



Memory Final Degree Project

EVALUATION OF THE CHEMICAL RISK IN DRINKING WATER TREATMENT PLANT

Figueres Drinking Water Treatment Plant

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RESUM

Garantir aigua potable segura i accessible és un objectiu crucial de salut pública a tot el món. Les plantes de tractament d'aigua potable (EPAT) tenen un paper fonamental en aquesta missió tractant l'aigua bruta per complir els estàndards de seguretat. Tanmateix, el canvi climàtic està provocant esdeveniments meteorològics més freqüents i greus, com ara sequeres i inundacions, que poden comprometre la qualitat de les fonts d'aigua bruta. Les sequeres redueixen la disponibilitat d'aigua i augmenten les concentracions de contaminants, mentre que les inundacions poden contaminar les fonts d'aigua amb patògens i productes químics. Aquestes condicions requereixen un procés de tractament més robust i adaptable per mantenir la seguretat de l'aigua.

Per abordar aquests reptes, les EDAR han d'adoptar tecnologies de tractament resistents que puguin eliminar eficaçment els contaminants en condicions canviants. Aquestes tecnologies inclouen processos avançats d'oxidació, filtració per membrana i l'ús de desinfectants alternatius, l'estudi se centra en tècniques avançades d'oxidació de l'ozó. Aquests mètodes estan dissenyats per gestionar una àmplia gamma de qualitats de l'aigua i es poden ajustar per satisfer les condicions canviants causades pel canvi climàtic. Les tecnologies de tractament resilients són essencials per adaptar-se a aquests canvis i garantir el subministrament continu d'aigua potable. La tesi final consisteix a avaluar la tècnica avançada d'oxidació mitjançant ozó a la Planta de Tractament d'Aigua Potable de Figueres. Això implica identificar contaminants potencials, avaluar el seu impacte en la qualitat de l'aigua i determinar l'eficàcia dels mètodes de tractament existents. L'estudi pretén destacar les àrees on calen millores i suggerir estratègies per millorar la resiliència dels processos de tractament.

En conclusió, aquesta tesi subratlla la importància de les tecnologies de tractament resilients per garantir l'aigua potable segura i accessible enmig dels reptes que planteja el canvi climàtic. Mitjançant l'avaluació dels riscos químics i la proposta d'estratègies adaptatives, l'estudi contribueix als esforços en curs per protegir la salut pública mitjançant pràctiques fiables de tractament de l'aigua.

RESUMEN

Garantizar agua potable segura y accesible es un objetivo crucial de salud pública en todo el mundo. Las Plantas de Tratamiento de Agua Potable (ETAP) juegan un papel fundamental en esta misión al tratar el agua cruda para cumplir con estándares de seguridad. Sin embargo, el cambio climático provoca fenómenos meteorológicos más frecuentes y severos, como sequías e inundaciones, que pueden comprometer la calidad de las fuentes de agua cruda. Las sequías reducen la disponibilidad de agua y aumentan las concentraciones de contaminantes, mientras que las inundaciones pueden contaminar las fuentes de agua con patógenos y productos químicos. Estas condiciones requieren un proceso de tratamiento más robusto y adaptable para mantener la seguridad del agua.

Para abordar estos desafíos, las ETAP deben adoptar tecnologías de tratamiento resilientes que puedan eliminar eficazmente los contaminantes en condiciones cambiantes. Estas tecnologías incluyen procesos de oxidación avanzados, filtración por membrana y el uso de desinfectantes alternativos; el estudio se centra en técnicas avanzadas de oxidación del ozono. Estos métodos están diseñados para gestionar una amplia gama de calidades de agua y pueden ajustarse para satisfacer las condiciones cambiantes causadas por el cambio climático. Las

tecnologías de tratamiento resilientes son esenciales para adaptarse a estos cambios y garantizar el suministro continuo de agua potable.

El trabajo final de carrera consiste en evaluar la técnica avanzada de oxidación mediante ozono en la Planta Depuradora de Agua Potable de Figueres. Esto implica identificar contaminantes potenciales, evaluar su impacto en la calidad del agua y determinar la efectividad de los métodos de tratamiento existentes. El estudio tiene como objetivo resaltar áreas donde se necesitan mejoras y sugerir estrategias para mejorar la resiliencia de los procesos de tratamiento.

En conclusión, este trabajo de fin de grado subraya la importancia de las tecnologías de tratamiento resilientes para garantizar agua potable segura y accesible en medio de los desafíos que plantea el cambio climático. Al evaluar los riesgos químicos y proponer estrategias de adaptación, el estudio contribuye a los esfuerzos continuos para proteger la salud pública a través de prácticas confiables de tratamiento del agua.

ABSTRACT

Ensuring safe and accessible drinking water is a crucial public health objective worldwide. Drinking Water Treatment Plants (DWTP) play a fundamental role in this mission by treating raw water to meet safety standards. However, climate change leads to more frequent and severe weather events, such as droughts and floods, which can compromise the quality of raw water sources. Droughts reduce water availability and increase contaminant concentrations, while floods can contaminate water sources with pathogens and chemicals. These conditions require more robust and adaptable treatment process to maintain water safety.

To address these challenges, DWTPs must adopt resilient treatment technologies that can effectively remove contaminants under changing conditions. These technologies include advanced oxidation processes, membrane filtration, and the use of alternative disinfectants, the study focuses on advanced ozone oxidation techniques. These methods are designed to manage a wide range of water qualities and can be adjusted to meet changing conditions caused by climate change. Resilient treatment technologies are essential to adapt to these changes and ensure the continuous supply of drinking water.

The final degree project is to evaluate the advanced technique oxidation using ozone in the Drinking Water Treatment Plant of Figueres. This involves identifying potential contaminants, assessing their impact on water quality, and determining the effectiveness of existing treatment methods. The study aims to highlight areas where improvements are needed and suggest strategies to improve the resilience of treatment processes.

In conclusion, this final degree project underscores the importance of resilient treatment technologies to ensure safe and accessible drinking water amid the challenges posed by climate change. By assessing chemical risks and proposing adaptive strategies, the study contributes to ongoing efforts to protect public health through reliable water treatment practices.

REFLECTION ON ETHICS

The use of ozone as a pre-oxidant in drinking water treatment is becoming increasingly common (Siddiqui, 1997). It is important to take responsibility for conducting studies on how to evolve these techniques and improve our lives. Personally, articles from other authors have been used, with proper citation to avoid plagiarism and respect intellectual property. Moreover, there has been a conscious effort to ensure transparency in data manipulation, avoiding image falsification, and ensuring the reproducibility of experiments. The use of other reference works for data analysis has also been acknowledged, with proper citations throughout the work.

REFLECTION ON SUSTAINABILITY

Nowadays, we suffer a significant effect: climate change. It is an important challenge that we must live and address to prevent further damage, as rising temperatures and drought periods affect water quality. In our work, we conducted analyses and methods because the waste management generated was, for solid waste, plastic syringes and filters. On the other hand, the liquid waste treated included water and small amounts of ascorbic acid, sodium hypochlorite, and hydrochloric acid. To avoid creating a small impact and not polluting part of the environment by pouring these wastes down the drain, they were disposed of in the appropriate containers.

REEFLECTION ON GENDER PERSPECTIVE

Science and research often reflect gender biases and stereotypes that can influence how research questions are formulated, how data is collected, and how results are interpreted. These biases can perpetuate inequalities and limit the full participation of women in science. Additionally, the wage gap demotivates women and reflects an unequal valuation of their work, while impostor syndrome causes many women to doubt their abilities, limiting their opportunities. Addressing these issues and promoting a supportive environment is crucial for more inclusive and representative research. By fostering diversity and equity in scientific fields, we can enhance innovation, improve research outcomes, and ensure that all voices are heard and valued.

1. INTRODUCTION

1.1 Access to safe water

Water is an essential resource for life, health and human development. Access to clean and safe drinking water is not only a necessity but also a fundamental right recognized by the United Nations (Gleick, 1998). Without access to safe water, the risks to human survival and quality of life are immediate and severe. Despite technological advances and improvements in water resource management, significant challenges remain in ensuring this right for everyone (Sorenson, 2011).

Human activities have significantly altered the characteristics of water resources, leading to contamination levels that render the water unfit for human consumption. To ensure that water is of highly quality and free from pathogenic microorganisms, toxic substances, and harmful agents, it must undergo proper treatment processes. This ensures that the water meets safety standards and is safe for human consumption (Chulluncuy, 2011). Quantity, quality, and continuity are the three fundamental requirements for companies involved in drinking water management. Water is a scarce and essential resource for life and must be managed appropriately to ensure its reasonable use and sustainability.

In global initiatives, recognizing these critical issues, the United Nations has made access to clean water a global priority through the Sustainable Development Goals (SDGs), specifically SDG 6, (United Nations, 2024) which aims to ensure availability and sustainable management of water and sanitation for all by 2030. Achieving this goal requires substantial investment in infrastructure, technology, and education to improve water quality and accessibility. Environmental sustainability is also a crucial aspect of ensuring long-term access to clean water. Over-extraction of groundwater, pollution of water bodies and climate change pose significant threats to water availability. Sustainable water management practices, such as protecting natural water sources, reducing pollution and implementing water-saving technologies, are essential to address these challenges. Integrating these practices into national policies and local management strategies is key to securing water resources for the future generations. (Gleick, 1998).

1.2 Drinking Water Treatment Plants (DWTPs)

In order to ensure the correct quality of water for the consumer, free of pathogenic microorganisms, toxic substances and harmful to health, it undergoes potable treatment in Drinking Water Treatment Plants (DWTPs). Drinking water treatment is the physical-chemical process of removing various contaminants and microorganisms that pose a risk to human health or give the water an unfavourable organoleptic look or quality. This ensures that all customers receive high quality water (Rietveld, 2010).

