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Memòria del Treball de Fi de Grau

A Comprehensive Study of Chemical and Microbial Risks of Drinking Water

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ABSTRACT

This study investigates the efficacy of water treatment processes in mitigating chemical and biological risks associated with drinking water. The assessment focuses on two main areas: chemical risk related to chlorination and disinfection by-products (DBPs), and biological risk indicated by assimilable organic carbon (AOC) levels. In the analysis of chlorination and DBPs formation potential, water samples from Montfullà and Figueres treatment plants underwent sequential treatment stages, including ozonation and activated carbon (AC) filtration. Results indicate varying degrees of reduction in Trihalomethanes (THMs) formation potential across treatments, with ozonation demonstrating effectiveness in some instances. Additionally, correlation analyses reveal strong associations between UV absorbance, turbidity, fluorescence peaks, and THM formation potential, providing valuable insights for water quality monitoring. Regarding biological risk, AOC levels were measured at different treatment stages in the Figueres plant, showing a reduction in microbial populations post-ozonation and a further decrease after AC filtration. Challenges in data acquisition due to contamination issues underscore the need for advanced methodologies such as flow cytometry for improved microbial quantification. This undergraduate thesis lays the groundwork for future research, transitioning into a Master's thesis to explore advanced techniques and address limitations, aiming to enhance the efficiency and accuracy of water treatment processes to ensure safe drinking water supply.

Keywords: water treatment, chlorination, disinfection by-products, ozonation, activated carbon filtration, Trihalomethanes, Assimilable Organic Carbon, UV absorbance, fluorescence, flow cytometry.

RESUM

En aquest estudi s’investiga l'eficàcia dels processos de tractament de l'aigua per mitigar els riscos químics i biològics associats a l'aigua potable. L'avaluació es centra en dues àrees principals: el risc químic relacionat amb els subproductes de cloració i desinfecció (DBP) i el risc biològic indicat pels nivells de carboni orgànic assimilable (AOC). En l'anàlisi del potencial de cloració i de formació de DBPs, les mostres d'aigua de les depuradores de Montfullà i Figueres es van sotmetre a etapes de tractament seqüencials, incloent ozonització i filtració de carbó actiu (AC). Els resultats indiquen diferents graus de reducció del potencial de formació de Trihalometans (THM) entre els tractaments, on l'ozonització demostra eficàcia en alguns casos. A més, les anàlisis de correlació revelen fortes correlacions entre absorbàncies UV, terbolesa, pics de fluorescència i el potencial de formació de THM, proporcionant informació valuosa per al seguiment de la qualitat de l'aigua. Respecte al risc biològic, es van mesurar els nivells d'AOC en diferents etapes de tractament a la planta de Figueres, mostrant una reducció de les poblacions microbianes després de l'ozonització i una nova disminució després de la filtració AC. Els reptes en l'adquisició de dades a causa de problemes de contaminació subratllen la necessitat de metodologies avançades com la citometria de flux per millorar la quantificació microbiana. Aquesta treball de grau estableix les bases per a futures investigacions, desenvolupant-se en una tesi de màster

per explorar tècniques avançades i abordar les limitacions, amb l'objectiu de millorar l'eficiència i la precisió dels processos de tractament d'aigua per garantir el subministrament segur d'aigua potable.

Paraules clau: tractament de l'aigua, cloració, subproductes de desinfecció, ozonització, filtració de carbó actiu, Trihalometans, carboni orgànic assimilable, absorbància UV, fluorescència, citometria de flux.

