied and regulated to limit their concentrations in water, thereby mitigating the associated risks, managing less common disinfection by-products that occur in advanced treatments remains an important challenge. This emphasizes the need to integrate additional processes to eliminate the newly formed transformation products, resulting in increased energy and operating costs for the treatment system [56,57].

In addition to being efficient at degrading micropollutants like other treatment technologies, lagoons also act as valuable ecosystems. The Cabezo Beaza lagoons are home to a wide variety of waterbirds, with around 30 species regularly visiting throughout the year, particularly those listed in national and international conservation appendices. This wetland acts as a vital foraging habitat for these birds, playing a key role in the conservation of ecologically important species [58]. Integrating such natural ecosystems, such as the Cabezo Beaza lagoons, into wastewater treatment projects could provide synergistic benefits by not only treating pollutants but also providing ecological support. This contributes to a more sustainable approach to water management.

4. Conclusions

Extensive research was carried out to assess the impact of the Cabezo Beaza wastewater treatment plant and the implementation of maturation lagoons in the Murcia Region, Spain. This study focused on the reduction of micropollutants, particularly the 12 substances listed in the new Urban Wastewater Treatment Directive. Notably, some of these substances have also been included in the EU Watch List (2022). The analysis revealed a significant improvement in the removal efficiency of the WWTP following the quaternary treatment. This improvement was particularly notable with the integration of the maturation lagoons and chlorination as the final step. This highlighted the significant differences in micropollutant removal between the WWTP secondary treatment and the inclusion of maturation lagoons. In particular, the final effluent after the lagoon treatment (post-chlorination) showed removal rates above 80% for most of the individual compounds assessed in this study. Moreover, the collective average elimination rate for the six substances with the highest percentages (amisulpride, metoprolol, hydrochlorothiazide, clarithromycin, diclofenac, and citalopram) met the 80% threshold required by the recent Directive. It is worth noting that the Directive's criteria, which require consideration of at least six micropollutants from the list, may not fully capture the variability in elimination efficiencies, operating conditions, and the presence of certain micropollutants in different WWTPs. This suggests the need for a more nuanced approach to ensure comprehensive assessment and effective management of water quality in wastewater treatment processes.

While this first indication suggests that lagoons have the potential to reduce contaminant levels, it is important to recognize that widespread implementation of lagoons as quaternary treatment is not yet fully established. The complexity of the biotic and abiotic mechanisms involved highlights the need for further research to fully understand the dynamics of these systems. Additionally, more research is needed to support these findings and explore the adaptability and scalability of lagooning in various ecological and geographical contexts. Despite the uncertainties, lagoons present an attractive option that deserves further consideration and evaluation in forthcoming wastewater treatment projects, with the objective of progressing toward sustainable and efficient solutions in water management.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/environments11060105/s1, Table S1: Final data for various samples from the influent, secondary treatment effluent, and lagoon effluent (post-chlorination). Data include the limit of quantification (LQ).

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