The stages of the water treatment process can be affected by a variety of circumstances. Research has indicated that the supply of surface water has been affected by climate change, and there have also been quality changes (Arheimer 2005). This feature has made managing drinking water more challenging, as has Catalonia's location in the Mediterranean region, where there are few and erratic precipitation.

1.2.1 Drinking water treatments

The selection of treatment processes at any Drinking Water Treatment Plant (DWTP) is heavily influenced by the quality and the quality of the incoming water. Depending on the origin of the water source the DWTPs could face different situations. Surface water sources, such as reservoirs often have different characteristics compared to rivers. Reservoirs function somewhat like large-scale settling tanks, where the water has a chance to become relatively clean due to the sedimentation of particulates over time. This natural process helps in improving the initial quality of the water, making it generally cleaner than water from rivers, which are subject to constant movement and potential contamination from various sources (Müller, 2012). Below are the main treatment processes carried out in a DWTP (Gibert, 2015):

a) Pre-oxidation

Pre-oxidation is the first step in many water treatment plants, especially when the raw water contains high concentrations of organic and inorganic matter. This stage uses oxidizing agents such as ozone, chlorine, sodium hypochlorite or potassium permanganate to break down contaminants, enhancing the efficiency of subsequent processes. The choice of oxidant depends mainly on the type and concentration of contaminants. For example, ozone is highly effective at breaking down organic compounds and certain inorganic contaminants like iron and manganese. Chlorine and sodium hypochlorite are commonly used for disinfection purposes and to control biological growth. Pre-oxidation also helps control taste, odour and compounds that can form harmful disinfection by-products during treatment (Rajagopaul, 2008).

b) Coagulation and flocculation

After pre-oxidation, the water undergoes coagulation and flocculation stages. This stage is crucial in drinking water treatment for several key reasons such as impurity removal, efficiency, versatility, public health and regulatory compliance. During coagulation, coagulants (such as aluminium sulphate or ferric chloride) are added to the water to neutralize the electrical charges of suspended particles, allowing them to aggregate into larger flocs. Flocculation is a mechanical process where the water is gently stirred to facilitate the formation of larger and denser flocs that can be more easily removed during sedimentation (Korshin et al, 2009).

c) Sedimentation

In the sedimentation stage, the flocculated water is introduced into large tanks where the heavy flocs settle to the bottom by gravity, separating from the clarified water that remains at the top. This stage removes a significant number of suspended particles and organic matter, reducing the contaminant load that needs to be treated in subsequent stages.

d) Filtration

Filtration is a crucial stage in the water treatment process. The clarified water passes through filters made up of layers of sand, gravel and activated carbon. These filters remove any remaining particles, including bacteria, viruses and other microorganisms. Activated carbon is particularly effective in removing organic compounds and chemicals that can affect the taste and odour the water (Sánchez, 2006). There are different types of activated

carbon are used for this stage. So, depending on those characteristics we can define the Granular Activated Carbon (GAC), Powdered Activated Carbon (PAC), and Extruded Activated Carbon (EAC).

e) Disinfection

Disinfection is the final essential step to ensure that the water is safe for human consumption. Disinfectants such as chlorine, chlorine dioxide, ozone or sodium hypochlorite added to eliminate any pathogenic microorganisms that may have survived the previous processes. The dosage of the disinfectant and the contact time are carefully controlled to ensure the effectiveness of the process without forming several amounts of harmful by-products.

1.3 Sustainability and climate change

Sustainability in water resource management is a critical challenge, especially in the context of climate change. Climate change impacts, such as altered precipitation patterns, increased temperatures and the frequency of extreme weather events like droughts and floods, significantly affect water availability and quality. These changes pose substantial risks to the reliability of water supplies and the effectiveness of traditional water treatment processes (Arheimer, 2005). To address these challenges, water treatment plants must adopt sustainable practices that not only enhance their operational efficiency but also minimize their environmental footprint. This includes reducing energy consumption, utilizing renewable energy sources, optimizing chemical usage, and implementing advanced technologies that are more resilient to climate variability. (Wu, 2015).

Furthermore, sustainable water management practices must also involve protecting and restoring natural water sources, reducing pollution, and promoting water conservation. This holistic approach ensures that water treatment plants can continue to provide high quality water even as environmental conditions change (Cosgrove, 2015). By adopting these sustainable practices, water treatment plants can better cope with the impacts of climate change, ensuring a reliable supply of safe drinking water for future generations. Integrating sustainability into every aspect of water treatment operations is essential for building a resilient and secure water future.

1.4 Resilient treatments

The increasing impacts of climate change, including shifts in precipitation patterns, rising temperatures, and more frequent extreme weather events, directly affect the quality of raw water sources. These changes can lead to fluctuations in the levels of contaminants, making the treatment process more challenging. To maintain the quality of treated water, treatment plants must implement resilient treatment methods that can adapt to these variations without compromising the final water quality (Skwaruk, 2021).

One example of resilient treatment is the ability to modify coagulation processes: Coagulation is critical for removing particulate matter and organic compounds from water. By adjusting coagulant types and dosages in response to changing water quality, treatment plants can effectively manage varying contaminant loads. For example, during periods of high turbidity or organic content, increasing the coagulant dosage can help maintain effective removal rates (Fiksel, 2003).

Advanced Oxidation Processes (AOPs) represent another set of resilient treatments that can address emerging contaminants and improve overall water quality. AOPs use powerful oxidants such as ozone, hydrogen peroxide and ultraviolet light to break down complex organic molecules that are resistant to conventional treatment methods. These processes are particularly effective against pharmaceuticals, endocrine-disrupting compounds and other micropollutants that can pose risks to human health. Additionally, integrating membrane technologies, such as ultrafiltration and reverse osmosis, into the treatment train can enhance resilience (Djebou, 2016). These technologies provide robust barriers against a wide range of contaminants, ensuring consistent water quality even when raw water conditions fluctuate significantly.

Incorporating **real-time monitoring** and adaptive management systems further enhances the resilience of water treatment plants. These systems allow operators to continuously monitor water quality parameters and adjust treatment processes dynamically in response to detected changes. This proactive approach ensures that treatment plants can swiftly respond to unexpected variations in water quality, maintaining the safety and reliability of the water supply (Kamyab, 2023).

Finally, by adopting resilient treatment strategies, water treatment plants can effectively navigate the challenges posed by climate change and other environmental stressors. These strategies ensure that the quality of treated water remains high, safeguarding public health and meeting regulatory standards, regardless of variations in raw water conditions. (Nwokediegwu, 2024)-

1.4.1 Ozone chemistry

Chemically, ozone acts as a powerful oxidant. When it comes into contact with contaminants, it oxidizes them, breaking down complex organic molecules into simpler, less harmful compounds, oxidizing heavy metals into more easily removable forms and destroying microorganisms. This figure (see Figure 1) illustrates the effects of ozone in drinking-water treatment. Disinfection and oxidation can occur simultaneously if ozone reactions are responsible for the oxidation. However, if compounds resistant to ozone need to be oxidized, ozone must be converted into OH radicals. This conversion decreases disinfection efficiency. Therefore, optimizing disinfection and oxidation necessitates a careful evaluation of the overall process. (Manasfi, 2021). Ozone can act through direct oxidation, breaking down organic pollutants and pathogens by disrupting their molecular structures. Additionally, ozone generates hydroxyl radicals ('OH), which are more reactive than the ozone molecule itself, in a process known as indirect oxidation (Duan, 2021).

However, it is crucial to eliminate residual ozone before the water is distributed for consumption. Residual ozone can be harmful if ingested and may affect the taste and odour of the water. Therefore, several methods are employed to remove it, ensuring the water is safe and palatable. One common method for removing residual ozone is aeration, allowing the ozone to decompose naturally into oxygen. This process is effective due to the unstable nature of ozone. Another method involves passing the water through activated carbon filters, which absorb and eliminate the ozone residuals and helps to remove other organic compounds.

The use of ozone in water treatment is highly effective in eliminating a broad spectrum of contaminants and microorganisms and acts more rapidly than other disinfection methods. Furthermore, ozone does not leave

harmful chemical residues after its decomposition. However, the equipment required for generating and applying ozone can be costly, and precise monitoring and control are necessary to ensure the complete removal of residual ozone (Rougé, 2020).

In conclusion, ozone is a highly effective tool for disinfecting and purifying drinking water. Its ability to remove a wide range of contaminants quickly and efficiently makes it a valuable component of water treatment processes. By employing appropriate methods to eliminate residual ozone, water treatment plants can ensure the safety and quality of the water supply, safeguarding public health and meeting regulatory standards.

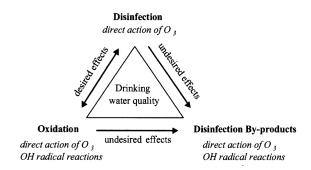


Figure 1: Schematic representations of the effects of ozone in drinking water treatment. (Manasfi, 2021)

2. OBJECTIVES

The main objective of this study is the evaluation of the treatment process in a Drinking Water Treatment Plant (DWTP) situated in Figueres, focusing on the characterisation of the chemical risks associated to the different treatments.

The specific objectives are as follows:

a) To assess the impact of ozone treatment on chemical water quality.

Evaluates the role of pre-oxidation with ozone in improving water quality and involves assessing the effectiveness of the current treatment processes in reducing chemical contaminants in raw water. The evaluation will be conducted using several indicators such as the measurement of the effectiveness of ozone pre-oxidation in reducing specific contaminants, assess the overall impact on the chemical quality of water and assess the ultraviolet absorbance at 254 nm (UV254) and the Excitation and Emission Matrixes (EEM).

b) To evaluate the efficacy of treatment in reducing chemical risks in reclaimed water.