RESUMEN

En este estudio se investiga la efectividad de los procesos de tratamiento de agua para mitigar los riesgos químicos y biológicos asociados con el agua potable. La evaluación se centra en dos áreas principales: el riesgo químico relacionado con los subproductos de la cloración y la desinfección (DBP) y el riesgo biológico indicado por los niveles de carbono orgánico asimilable (AOC). En el análisis del potencial de cloración y formación de DBPs, las muestras de agua de las depuradoras de Montfullà y Figueres se sometieron a etapas de tratamiento secuenciales, incluyendo ozonización y filtración con carbón activado (CA). Los resultados indican distintos grados de reducción en el potencial de formación de Trihalometanos (THM) entre tratamientos, y la ozonización demuestra eficacia en algunos casos. Además, los análisis de correlación revelan fuertes asociaciones entre la absorbancia de los rayos UV, la turbidez, los picos de fluorescencia y el potencial de formación de THM, lo que proporciona información valiosa para el seguimiento de la calidad del agua. En cuanto al riesgo biológico, se midieron los niveles de AOC en diferentes etapas de tratamiento en la planta de Figueres, mostrando una reducción de las poblaciones microbianas después de la ozonización y una mayor disminución después de la filtración AC. Los desafíos en la adquisición de datos debido a problemas de contaminación subrayan la necesidad de metodologías avanzadas, como la citometría de flujo, para mejorar la cuantificación microbiana. Esta tesis de pregrado sienta las bases para futuras investigaciones, pasando a una tesis de maestría para explorar técnicas avanzadas y abordar las limitaciones, con el objetivo de mejorar la eficiencia y precisión de los procesos de tratamiento de agua para garantizar el suministro de agua potable.

Palabras clave: tratamiento de agua, cloración, subproductos de la desinfección, ozonización, filtración con carbón activado, Trihalometanos, Carbono Orgánico Asimilable, absorbancia UV, fluorescencia, citometría de flujo.

REFLECTIONS

Ethical:

Authorship policy in scientific research should guarantee transparency, fairness, and integrity in the recognition of contributors. However, the promotion of responsibility and the recognition of the contribution of the members also entail certain problems like the undue exclusion of people from authorship or the inclusion of people with no substantial role or contribution to the project. These situations can arise due to the interests of researchers because of the need to publish for reasons of promotion or funding, or simply due to inappropriate practices within the same research group. Thus, can end up generating disagreement among members and end up being detrimental to the reputation of the research group, due to the lack of consistency when applying the authorship policy. To improve this situation, it is necessary to establish clear policies, promote a culture of fair recognition and involve institutions and funding bodies.

Sustainability

We face pressing challenges today, with global warming at the forefront. Addressing the urgent need to reduce pollutant waste is paramount in our efforts to this crisis. This study focuses on ozonization as a disinfecting agent, notable for its ability to operate without generating waste or requiring additional reagents. Considered a sustainable water treatment solution, it holds promise for minimizing environmental impact. However, it's essential to acknowledge its considerable energy cost and consider its energy management. In evaluating new applications, a comprehensive cost-benefit analysis is crucial, considering various perspectives to establish sustainability indicators.

Gender Perspective

Gender stereotypes persist in influencing access to higher positions, thereby perpetuating traditional male-dominated societal norms. This issue was underscored by the Spanish Ministry of Science in 2021, revealing that only 13% of female researchers were active in STEM fields (Spanish Ministry of Science and Innovation, 2021). The disparity is further evident in the percentages of permanent female researchers in groups such as LEQUIA (33%) (LEQUIA, 2024).

The project team with which I collaborate, is predominantly composed of women, with a representation of 60%. This challenges the prevailing gender imbalance in STEM fields. Addressing gender bias in scientific research is crucial, as demonstrated by the scarcity of women in leadership positions and their disproportionate representation in subordinate roles

1. INTRODUCTION

Drinking water treatment plants (DWTP) are pivotal in ensuring the health and well-being of communities. Their primary role is to protect public health by eliminating harmful contaminants, including pathogens, chemicals, and pollutants, which could otherwise lead to waterborne diseases and health risks. By adhering to stringent regulatory standards, these facilities provide a reliable supply of clean, safe drinking water (DW) that meets consumers' expectations.

Water treatment plants not only ensure health and safety but also contribute to the improvement of water aesthetics. They tackle issues related to taste and odour, making the water more palatable and encouraging people to consume more water for hydration. Moreover, these facilities are equipped to remove particulates and turbidity, resulting in clear and visually appealing water.