This objective focuses on assessing how effectively the current treatment processes reduce chemical risks in reclaimed water, specifically looking at the potential for trihalomethane potential formation (THM-FP). Evaluating THM-FP will provide insights into the effectiveness of the overall treatment process and help identify areas for improvement to reduce chemical risks in the treated water.

c) To study the effects of dry periods on water quality.

This objective focuses on understanding how dry periods and changes in reservoir conditions impact the quality of the raw water and the associated chemical risks. During dry periods, water levels in reservoirs can drop, leading to increased concentrations of contaminants and changes in water chemistry. The findings will provide insights into how climate variability and reservoir management practices affect water quality and inform strategies for mitigating these impacts.

3. METHODOLOGY

3.1 Study case: Figueres DWTP

Figueres de Serveis SA (Fisersa) is a multi-municipal company that directly manages various services. The company is responsible of the treatment and supply of drinking water to Figueres and surrounding areas, among others. The DWTP is situated in Girona, in the northeast of Catalonia, at the highest point in the city of Figueres (see Figure 2). The plant draws surface water from the Boadella-Darnius reservoir, which has a maximum capacity of 62 hm³ and is currently at 22,91% of its capacity. This reservoir is located on the lower valley of the Arnera river, which is a tributary of the Muga river, with both rivers feeding into the reservoir (Fisersa, 2024).



Figure 2: Geographic situation of Figueres DWTP and reservoir Boadella-Darnius, (own source).

The Figueres DWTP treats a maximum flow of 0,25 m³/s with a maximum hydraulic intake of 0,30 m³/s. The treatment process at the Figueres Drinking Water Treatment Plant consists of seven stages (See Figure 3):

- 1. Water intake: Capturing water from the reservoir Boadella–Darnius.
- 2. **Ozonation:** Applying ozone for pre-oxidation for Natural Organic Matter (NOM) removal, colloidal particles and macromolecules elimination and improving the performance of coagulation-flocculation and even the sedimentation stage.
- 3. Coagulation-Flocculation: Adding coagulants to aggregate small particles into larger flocs.
- 4. Sedimentation: Allowing the flocs to settle, separating from the clarified water.
- 5. Activated Carbon Filtration: Passing the water through activated carbon filters to remove remaining organic contaminants and improve taste and odour.

- 6. UV Disinfection: Using ultraviolet light to disinfect the water by deactivating harmful microorganisms.
- 7. Final disinfection with sodium hypochlorite (NaClO): Adding sodium hypochlorite to ensure the water remains disinfected throughout the distribution system.

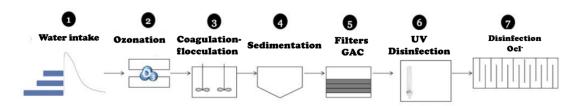


Figure 3: Treatment train of Figueres DWTP (adapted from Laura Ferràndez master's final thesis).

The treatment train at the Figueres DWTP begins with a shared ozonation unit with a capacity of 576 m³. This is followed by two coagulation units and two flocculation units, which are used according to demand and alternated each month. After the coagulation-flocculation process, line 1 contains six sedimentation tanks. The older sedimentation tanks are funnel-shaped, approximately 7 meters deep, with a maximum flow rate of 0.015 m³/s each. In contrast, the two newer sedimentation tanks are 4 meters deep. In these tanks, water is introduced in pulses rather than continuously, which enhances sedimentation. All sedimentation tanks are equipped with lamella systems that help retain organic matter flocs on the walls as the water ascends, allowing the formed sludge to settle. The plant also has eight filters where the water passes through a material called Granular Activated Carbon (GAC). The activated carbon primarily performs an adsorption process, where compounds that could impart unpleasant taste and appearance to the water adhere to the carbon. These filters have capacities of 32,7 m³ and 17.6 m³. Finally, the water, once filtered, is unified from the eight activated carbon filters, and undergoes disinfection processes using ultraviolet (UV) radiation and sodium hypochlorite disinfection.

3.2 Real Plant Sampling

Weekly visits were conducted to the Figueres DWTP to observe and understand the various unit processes involved in water treatment and the methods used for sampling water characteristics. Accompanied by the plant operator, each visit included a detailed examination of the treatment processes and the collection of water samples from key points in the treatment train. The different sampling points were:

- Plant Inlet: The raw water entering the treatment plant.
- **Post-Ozonation:** After the ozone pre-oxidation process.
- Sedimentation tanks: water from the sedimentation tanks
- Filters: Water after passing the activated carbons filters.
- Unified filter Outlet: the filtrated water combined without disinfection step.

For the **sampling procedure**, amber-coloured glass bottles of 1 L capacity, properly labelled, were used for collecting the samples and a portable cooler was employed to transport the samples. Additionally, a 25 L container was used to collect raw water sample from the plant inlet for further laboratory analysis at the University facilities. The maximum time allowed for analysing the samples was three days and during this

period, the samples were preserved at a temperature between 5 and 10°C. This systematic approach to real plant sampling ensured comprehensive monitoring of water quality throughout the treatment process, providing valuable data to assess and optimize the plant's operations.

3.3 Set-up of pre-oxidation with ozone

Among all the treatment processes carried out at the Figueres DWTP, special attention is given to the ozonation stage since is one of the primary objectives of this study is understanding how this <u>oxidation process</u> with ozone is effective in eliminating organic and inorganic contaminants.

3.3.1 Ozone generation

The conditions as well as the applications requires an optimal arrangement to be developed for the experiments and ozone generation. The first step is ozone must be produced in-situ as ozone is a highly aggressive and unstable oxidant. A further 30 L stainless tank was obtained and added to the set-up where it was positioned inside fume hood for guaranteed safety and control on the entire system.

The complete set-up consisted of the following components (See Figure 4):

- **Oxygen Concentrator:** this device is used to capture and concentrate oxygen from the air, which is then fed into the ozone generator.
- Ozone Generator: The concentrated oxygen is converted into ozone, where oxygen passes through a highvoltage electric field, splitting the oxygen molecules into atoms that recombine to form ozone. This piece of equipment is crucial because ozone can't be stored or transported due to its high reactivity and short halflife.
- Stirrer with three-blade propeller: To ensure through mixing of the ozone with the water and converted all homogenous. This ensures that the ozone is evenly distributed throughout the water, maximizing contact and oxidation efficiency.
- 30 L stainless steel tank: This tank was specifically chosen for its resistance to corrosion and ability to withstand the oxidative environment. The tank holds the water to be treated and allows for controlled experimentation.

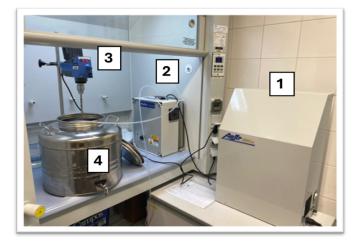


Figure 4: Pre-oxidation with ozone set-up. Own source.

The process begins with oxy concentrator capturing and purifying oxygen (1), which is then directed to the ozone generator (2). The generator produces ozone, which is immediately introduced into the water contained in the stainless-steel tank (4) with a tube connected to those devices. The dosing followed operating conditions chosen based on previous experimental tests (see results 4.2.5). The stirrer with the three-blade propeller (3) ensures that the ozone is thoroughly mixed with the water, promoting effective oxidation of contaminants.

3.3.2 Residual ozone: measurement and possible removal

Once the oxidation is performed, a small amount of residual ozone may remain in the water. It is important to destroy it if is present in high amounts to prevent adverse effects in later treatment stages.

The Lovibond method is a colorimetric procedure used to determine the concentration of residual ozone in water. It relies on the reaction of ozone with a chemical reagent that produces a colour change, which can be measured and quantified to determine the ozone concentration. Below are the fundamental principles, the reagents used, the colour measurement process, and the conversion of this coloration into a concentration value in mg/L. The reagents in the Lovibond method for determining residual ozone are:

- DPD (N, N-diethyl-p-phenylenediamine).
- Phosphate buffer
- Potassium chloride

The Lovibond method is based on the property of ozone to oxidize specific chemical compounds, producing a colour change in the solution. The intensity of the developed colour is proportional to the concentration of ozone present in the sample. This coloration is compared to predefined colour standards using a Lovibond colorimeter, allowing the quantification of ozone concentration in terms of mg/L.

By setting up this system, the experiments can be conducted under controlled conditions, allowing for precise evaluation of the pre-oxidation process and its impact on water quality. This approach helps to assess the effectiveness of ozone in reducing organic and inorganic pollutants, as well as pathogenic microorganisms, thus enhancing the overall treatment process at the Figueres DWTP.

3.4 Sample characterisation: Physicochemical analysis

Once the samples were obtained, they were analysed at the Lequia laboratories at the Faculty of Sciences. To achieve the established objectives in drinking water treatment, it is crucial to understand the different analytical techniques that allow us to analyse the substance we are interested in. The primary objective of chemical analysis in drinking water treatment is to detect and quantify contaminants to ensure the water is safe for consumption. This requires a comprehensive approach using various analytical techniques. The following are the standardized methods used for analytics methods, pH, Absorbance UV254, turbidity and Non Purgeable Organic Carbon (NPOC). Here is an overview of the methodologies and applications of these techniques:

pH: The potentiometric method 4500 H+ from Standard Methods was used to measure pH. A portable pH meter (pH 110). For pH adjustment, 0,1 N sodium hydroxide and 0,1 N hydrochloric acid solutions were used. It provides information on whether the sample has acidic (pH<7), neutral (pH=7) or basic (pH>7) characteristics.

Turbidity: Turbidity is a measure of the clarity of transparency of the water. It refers to the presence of suspended particles, which can be organic or inorganic in nature. To measure turbidity, a Hach TU5200 turbidimeter was used, which was previously calibrated with appropriate standards. The protocol used to prepare the sample involves introducing a 1 NTU standard into the device to verify it. Then, approximately 10 mL of the sample is added to a glass cuvette and inserted into the device to read the turbidity.

UV-Vis Absorbance: Absorbance is a quantitative measure of a substance's ability to absorb light at a specific wavelength. An Agilent Cary 3500 compact UV-Vis absorption spectrophotometer was used. In the context of water treatment, it is used to indirectly determine the concentration of certain contaminants or substances present in the water, such as organic compounds, heavy metals and other dissolved substances. The spectrophotometer detects this dissolved organic matter. From the scan (full spectrum of wavelengths between 180-1100 nm) provided by the device, we highlight the absorbance at 254 nm as it is the wavelength most easily absorbed by the organic matter present in a sample. Thus, it provides information about the content of organic matter. Prior to the analysis of this spectrum, it is necessary to follow a sample pretreatment protocol; filtration at 0,45 µm with a nylon filter to eliminate possible suspended particles. The sample is then placed in a glass cuvette for characterization. To perform the blank (Mili Q water) before measurement, a baseline is first carried out, which refers to the reference value used to establish a comparison for the absorbance measurement of the samples.

NPOC (Non Purgeable Organic Carbon): is an indirect measure of the amount of organic carbon present in a water sample that cannot be removed by purging with an inert gas. This parameter indicates the concentration of dissolved organic compounds in the water. The measurement of NPOC is performed using a Total Organic Carbon (TOC) analyser, which follows these steps: volatile organic carbon is removed by purging with an inert gas, inorganic carbon is removed by acidification to convert carbonates and bicarbonates to CO₂, and the remaining organic carbon is oxidized by combustion. Finally, the NPOC is determined by measuring the generated carbon dioxide.

For sample preparation, the protocol involves first checking the sample's pH and acidifying it to a pH range of 2-3. Acidification is done to eliminate the inorganic carbon fraction, converting it to CO_2 . Then using a 0,45 μ m filter and a syringe, approximately 15 mL of the sample is added to the vial.

Fluorescence Spectroscopy: is an analytical technique that allows the characterization and represents various organic matter compounds present in water. Fluorescence is a highly sensitive and selective technique capable of detecting and quantifying substances at very low concentrations. Its theoretical foundation is based on the processes of photon excitation and emission, while technically it is performed using specialized equipment that allows for precise analysis of the fluorescence light emitted by samples (Bridgeman, 2011). This technique is essential in many scientific fields due to its ability to provide detailed information about the composition and properties of various substances. The characterization of fluorescent organic matter was conducted using a Cary Eclipse fluorescence spectrometer equipped with quartz cells. The fluorescence representation is a graph generated from a set of two-dimensional data, where three distinct zones can be identified: the T peak (protein-like substances), A peak (humic substances) and C peak (fulvic substances). In the study, three regions of

organic matter were identified: humic acids, fulvic acids and protein-like substances characterized by tryptophan. The results analysed as shown in Figure 5, clearly identified three peaks A, C and T corresponding to fulvic, humic and protein-like fractions of organic matter, respectively.

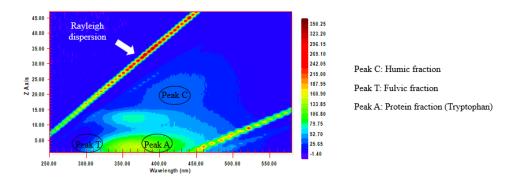


Figure 1: Schematic of fluorescence with fractions of organic matter and corresponding peaks. Own source.

Before analysis, the water sample is filtered using a 0,45 µm filter with a syringe and placed in a quartz cuvette. This filtration step is crucial in the preparation of water samples for analysis, as it ensures that particulate matter, including microorganisms and dissolved organic compounds are effectively removed. In summary, the choice 0,45 µm filter is based on the need to maintain a good balance between sample clarification and the preservation of dissolved substances to be analysed, while also ensuring an efficient and cost-effective practice. This step helps in obtaining a clear and uncontaminated sample, which is essential for precise detection and quantification of target analytes. The analysis conditions involve scanning with intervals of 5 nm between 200 and 400 nm for excitation and between 280 and 500 nm for emission.

3.4.1 Chemical risk: THMs analysis and chlorine disinfection

Chlorine Demand Test

The chlorination procedure was aimed at assessing chlorine demand in water simples determining the formation of disinfection by-products, such as THMs. A sodium hypochlorite solution with an initial concentration of 150.000 ppm was used as a disinfecting agent. A series of dilutions was prepared, reaching a chlorine concentration of 2 ppm. For each treated water sample, two doses of chlorine were applied, resulting in two samples with initial chlorine concentrations ranging from 2 to 4 ppm.

After a 24 and 48 hours reaction period, residual chlorine concentration was measured using a portable Hanna chlorine tester. To measure the unreacted chlorine concentration, a Hana device using the N, N-diethyl-p-phenylenediamine (DPD) method is used. This method is based on the chemical reaction between residual chlorine and the DPD reagent, producing a pink-red complex. The colour intensity is proportional to the residual chlorine concentration in the sample. For analysis, 10 mL of the sample is placed in a glass vial for a blank reading. Then, the DPD reagent is added, and the intensity of the pink colour indicates the free chlorine concentration in mg/L.

The sample with the chlorine level closest to 1 ppm was chosen for GC-MS THM analysis. Chlorination was stopped using ascorbic acid.

THM Formation Potential (THM-FP)

Trihalomethane Formation Potential (THM-FP) analysis is an analytical method used to examine how these halogenated organic compounds, which can be volatile and semi-volatile, form in drinking water post-treatment.

The analysis of trihalomethanes (THMs) was performed using a headspace gas chromatography coupled with a mass spectrometer (GC-MS). This analytical approach facilitated the separation and quantification of THMs by analysing the volatile compounds present in the gas phase above the sample. This technique allowed for a comprehensive assessment of THMs based on their unique characteristics assessment of THMs based on their unique characteristics in the vapor phase. To calibrate the GC-MS, the THM calibration mix CRM48140 was used. To determine THMFP, the trihalomethanes present in water are not measured directly. The samples potential to form THMs under controlled conditions simulating the disinfection process is evaluated. This includes factors like disinfectant type, concentration, contact time, temperature, light/dark conditions and agitation. calculated to chlorinate the samples. The chlorinated samples are allowed to react for 24 and 48 hours at room temperature and in darkness to simulate real conditions. The residual free chlorine concentration is measured post contact time and samples with values closest to 1 ppm of free chlorine (Real Decreto, 03/2023) are selected for THM determination. Approximately 12 mL of the sample is placed in vials for GC-MS analysis leaving sufficient headspace for proper volatilization. These protocols are designed to analyse trihalomethanes (THMs) form when organic matter in the water reacts with chlorine used for disinfection. Therefore, the goal of water purification is to remove as much organic matter as possible so that chlorination does not exceed the regulated THM limit of 100 ppb. (Real Decreto, 3/2023).

Gas Chromatography operation: **Sample injection**: The sample is vaporized and injected into the carrier gas flow. **Chromatography Column**: The vaporized sample is transported through a capillary column coated with a stationary phase. Components separate based on their affinity for the stationary phase and their boiling points. **Detector**: Once separated, the components exit the column at different times (retention times) and enter the mass spectrometer.

Mass spectrometry operation: **Ionization**: Separated components are bombarded with electrons to create charged ions. **Mass analysis**: Generated ions are separated according to their mass to charge ratio (m/z) in a mass analyser. **Detection and identification**: Separated ions are detected and recorded, producing a mass spectrum that shows ion intensity as a function of their m/z ratio.

This spectrum provides detailed insights into the composition of the sample, enabling the identification and quantification of THMs. The goal of the THMFP analysis is to ensure that the chlorination process in water treatment does not exceed the regulated THM limits, ensuring safe drinking water. The GC-MS method identifies the four main THM compounds by their m/z ratio at specific retention times: (Figure 6):

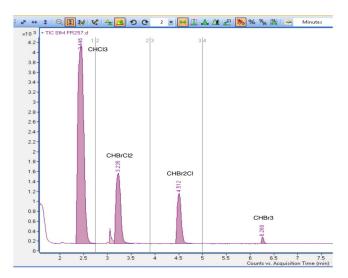


Figure 2: Graphical representation and data of the THM formation potential area. Own source.

- 1. Chloroform (CHCl₃), retention time, 2,5 minutes.
- 2. Bromodichloromethane (CHBrCl₂), retention time, 3,24 minutes.
- 3. Dibromochloromethane (CHBr₂Cl), retention time, 4,5 minutes.
- 4. Bromoform (CHBr₃), retention time, 6,3 minutes.

3.5 Meteorological data acquisition to evaluate dry period

During the study period, a significant drought was observed, which caused alarm. This drought greatly affected the Boadella-Darnius reservoir, causing its capacity to drop to approximately 7%, a very low level. To study the effects on water, data were collected from the Arnera river, the Muga river, and the state of the reservoir, including rainfall days. Data on river flow rates and the reservoir capacity and volume were gathered. These data were extracted from the website (Aigua en temps real, 2024). The acquisition and analysis of meteorological data are essential for evaluating the effects of dry periods on water quality. By understanding these relationships, can better predict and manage the formation of disinfection by-products, ensuring safer and more effective water treatment processes. This approach helps optimize water quality management during varying climatic conditions.