Global warming and its environmental repercussions are intensifying the frequency and severity of natural disasters, including hurricanes, floods, and wildfires, which can disrupt both water sources and infrastructure. In such scenarios, the adaptability of DWTPs becomes invaluable as it ensures uninterrupted access to safe DW. This not only safeguards public health but also enhances climate resilience, a fundamental aspect of addressing the broader global warming challenge.

In the context of global warming, the role of DWTPs gains added significance. These facilities serve as pillars of public health, economic development, and environmental sustainability. Through efficient water treatment and the removal of contaminants, they contribute to the mitigation of climate change's impact on aquatic ecosystems. Furthermore, their responsible management of energy and resources aligns with global efforts to reduce greenhouse gas emissions and combat global warming, making them indispensable components of modern infrastructure.

1.1 Role and Impacts of Natural Organic Matter in DW

Natural Organic Matter (NOM) refers to a complex mixture of naturally occurring organic compounds found in surface water, groundwater, and other natural water sources. NOM originates from the decomposition of organic materials, such as leaves, algae, and microorganisms, in aquatic environments. It consists of a diverse array of organic molecules, including humic substances, fulvic acids, tannins, and other organic compounds. NOM is a ubiquitous component of natural waters (Maqbool *et al*., 2020) and plays a significant role in the context of DW treatment and water quality:

- Complex Analytical Challenges: NOM poses complex analytical challenges for DW treatment facilities. Its composition is highly diverse and can vary significantly depending on the source of water. Accurately characterizing and quantifying NOM components require sophisticated analytical techniques and equipment, making NOM analysis both time-consuming and resource-intensive (Krasner, S. W, 1996, Pan, Y., 2016). These

analytical challenges are essential to address as they impact the understanding of the specific NOM content and reactivity in the treatment process.

- Formation of Assimilable Organic Carbon (AOC) and Increases Microbial Risks: NOM can also contribute to the formation of AOC, which is an important consideration in DW treatment. AOC represents the fraction of NOM that can be utilized as a carbon source by microorganisms, particularly bacteria (U.S. EPA, 2002). Increased AOC levels in treated water can stimulate microbial growth in distribution systems, potentially leading to biofilm formation and microbiological regrowth. This, in turn, can increase the risk of water quality deterioration (van der Kooij *et al*., 1982, Hambsch and Werner, 1993, U.S. EPA, 2002, Camper, 2004, Vital *et al*., 2010) and pose challenges for maintaining residual disinfection, as it consumes disinfectants like chlorine. Controlling and minimizing AOC levels is critical to mitigate microbial risks and maintain water quality as the water travels through distribution networks.

- Source of Contaminants: NOM is a complex mixture of naturally occurring organic compounds derived from decaying vegetation and organic materials in aquatic environments (Beckett, R., & Ranville, J. 2006). While not inherently harmful, NOM can serve as a source of various contaminants, including organic and inorganic substances.

- Water Quality and Aesthetics: NOM in water can cause issues related to water quality and aesthetics (Dietrich, A. M. 2006, Zhang, T. *et al*, 2020,). It can lead to the development of unpleasant tastes and odours in DW. The compounds within NOM, such as geosmin and 2-methylisoborneol, are known for causing musty or earthy odours and flavours. These taste and odour problems can make the water unappealing to consumers, even if it is safe to drink (Mustapha, S. 2021, Srinivasan, R., & Sorial, G. A. 2011)

- Interference with Treatment Processes: The presence of NOM can interfere with various water treatment processes. For example, in coagulation and flocculation processes, NOM can act as a colloid, reducing the effectiveness of particle removal. In addition, it can negatively impact the efficiency of filtration by coating filter media and reducing the removal of suspended particles. This interference can complicate the removal of other contaminants and necessitate additional treatment steps (Jacangelo, J. G., 1995, Levchuk, I 2018)

- Formation of Disinfection Byproducts: NOM is a precursor for the formation of disinfection byproducts (DBPs) during the chlorination or chloramination of water. DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs), can have regulatory limits and health concerns (Hua *et al*., 2015, Li *et al*., 2014, Tian *et al*., 2013). The control of NOM in water treatment is essential to minimize the formation of DBPs and their potential health risks.