3.6 Data analysis

To systematically process and analyse the data collected from all the parameters, followed a structured approach to ensure accuracy and organization. All measured values and results were meticulously recorded and saved in an Excel sheet for comprehensive analysis. Below is an explanation of how the data values were processed and organized. One file contains multiple sheets, each with a distinct function. Description of each sheet and its purpose. The order that follows is description of analyses, objective and basic information, sample descriptions, results, UV-Visible Matrix, THM at 24h and 48 h and the last sheet contains data processing and correlation tables.

Once the individual test files are organized, the next step is to consolidate all the data from each test into a single, new Excel sheet. This new sheet consolidates all the corresponding data for each characterization from

each assay, i.e., all turbidity measurements from each assay in one sheet and similarly for each parameter. Once this file is completed with all the data, the corresponding graphs are created to evaluate the treatment train processes in a Drinking Water Treatment Plant, focusing on the characterization of the chemical risks associated with the different treatments.

To extract information from the fluorescence Excitation Emission Matrices (EEM), we employed the technique of recording the maximum intensities of specific peaks identified in the water samples. (Rodríguez, 2013).

To establish the relationship between the removal of natural organic matter and the potential for THM formation, the Pearson correlation coefficient was employed. This statistical measure quantifies the significance of the relationship between two variables, as well as the strength and direction of this relationship if it exists.

The Pearson correlation coefficient is denoted by "r" and ranges from -1 to 1. A value of -1 signifies a perfect negative correlation, where an increase in one variable corresponds to a proportional decrease in the other. Conversely, a value of 1 signifies a perfect positive correlation, where both variables increase proportionally. A value of 0 indicates no linear correlation between the variables.

$$r = \frac{\sum (X - \bar{X})(Y - \bar{Y})}{\sqrt{\sum (X - \bar{X})^2 \cdot \sum (Y - \bar{Y})^2}}$$
Equation 1.

Where X and Y represent the variables being correlated, and X⁻and Y⁻are their respective mean values. In this study, to comprehend the relationships among multiple variables, a correlation matrix was created. This matrix displays the correlation coefficients between various pairs of variables. The Excel data analysis tool was utilized to generate this matrix.

4. **RESULTS & DISCUSSION**

This section presents the results obtained from the study of chemical analysis of each stage of the treatment process and their characterizations are organized according to the following subtopics: the effect of ozone on water quality, the impact of different treatments on THM formation potential and chemical risk and the effects of dry periods on water quality.

4.1 Sampling at DWTP Figueres and all data information

In the context of evaluating and optimizing water treatment plant, a series of comprehensive assays were conducted over several months. These assays aimed to assess the effectiveness of various treatment stages and the impact of different pre-oxidation techniques, particularly ozonation, on water quality. The experiments were planned and executed to provide detailed insights into the treatment process. To ensure a thorough analysis, water samples were collected from multiple key points within the DWTP. These sampling points included the Raw water intake (EP), the Post-ozonation (O3), the Decantation stages (DEC123, DEC456 and DEC78), the Filtration stages (F123, F456 and F78). According to the sampling that have been carried out at the plant, they are summarized as follows (see Table1):

Assay	Sampling Date	Sample point	Volume reservoir	Capacity
			(hm^3)	(%)
1	18/3/2024	EP, O ₃ , DEC123, DEC78, F3, F4 and F7	7,10	11,62
2	9/4/20224	EP, O ₃ , DEC123, DEC78, F3, F4 and F7	7,23	11,83
3	15/4/2024	EP, O ₃ , DEC123, DEC78, F3, F4 and F7	7,14	11,70
4	22/4/2024	EP, O ₃ , DEC123, DEC78, F3, F4 and F7	7,03	11,46
5	29/4/2024	EP, O ₃ , DEC123, DEC78, F1, F5 and F8	7,29	12,01
6	6/5/2024	EP, O ₃ , DEC123, DEC78, F3, F6 and F7	9,99	16,40
7	13/5/2024	EP, O ₃ , DEC456, DEC78, F1, F5 and F8	10,31	16,88
8	20/5/2024	EP, O ₃ , DEC123, DEC78, F3, F6 and F7	10,69	17,51
9	27/05/2024	EP, O ₃ , DEC123, DEC456, F3, F4 and F7	13,31	21,80

Table 1: Information about all characteristics to understand the results.

4.2 Assessment of ozone pre-oxidation in the performance of water quality

These results obtained from the chemical analysis of each stage of the treatment process and their characterizations are organized according to the following parameters:

4.2.1 Turbidity

Turbidity is an indicator for the selection of the water treatment technology. In addition, this parameter can be measured on real time, and it is also an important indirect indicator for waterborne diseases (Payment and Hunter, 2001). Next (see Graphic 1 and 3), displays the average turbidity across different stages of the treatment process at the DWTP in Figueres. First, can see the raw water, EP. This is the initial turbidity level of the raw water before any treatment. The high turbidity indicates the presence of suspended particles, organic matter and other impurities and contaminants in the water. After the ozone pre-oxidation (O₃) stage, turbidity increases slightly. Ozone is a powerful oxidant that breaks down organic and inorganic substances, which can initially increase turbidity by creating smaller particles from larger ones. These particles are then targeted in subsequent treatment stages. However, a significant reduction in turbidity is observed during the coagulation-flocculation stages. At DEC123, turbidity drops drastically to approximately 0.7 NTU. This stage involves adding chemicals that cause small particles to clump together into larger flocs, which can then settle out of the water, thus significantly reducing turbidity. In the subsequent stage, DEC456 turbidity slightly increases to about 1.3 NTU. This minor increase might be due to variations in the flocculation process or the presence of residual flocs that have not settled completely or are dirty. Continuing with the DEC78, turbidity further decreases to around 0.3 NTU, indicating effective removal of particulate matter and improved water clarity. The filtration stages that follow are highly effective in maintaining low turbidity levels. During the filtration stages F1/F3, turbidity is reduced to approximately 0.1 NTU as the filters trap fine particles. This very low level of turbidity is maintained through the subsequent filtration stages F4/5/6, where turbidity remains at about 0.1 NTU. In the other filters stage F7/8, there is a slight increase in turbidity to approximately 0.2 NTU, possibly due to minor operational variations. However, the overall turbidity remains very low, highlighting the efficiency of the filtration process in removing particulate matter. This graphic illustrates the effectiveness of each treatment stage in reducing turbidity.

Also, the analysis of this graphic demonstrates the significant impact of ozone pre-oxidation on water quality. Initially increases turbidity because is raw water that it comes from the reservoir. However, this stage enhances the subsequent coagulation-flocculation process by making the particles easier to coagulate and remove. The result is a significant reduction in turbidity, of 87,57%, particularly during coagulation-flocculation and filtration. Therefore, ozone pre-oxidation is highly effective in improving water clarity and quality by aiding the removal suspended particles through the treatment process.

4.2.2 Absorbance UV254

In this study, performed multiple trials were conducted to measure the UV254 absorbance at different stages of the drinking water treatment process at the DWTP in Figueres (see Graphic 1 and 4). The UV254 absorbance is a crucial parameter as it indicates the presence of aromatic organic matter in the water. The average results of these trials were compiled to create a single bar graph, representing the overall trend in UV254 absorbance throughout the treatment train. This section will describe and interpret these results, highlighting the effectiveness of each treatment stage.

The initial measurements (EP) were taken from the raw water entering the treatment plant. As expected, the UV254 absorbance was highest at this stage, absorbance value 0.047, indicating a substantial presence of aromatic organic compounds. These compounds are commonly found in untreated surface water, originate from natural organic matter and various pollutants (Hudson, 2007). The high absorbance value at this stage underscores the necessity for extensive treatment to ensure the water meets drinking standards.

The first significant treatment step was pre-ozonation. The introduction of ozone into the water resulted in a marked decrease in UV254 absorbance. Ozone, known for its powerful oxidative properties, effectively breaks down complex organic molecules, including aromatic compounds. This reduction was 46,81%, which indicates that the ozonation process is highly effective in degrading these compounds, significantly improving the water quality by reducing potential precursors to harmful byproducts.

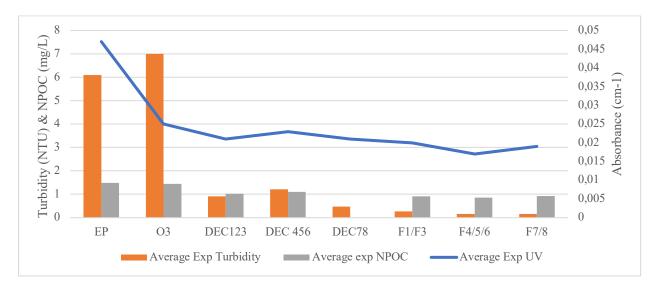
Following pre-ozonation, the water underwent coagulation-flocculation. This stage further reduced at the middle of the UV254 absorbance value, 0.025 cm⁻¹. Coagulation and flocculation processes work by aggregating smaller particles and dissolved organic matter into larger flocs, which can then be removed from the water. The additional decrease in absorbance at this stage, of 13,85%, highlights the efficiency of these processes in eliminating contaminants that were not fully oxidized during ozonation. Subsequently, the water was filtered, leading to a continued reduction in UV254 absorbance. Filtration is crucial for removing any remaining particulates and finer organic matter that passed through the previous stages. The sustained decrease in absorbance through filtration demonstrates the process effectiveness in polishing the water, ensuring that most of the organic contaminants are removed, resulting in significantly cleaner water. Filters presents lowest values, under 0.02 cm⁻¹, these values are close to 0 and present a clean water.