1.2 Drinking Water Treatment Operations

DWTPs employ a variety of treatment processes to ensure the delivery of safe and clean DW. These processes are typically implemented in a specific order to effectively remove contaminants and provide high-quality DW. Here are some common treatments used in DWTPs:

- Ozonation: Ozone is a powerful oxidizing agent used to break down and remove organic and inorganic contaminants in water. It can effectively oxidize pathogens, taste and odour compounds, and other impurities. Ozone preoxidation is often employed as a preliminary step to initiate the breakdown of complex contaminants, making subsequent treatment processes more effective (Lin *et al*., 2022).
- Coagulation/Flocculation (C/F): During coagulation, chemicals called coagulants (commonly aluminium sulfate or ferric chloride) are added to the water. These chemicals neutralize the electrical charges on particles, allowing them to come together and form larger aggregates. In the flocculation step, gentle mixing promotes the formation of larger, settleable particles (flocs) from the smaller coagulated particles. These flocs can trap and absorb impurities, such as suspended solids, microorganisms, and some dissolved substances (Korshin *et al*., 2009).
- Activated Carbon (AC) Adsorption: AC is widely used for the removal of organic compounds, taste and odour compounds, and some chemicals like pesticides and industrial pollutants. Granular activated carbon (GAC) or powdered activated carbon (PAC) is added to the water, and the porous structure of activated carbon adsorbs and traps contaminants as they pass through. This process is highly effective in improving water quality and taste (Ding *et al*., 2019).
- Chlorine Disinfection: Chlorine is commonly used for disinfection in DWTPs. It effectively kills or inactivates bacteria, viruses, and other pathogens that may be present in the water. It also provides residual disinfection to protect against recontamination during distribution (Hua & Reckhow, 2007).

These treatment processes are typically used in combination and may be followed by additional steps such as sedimentation, filtration, and pH adjustment to further refine water quality. The specific order and combination of treatments can vary depending on the source water quality, local regulations, and the desired water quality goals. The goal of DWTPs is to provide safe, palatable, and reliable DW to the community while complying with regulatory standards and addressing local water quality challenges.

1.3 Microbial Risks and Chemical Risks in Drinking Water

Balancing microbial risks and chemical risks in NOM removal is a critical aspect of designing and operating effective DWTPs. The treatment processes mentioned earlier, such as ozonation, coagulation/flocculation, activated carbon adsorption, and chlorine disinfection, play pivotal roles in addressing both microbial and chemical contaminants. However, achieving the balance for NOM removal and DBPs minimization requires a

comprehensive understanding of the characteristics of the source water, the potential risks involved, and the efficiency of each treatment step.

Microbial risks in drinking water primarily involve the presence of bacteria, viruses, and other microorganisms that can cause waterborne diseases (Cabral, J. P. 2010). Chlorine disinfection is a commonly employed method to eliminate or inactivate these microorganisms (Sommer *et al*.2008, WHO 2011). However, the effectiveness of chlorine can be influenced by factors such as contact time, temperature, and the presence of organic matter. High levels of NOM can react with chlorine, forming disinfection by-products (DBPs) and reducing the available chlorine for microbial inactivation (Mazhar, M. A., *et al*, 2020).

The formation of assimilable organic carbon (AOC) during the breakdown of NOM further complicates microbial risk management. AOC serves as a nutrient for microorganisms, potentially leading to biological regrowth in the distribution system (Escobar, I. C., 2001). Therefore, a delicate balance must be maintained to ensure sufficient disinfection without compromising the water's aesthetic qualities and safety.

While chlorine effectively controls some microbial risks, it also poses chemical risks by fostering the formation of DBPs, including trihalomethanes (THMs) and haloacetic acids (HAAs) (Koley, S., 2024), subject to regulatory limits due to health concerns. Striking the right balance involves optimizing the dosage of chlorine to achieve effective microbial disinfection while minimizing DBP formation. Advanced monitoring and control systems are crucial in real-time tracking of chlorine levels, organic matter content, and DBP concentrations. This allows for adjustments to chlorine dosage to maintain effective disinfection while minimizing the production of DBPs (Sandaa, K.,2019).

To achieve an optimal balance between microbial and chemical risks, DWTPs are increasingly incorporating advanced monitoring and control systems. Real-time monitoring of water quality parameters, including microbial indicators and chemical concentrations, allows for prompt adjustments to treatment processes. Automated control systems can optimize chemical dosages based on the variability of source water characteristics, ensuring consistent and reliable water quality.

Moreover, the integration of advanced analytical techniques helps in characterizing NOM components more accurately, addressing the challenges associated with its diverse composition. By gaining a deeper understanding of NOM, treatment plants can develop more effective strategies to manage its impact on both microbial and chemical aspects of water quality. (Chen, W., & Yu, H. Q. 2021)

Thus, the role of DWTPs extends beyond mere water treatment; they are essential guardians of public health, environmental sustainability, and resilience in the face of climate change. Achieving the delicate balance between microbial and chemical risks requires a holistic approach, combining advanced technologies, rigorous monitoring, and a nuanced understanding of water chemistry. As water treatment continues to evolve, DWTPs will play a crucial role in providing communities with not only safe and palatable drinking water but also in adapting to emerging challenges in a changing global environment.

1.4 Chemical Analysis of Drinking Water

Understanding how well we remove organic matter is really important for DWTPs. It helps us know if our treatment processes are working effectively and meeting quality standards. Trihalomethanes are especially important to watch out for because they can affect human health.

In DWTPs, we use lab tests like Total Organic Carbon and Visible Ultraviolet Absorbance to check how much organic matter is being removed. Using UV Absorbance at wavelengths of 254 nm and absorbance ratios 210/254, 250/365, 254/203, 254/436, 265/465, 270/400, 280/350 and 465/665 (Table 1.1), provide a more detailed characterization of the organic matter present in a sample than the absorbance values at a single wavelength.

Table 1.1: Spectral absorbance ratios and their characteristic references

Absorbance Ratio	Reference	Indicator/Characteristic
220/280	Yang *et al* (2016)	Characterization of organic matter absorbance spectra
254/203	Hur *et al* (2006)	The relative proportion of unsaturated to saturated fractions
465/665	Chen *et al* (1977)	Degree of condensation of aromatic carbon network
265/465	Rodríguez *et al* (2016)	Characterization of fulvic acids and macromolecules
254/436	Jaffé *et al*. (2004)	Composition of indigenous versus terrestrial organic matter
280/350	Changchun *et al*. (2021)	Activation of polyhydroxyaromatics in natural organic matter
250/365	De Haan and De Boer (1987)	Changes in the relative size of dissolved organic matter molecules
210/254	Her *et al* (2003)	Characterization of NOM macromolecules based on aromaticity

However, these tests do not give us detailed information about the type of organic matter. So, we need to use more advanced techniques like fluorescence spectroscopy to better understand NOM. This analysis technique allows for the rapid and sensitive characterization of organic matter. Fluorescence is a property of some organic and inorganic molecules that release energy in the form of light when excited by a high-energy light source. The goal is to evaluate natural fluorescent groups such as humic, fulvic fractions, and fluorescent proteins in a water sample.

The Excitation-Emission Matrix (EEM) is an increasingly used measure in fluorescence spectroscopy. It is a three-dimensional scan that generates a contour plot relating the excitation wavelength to the emission wavelength and fluorescence intensity. Organic matter in water shows discrete intensity peaks at different excitation and emission wavelengths; therefore, from the data found with EEM, it is possible to determine the presence and concentration of specific fluorophores, which are fractions of fluorescent organic matter (Bieroza *et alet al*., 2009).