In conclusion, see graphic 1 clearly illustrates the significant impact of ozonation on reducing UV254 absorbance values, indicating a substantial decrease in the concentration of organic compounds in the water. This pre-oxidation step with ozone not only directly reduces the organic load but also enhances the efficiency of subsequent treatment processes. The overall effect is a marked improvement in water quality, with lower levels of organic precursors that could form harmful disinfection byproducts. This highlights the importance of incorporating ozonation in the treatment process to achieve safer and cleaner water.

4.2.3 NPOC

Non-Purgeable Organic Carbon is a key parameter in assessing water quality, representing the organic carbon content that remains in the water after purging with a gas. It provides a measure of the total organic compounds present, which can include various pollutants. Monitoring NPOC levels helps evaluate the efficiency of water treatment processes in removing organic pollutants. The following graphic (Graphic 1 and 8) illustrates the changes NPOC levels throughout different stages of the water treatment process for various assays at the Figueres Drinking Water Treatment Plant (DWTP).

Across the assays, the initial NPOC levels at the plant entry (EP) are consistently high, with concentrations around 1.3 to 2.7 mg/L. This indicates a significant presence of organic pollutants in the raw water entering the treatment plant. In the pre-ozonation stage, there is a noticeable reduction in NPOC levels for all assays. Ozone is effective in breaking down complex organic molecules, which leads to a decrease in NPOC. This stage demonstrates the role of ozone in enhancing water quality by reducing organic carbon content. The decantation stages (DEC 123 and DEC78) further reduce NPOC levels, albeit to varying extents. The effectiveness of these stages depends on the specific assay, but generally, a consistent decrease NPOC is observed. In some cases, such as in assay 5 the reduction in significant, while in others, like assay 7, reduction is moderate. An anomaly is observed in assay 7, where DEC78 shows a slight increase in NPOC levels, this small increase has been due to rain which has increased the last tests. Final treatment stages, including filtration units F123, F456 and F78, consistently show the lowest NPOC levels. These stages are crucial in polishing the water, ensuring that the organic carbon content is minimized before the water is considered potable. In all assays, the F78 stage shows the lowest NPOC levels, indicating the cumulative effectiveness of the entire treatment train.



Graphic 1: Average parameters UV, Turbidity and NPOC represented all evolution along the treatment train.

In summary, the results across all assays indicate that the Figueres DWTP effectively reduces NPOC levels through its multi-stage treatment process. Ozone effectively breaks down complex organic molecules, leading to lower NPOC levels and enhanced biodegradability of the remaining organic matter. Overall, the data indicates that the initial treatment stages are highly effective in reducing all these parameters which then stabilize in the

following stages. This trend reflects the effectiveness of the water treatment process in improving water quality by removing particulate and organic contaminants. The relatively stable values in the later stages suggest sustained treatment efficiency, ensuring the production of high-quality water.

4.2.4 Fluorescence EEM

The analysis of fluorescence Excitation-Emission Matrix (EEM) results focuses on three distinct peaks: humic acids (peak C), fulvic acids (peak A) and protein-like substances (peak T). Each peak's intensity is tracked across different stages of the water treatment process at the DWTP in Figueres, providing insights into the efficiency of each stage in reducing these organic compounds. The results indicate significant changes in the intensity of these three peaks throughout the treatment stages, which are interpreted to understand the efficacy of each process (see Graphic 2).

Humic Acids Peak

Starting with humic acids, the fluorescence intensity at the initial step (EP), indicates a substantial presence of these compounds in the raw water. However, a significant reduction, of 61,91%, is observed after the preozonation stage (O₃). This decrease highlights the effectiveness of ozone in breaking down humic acids through oxidation. Following ozonation, the intensity continues to decline in the DEC123 stage, showing further removal of humic substances. Unexpectedly, there is an increase in intensity at the DEC456 stage. This anomaly suggests possible operational inefficiencies or challenges in completely removing humic acids at this decantation stage, potentially due to maintenance issues. Subsequent stages, including DEC78 and the filtration stages (F123, F456, F78), show a continuous decrease in intensity, confirming the overall effectiveness of the treatment process in reducing humic acid concentrations.

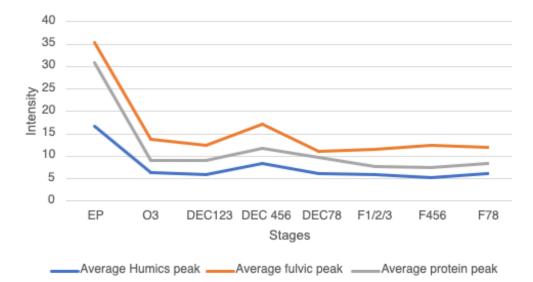
Fulvic Acids Peak

The pattern for fulvic acids is like the previous one. The raw water sample (EP) shows a high initial intensity, which significantly decreases, of 61,03%, after pre-ozonation, reflecting the ozone's ability to degrade fulvic substances effectively. The trend of reduction continues in the DEC123 stage. However, like humic acids, an increase in intensity is observed at the DEC456 stage. Despite this, the intensity decreases in the following stages, with the final treatment processes successfully lowering the fulvic acid levels.

Protein peak

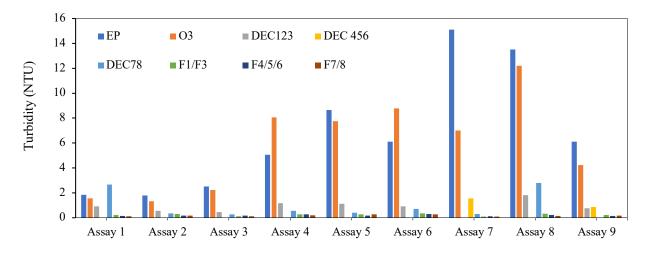
For protein-like substances, the highest intensity is also seen at the raw water sample. After pre-ozonation, the intensity drops, although the reduction, of 70,94%, is less significant compared to humic and fulvic acids fractions. This suggests that while ozone is effective, protein-like substances might be more resistant to oxidation. As the water moves through the DEC123 stage, the intensity continues with the trends observed for humic and fulvic acids. This recurring anomaly highlights the need for further investigation into the decantation process at this stage. The subsequent stages show a moderate decrease in intensity, with final values not exceeding an intensity of 10, demonstrating effective removal of protein-like substances through the treatment process.

In summary, the fluorescence EEM analysis reveals that the pre-ozonation is highly effective in reducing the concentrations of humic acids, fulvic acids and protein-like substances. The DEC456 stage consistently shows anomalies, suggesting operational issues that need to be addressed to ensure optimal performance and it is also since few samples have been taken compared to the other decanters. The scientific implications of these results underscore the importance of integrating ozonation in modern water treatment protocols to achieve superior water quality standards.

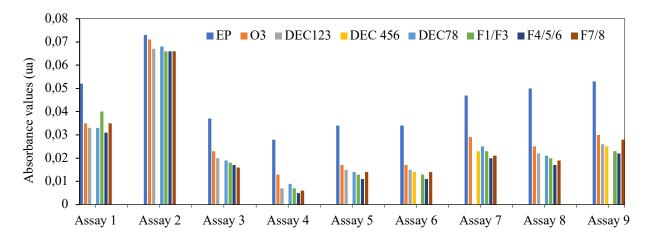


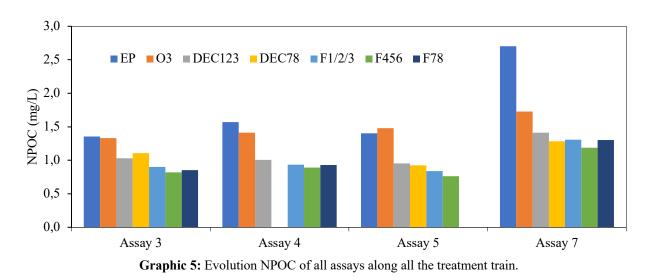
Graphic 2: Average of all peaks, humics, fulvics and protein along the treatment train.

Overall, the treatment processes are effective in significantly lowering the levels of these organic contaminants, ensuring the delivery of high-quality drinking water. Below are the separate assays conducted for each parameter. Each parameter's evolution over this period is shown. The importance of ozonation in the treatment train is particularly noteworthy. As previously discussed, ozonation plays a crucial role in improving water quality. The detailed analysis of each parameter in these assays highlights the significant impact of ozonation and other treatment stages on reducing turbidity, NPOC and UV absorbance. These results emphasize the critical contribution of each treatment stage in the overall effectiveness of the water treatment process.



Graphic 3: Evolution turbidity along all the treatment train.





Graphic 4: Evolution absorbance of all assays along all the treatment train.

4.2.5 Assessment of pre-oxidation unit at Lab-scale

The impact of ozone pre-oxidation on water quality was evaluated by analysing several parameters. The ozone generation system was meticulously configured to ensure optimal performance, considering factors such as ozone concentration, contact time and water flow rates. These parameters were systematically adjusted and monitored throughout the experimental period to maintain consistency and reliability in the treatment process.

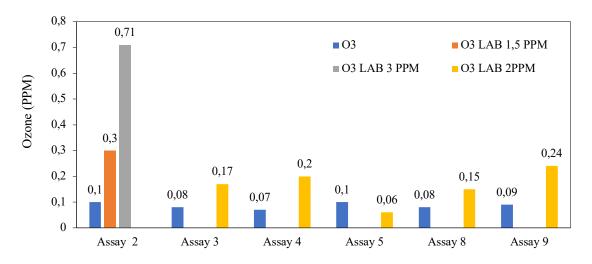
The operational conditions were rigorously documented, detailing variations in ozone dosage and reaction kinetics under different scenarios. This section provides a comprehensive overview of the setup process, emphasizing the meticulous approach taken to achieve reliable ozone-based water treatment at the Figueres DWTP (see Table 2).