Based on the literature (Chen *et alet al*. 2003), several EEM fluorescence regions could be defined, theoretically containing specific constituents with distinctive fluorometric properties of organic matter. In this case, fluorescence peaks with excitation wavelengths less than 250nm and emission wavelengths less than 350nm are related to aromatic proteins like tyrosine. Peaks found in excitation wavelengths between 250 – 280 nm and emission wavelengths less than 380nm are linked to materials resembling soluble microbial byproducts. Additionally, for organic compounds like humic acids, fluorescence peaks are found at excitation wavelengths

less than 380nm and emission wavelengths greater than 380nm. Lastly, fulvic acids can be found in peaks with excitation wavelengths <250nm and emission wavelengths >350nm. The simplified graph by Bridgeman *et alet al*. (2011) can be observed in Figures 1.1 and 1.2. Similarly, Coble (1996) in his study includes another classification alternative to fluorescence regions, in which humic-type fluorescence is divided into two peaks, peak A and C, and protein-type fluorescence indicated as peak B (tyrosine type) and peak T (tryptophan type).

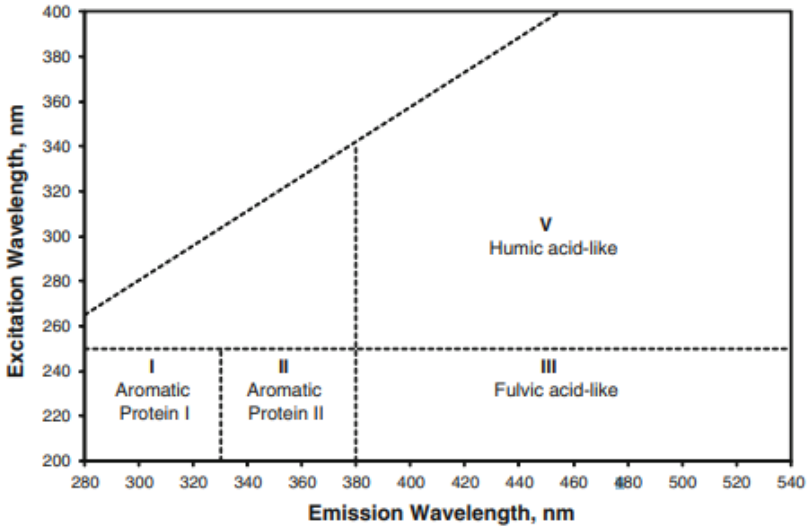

Figure 1.1. EEM fluorescence regions (Bridgeman *et alet al*., 2011).

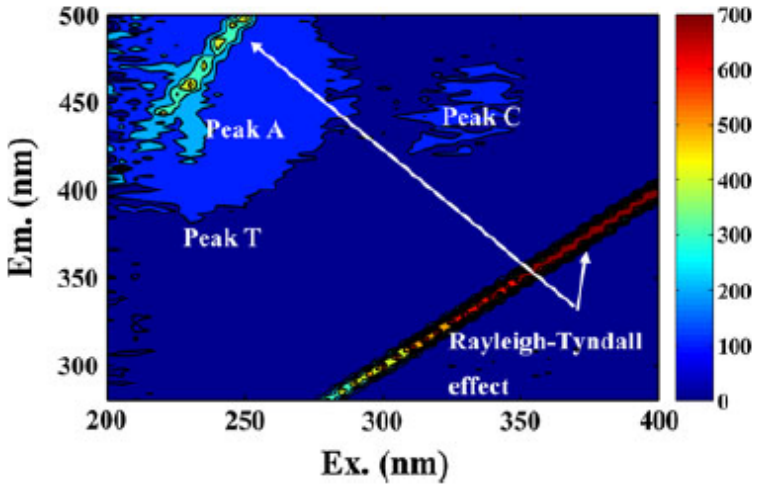

Figure 1.2. Excitation-Emission Matrix with typical fluorescence characteristics (Bridgeman *et alet al*. 2011).