Table 2: Data to work in optimal operational conditions.

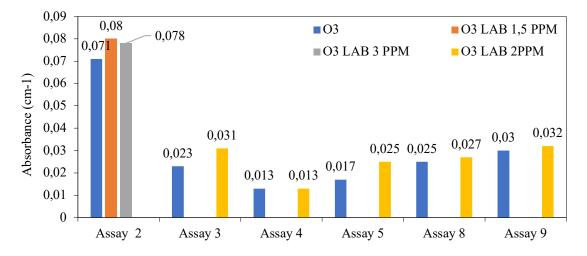
Ozonated Volume	Ozone concentration	Air flow rate	Contact time	O ₃ Gas Concentration
25 L	1-3 ppm	5 L/min	1-3 min	10.2 g/m^3

Once the operating conditions are applied and we have the set-up ready, ozonation is carried out. Once the whole process of ozonizing the sample is finished, what is done is with the method DPD-Lovibond.

As can be seen in the following graphic (see Graphic 6) shows a comparison residual ozone DWTP vs LAB. To evaluate the effects of ozone dosage applied in the laboratory, compared the absorbance data from lab experiments with those from the DWTP (see Graphic 7). The graphic 7 provided shows the absorbance of samples from various assays, comparing the residual ozone levels between DWTP and LAB under different ozone concentrations.

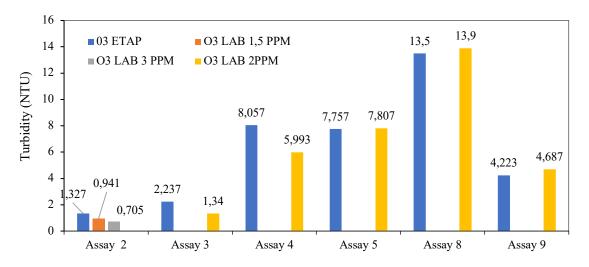


Graphic 6: Comparison of residual ozone about these assays, between LAB conditions and monitoring ETAP.



Graphic 7: Comparison of residual ozone about these assays, between LAB conditions and monitoring DWTP.

The data suggest that the DWTP results in slightly lower absorbance values compared to laboratory at similar or higher ozone doses, indicating more effective reduction. Higher ozone doses in the lab do not always correlate with a proportional decrease in absorbance. This comparative analysis underscores the need to tailor ozone dosages to achieve optimal removal efficiencies and highlights the potential differences in process efficiencies between controlled lab conditions and operational treatment plants (see Graphic 8).



Graphic 8: Comparison of turbidity ozone about these assays, between LAB conditions and monitoring DWTP.

4.3 THM-FP: How does the different treatments effect to the chemical risk?

The formation potential of trihalomethanes was assessed at various stages of the treatment process to evaluate the effect of different treatments to the chemical risk, using data from the specified period.

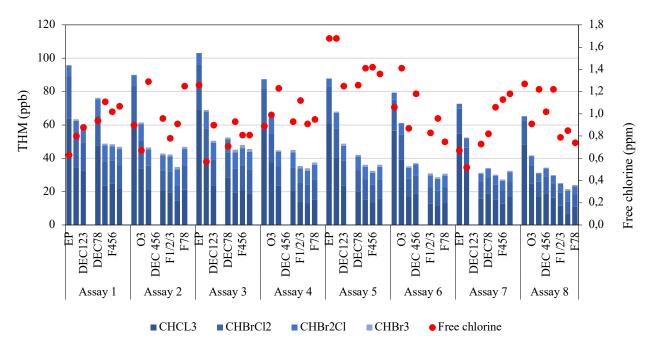
The graphs present the concentrations of the potential formation of trihalomethanes (THMs-FP) after 24 and 48 hours of contact with sodium hypochlorite at different stages of the water treatment process. THMs-FP, include the compounds: chloroform (CHCl3), bromodichloromethane (CHBrCl2), dibromochloromethane (CHBr2Cl) and bromoform (CHBr3), all of them considerate disinfection byproducts, formed when chlorine species react with organic matter in the water. The red dots represent the concentrations of free chlorine in mg/L.

THM-FP 24 hours

In the 24-hour graph (See graphic 9), we can observe that in the initial stages, especially the raw water stage (EP), THM-FP concentrations are very high, reaching above 100 ppb in some assays. This high initial concentration is due to the large amount of organic matter present in the raw water, which serves as a precursor for THM formation. As the water passes through the ozonation process (O₃), there is a significant reduction in THM-FP concentrations, indicating that ozonation effectively degrades organic precursors. The DEC123, DEC456 and DEC78 stages show a sustained reduction in THM-FP concentrations, while the final stages (F123, F456, F78) exhibit some variability but maintain lower concentrations compared to the initial stage. The overall trend indicates that the treatment process effectively reduces THMs-FP, although there are fluctuations in the final stages, possibly due to variations in treatment conditions or reactivation of residual chlorine with remaining organic matter.

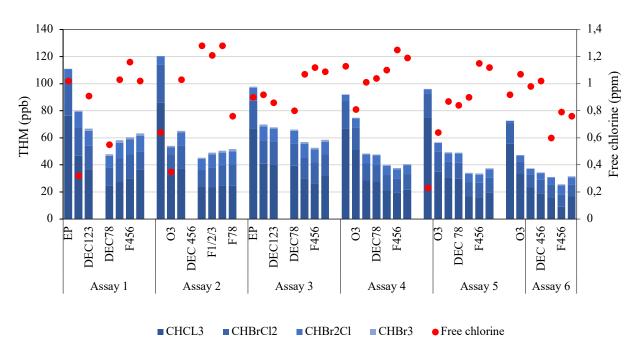
THM-FP 48 hours

The 48-hour graph follows a similar pattern to the 24-hour graph, with very high initial THM-FP concentrations in the raw water unit (EP) due to significant organic matter presence. As the water progress through the treatment process, especially after ozonation (O_3), there is a notable decrease in THM-FP concentrations. The DEC123, DEC456 and DEC 78 stages continue to show reduced THM-FP levels, highlighting the effectiveness of the



sedimentation and filtration process on removing precursors of this disinfection byproducts. The final stages (F123, F456 and F78) exhibit some variability but generally maintain lower concentrations (see Graphic 10).

Graphic 9: Analysis of THM-FP 24 hours of all assays along the treatment train.

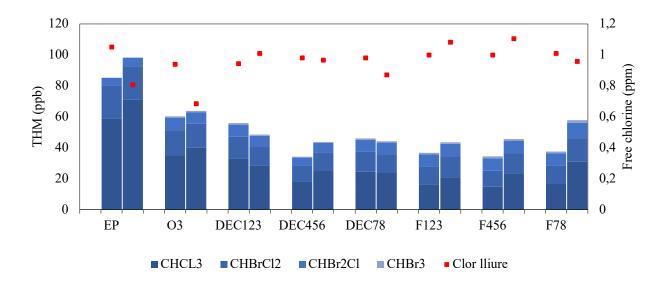


Graphic 10: Analysis of THM-FP 48 hours of all assays along the treatment train.

The analysis of both THM-FP 24 and 48 hours graphs indicates that the different treatments applied in the water treatment process generally **reduce the chemical risk** associated with THM formation. The significant initial THM-FP levels, due to high organic matter, are markedly decreased after ozonation and subsequent sedimentation and filtration stages. Although some variability is observed in the final stages, the overall trend stages. Although some variability is observed in the final stages, the overall trend stages, suggesting that the treatments effectively mitigate the chemical risk of THM formation. Thus,

it can be concluded that the different treatments employed do not increase the chemical risk but rather play a crucial role in significantly reducing the potential for THM formation, thereby enhancing water safety and quality.

Below is the graph with the averages of all the assays represented during the period of 24 first bar and 48 hours second bar. Explanation of the effect of contact time on chemical risk.



Graphic 9: Average analysis along all the treatment trains of THM-FP 24 and 48 hours.

Higher THMs concentrations are consistently observed at 48 hours, indicating the progressive increase in THM formation over time.

THMs are formed when chlorine reacts with natural organic matter in the water, a process that continues over time. As a result, the longer the water is exposed to chlorine, more THMs are produced. This is why we see significantly higher THM concentrations at the 48 hours. For example, stages such as filters tend to have lower THMs levels, indicating more effective treatments in reducing organic matter or the remaining chlorine no longer reacting.

After determining the THM-FP after the sequential organic matter removal of the samples. THM-FP was correlated with the chemical parameters. The table presents the correlation coefficients between various UV absorbance ratios and fluorescence peaks with THM-FP measured at 24 hours and 48 hours (see Table 3 & 4).

Firstly, we observe that UV254 which measures absorbance at 254 nm, has a positive correlation with CHCl₃ and CHBrCl₂ at both 24&48 hours. This indicates that higher absorbance at this wavelength, associated with the presence of aromatic compounds in dissolved organic matter, translates to higher THM formations. This relationship remains consistent over time, suggesting that UV254 can be a good indicator of THM-FP.

The wavelength ratios, such as UV254/203, 265/465, 254/436, among others, show a variety of correlations with THM formation. For example, UV254/203 has a positive correlation with CHCl₃ and CHBrCl₂ at 24 hours but negative correlation with total. THM. This pattern changes slightly at 48 hours, where the correlation with total THM becomes positive. This suggests that different compositions of organic matter affect THM formation

in diverse and complex ways. A notable case is the 210/254 ratio, which shows a consistent negative correlation with all types of THMs at both 24 and 48 hours, indicating that this parameter might be associated with lower THM formation.

Fluorescence peaks also provide valuable information. Humic, fulvic and protein peaks show strong positive correlation with THM formation. This especially evident for peak T, which has a correlation of 0.711 with total THM at 24 hours and 0.536 at 48 hours. These correlations suggest that organic components associated with these peaks are significant contributors to THM formation. This implies that the quality and type of organic matter present in the water are crucial factors in THM formation.

Overall, the data indicate that THM formation is strongly influenced by the properties of dissolved organic matter in the water. Absorbance UV254 emerges as a good predictor of THM formation, likely due to the presence of aromatic compounds. Fluorescence peaks, on the other hand, show that humic substances, fulvic acids, and proteins are important contributors to THM formation. These findings can be used to improve water treatment techniques, focusing on reducing certain types of dissolved organic matter to minimize THM formation and, consequently, enhance the quality of drinking water.

Table 3: Correlation coefficients of THM -FP at 24h with UV at different wavelengths and fluorescence.

				0		
	CHCl3	CHCl2Br	TOTAL THM	Humics	Fulvics	Proteins
UV254 (nm)	0,400	0,411	0,345	0,434	0,456	0,391
254/203	0,192	0,251	0,198	0,109	0,100	0,053
465/665	0,156	-0,003	0,122	0,617	0,589	0,556
265/465	-0,128	-0,200	-0,151	0,065	0,055	0,027
254/436	-0,107	-0,149	-0,108	0,042	0,028	0,004
280/350	-0,133	-0,069	-0,040	-0,072	-0,122	-0,053
250/365	0,054	0,048	0,123	-0,094	-0,101	-0,043
270/400	-0,107	-0,157	-0,099	0,047	0,042	0,051
210/254	-0,402	-0,418	-0,439	-0,289	-0,304	-0,283
Humics	0,744	0,495	0,688			
Fulvics	0,749	0,501	0,688			
Proteins	0,756	0,500	0,711			

Table 4: Correlation coefficients of THMFP at 48h with UV at different wavelengths and fluorescence.

	CHCl3 48h	CHCl2Br 48h	TOTAL THM	Humics	Fulvics	Protein
UV254 (nm)	0,385	0,400	0,318	0,434	0,456	0,391
254/203	0,327	0,242	0,271	0,109	0,100	0,053
465/665	0,145	-0,061	0,084	0,617	0,589	0,556
265/465	-0,202	-0,325	-0,237	0,065	0,055	0,027
254/436	-0,207	-0,258	-0,208	0,042	0,028	0,004
280/350	-0,022	-0,009	0,073	-0,072	-0,122	-0,053
250/365	0,047	0,083	0,122	-0,094	-0,101	-0,043
270/400	-0,444	-0,330	-0,401	0,047	0,042	0,051
210/254	-0,310	-0,127	-0,317	-0,289	-0,304	-0,283
Humics	0,595	0,263	0,500			
Fulvics	0,607	0,287	0,509			
Proteins	0,616	0,299	0,536			

4.4 Effects of dry period to water quality

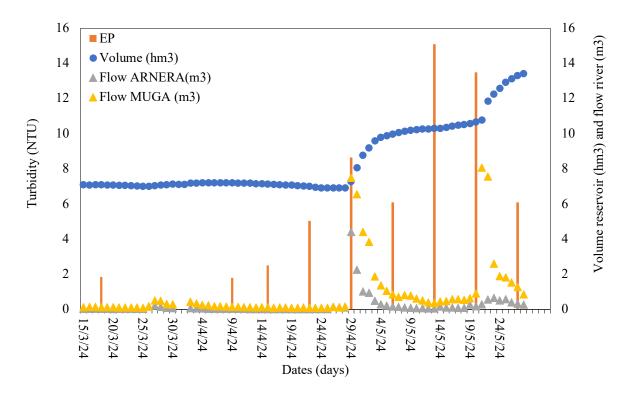
Studying turbidity levels is crucial to understanding how weather events, such as rainfall, can affect the quality of raw water entering the treatment plant. By looking at the behaviour of turbidity, reservoir capacity and river

flows, important patterns and correlations can be identified that help better manage water treatment processes, especially during periods of extreme weather conditions.

In this context, special attention is paid to variations in turbidity, reservoir volume and river flow during rainfall events. These data are essential for understanding how precipitation affects water quality and for designing treatment strategies that are effective during periods of heavy rain or prolonged drought.

The presented graph illustrates the evolution of turbidity (NTU) during various assays conducted between reservoir volume and the flow rates rivers. Focusing on the rainy period, it is evident that this period significantly impacts water turbidity. Initially turbidity remains at low levels but shown spikes on March 18th April 28th and May 20th. These sudden increases in turbidity suggest that the rains have caused a rise in suspended particles in the water. Intense rainfall can wash sediments, organic matter, and other contaminants from the catchment areas into the rivers and eventually, into the reservoir.

In summary, this phenomenon underscores the importance of monitoring water quality, especially during rainy periods, to adjust treatment processes and ensure a clean and safe water supply.



Graphic 10: Evolution of turbidity at the inlet DWTP Figueres between volume reservoir flow rates rivers Muga & Arnera.

The correlation table provides information on the relationships between trihalomethanes (THMs), turbidity, UV254 absorbance, and reservoir volume, which are critical to understanding water quality dynamics (see Table 5).

The data reveal that higher levels of organic matter, as indicated by UV254 absorbance, are positively correlated with increased chloroform (CHCl3) formation (0.497), while turbidity shows a negative correlation with levels of bromodichloromethane (CHCl2Br) (-0.662), which suggests that suspended solids can reduce its

concentration. Total THMs show a moderate correlation with UV254 (0.342), linking organic content to overall THM formation, but a strong negative correlation with reservoir volume (-0.754) highlights that larger volumes dilute precursors of THM, thereby reducing their levels.

Interestingly, turbidity itself is negatively correlated with THMs (-0.359) and with certain absorbance ratios, indicating that although turbidity measures particulate matter, it does not directly increase THM levels. This suggests that factors other than suspended solids, such as organic matter, play a larger role in THM formation.

In summary, the correlation table provides an integrated view of how different water quality parameters are interconnected and affected by weather conditions and treatment processes. This knowledge is essential for water treatment plants to adjust their processes effectively, ensuring safe and clean drinking water, especially during extreme weather events such as heavy rains or prolonged droughts.

Table 5: Correlation coefficients of turbidity and volume reservoir with UV at different wavelengths and fluorescence.

	THM-FP			Parameter				
	CHCl3	CHCl2Br	TOTAL THM	Turbidity	Volume	Humics	Fulvics	Proteins
UV254 (nm)	0,497	0,369	0,436	-0,142	-0,005	0,454	0,395	0,370
254/203	0,395	0,251	0,342	-0,051	0,323	0,621	0,587	0,544
465/665	-0,102	-0,364	-0,195	0,357	0,774	0,678	0,668	0,609
265/465	-0,107	-0,169	-0,185	0,001	0,606	0,462	0,394	0,280
254/436	0,183	0,124	0,249	0,166	-0,135	0,060	0,142	0,260
280/350	-0,944	-0,697	-0,880	0,020	0,174	-0,711	-0,721	-0,750
250/365	0,916	0,603	0,833	0,146	-0,178	0,721	0,751	0,794
270/400	-0,084	0,170	0,037	-0,395	0,040	-0,148	-0,161	-0,157
210/254	-0,829	-0,651	-0,786	0,110	0,003	-0,707	-0,699	-0,702
Turbidity	-0,212	-0,662	-0,359					
Volume	-0,634	-0,902	-0,754					
Humics	0,570	0,096	0,414					
Fulvics	0,549	0,071	0,399					
Proteins	0,614	0,148	0,481					

5. CONCLUSIONS

This study aimed to evaluate the treatment processes in the DWTP in Figueres, with a focus on characterizing the chemical risks associated with different treatments. The conclusions drawn from the study address each of the specific objectives set out at the beginning.

Pre-oxidation operation using ozone was assessed to determine its impact on chemical water quality, UV254 and EEM fluorescence. The findings demonstrate that ozone pre-oxidation significantly reduces the levels of specific contaminants in raw water. UV254 absorbance values consistently decreased after ozone treatment, indicating a reduction in organic matter that could contribute to the formation of disinfection by-products. EEM, analysis further supported these results by showing a noticeable reduction in the intensity of fluorescence peaks associated with organic pollutants. These indicators collectively confirm the effectiveness of ozone pre-oxidation in improving the chemical quality of water, optimizing this process can further enhance water safety standards.

Then, evaluation of the treatment processes efficacy in reducing chemical risks focused on the trihalomethanes formation potential (THM-FP). The results indicate that the current treatment processes are effective in mitigating the formation of THMs, a key group of disinfection by-products that pose chemical risks. The comparative analysis of THM-FP after different treatment stages revealed a significant reduction in THM-FP, highlighting the success of the plant's strategies in managing chemical risks.

The study also examined the impact of dry periods and reservoir changes on water quality and chemical risks. During dry periods, lower water levels were associated with higher concentrations of contaminants, likely due to reduced dilution and increased input of pollutants from surrounding areas. Monitoring of water quality parameter during these periods revealed elevated levels of certain chemical pollutants, which underscored the importance of seeing how it affected the parameter, turbidity. Changes in reservoir conditions, such as water level fluctuations, were found to significantly affect the chemical quality of raw water, influencing treatment effectiveness.

5.1 Future tasks

A future task that could be undertaken is to evaluate the use of sodium hypochlorite (NaClO) as an alternative pre-treatment method to substitute ozone. Sodium hypochlorite is widely used for its disinfectant properties, and its application could offer several benefits and challenges that need to be thoroughly investigate

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