1.5 Assimilable Organic Carbon

AOC is the fraction of carbon most easily consumed by bacteria, facilitating microbial regrowth (Nescerecka, A., *et alet al*. 2014). Within the dissolved organic carbon (DOC) portion of total organic carbon (TOC), two subsets exist: biodegradable dissolved organic carbon (BDOC) and assimilable organic carbon (AOC). AOC consists of low molecular weight organic compounds, generated through bacterial cell lysis or the biological and chemical hydrolysis of organic material. The AOC organic fraction is relatively small, typically ranging from 3 to 500 µg/L, constituting 0.1-8.5 percent of the DOC reservoir (Van der Kooij, D., *et alet al*, 1989).

The implementation of ozonation in water treatment processes has been investigated regarding its impact on AOC levels and subsequent bacterial regrowth. Full-scale system data analysis reveals a significant increase in AOC concentration following ozonation treatment. Moreover, this increase correlates with elevated bacterial counts within the distribution system, both in the short and long term. Thus, while ozonation may effectively target certain contaminants, its unintended consequence of elevating AOC levels and promoting bacterial regrowth underscores the importance of comprehensive monitoring and optimization strategies in water treatment (Escobar, I. C., & Randall, A. A. 2001).

The biological stability of DW is a critical aspect of ensuring the safety and quality of the quality supply. The scientific literature points out AOC can be used as a control parameter to optimize treatment processes, minimize microbial growth, and ensure the long-term stability and quality of treated water [Wingender & Flemming, 2011]. The implementation of ozonation in water treatment processes has been investigated regarding its impact on AOC levels and subsequent bacterial regrowth. Full-scale system data analysis reveals a significant increase in AOC concentration following ozonation treatment. Moreover, this increase correlates with elevated bacterial counts within the distribution system, both in the short and long term. Thus, while ozonation may effectively target certain contaminants, its unintended consequence of elevating AOC levels and promoting bacterial regrowth underscores the importance of comprehensive monitoring and optimization strategies in water treatment.

Pseudomonas fluorescens (P17) and *Spirillum sp*. (NOX) strains, were selected in published literature (Van der Kooij *et al*.1984) for the AOC measurement test based on their metabolic characteristics. Both species have been used as inoculums in AOC bioassays to characterize released metabolic organics during such analyses.

P17 is commonly used in water quality studies, specifically for determining AOC in water, which is crucial for assessing drinking water biostability. This strain is known for releasing organic metabolites during AOC analyses, and its characteristics have been extensively studied regarding water quality and microbial regrowth in drinking water distribution systems. Additionally, research has investigated its growth in tap water with various substrates and its transport through porous media. Thus, P17 holds significant importance in water quality and microbiology, particularly concerning AOC determination and microbial regrowth in water distribution systems.

NOX has been utilized alongside P17 in various studies, particularly for AOC analyses. The significance of this conjunction with P17 lies in their use as part of AOC. P17 metabolizes various compounds except carboxylic acids like oxalate. To address this limitation, NOX, which primarily thrives on carboxylic acids and can metabolize oxalate, is included. While P17 can metabolize a wide array of compounds but not carboxylic acids, NOX can metabolize carboxylic acids while excluding carbohydrates, alcohols, or aromatic acids. Additionally, NOX does not assimilate amino acids when grown in compound mixtures.

1.6 Case Studies

Montfullà

The Montfullà DWTP is located 7km from the city of Girona. It carries out the treatment of water from the Pasteral reservoir, located in the municipality of La Cellera de Ter. This reservoir, apart from its function as a generator of electricity of hydraulic origin, is used as a regulator of water resources of the lower section of the Ter River, since it serves the water supply in Barcelona and Girona.

The station has two treatment lines, the first to supply the city of Girona in high and low and the second to supply the Costa Brava (in high). The Montfullà DWTP treats 1,2 m^3/s of water, approximately 600 l/s for each line.

Both lines have the same treatment stages, starting with 1) capture, 2) pre-oxidation with chlorine dioxide, followed by 3) coagulation, 4) flocculation, 5) sedimentation, 6) sand filtration 7) active carbon filtration) and 8) disinfection. The treatment train can be seen in Figure 1.3.

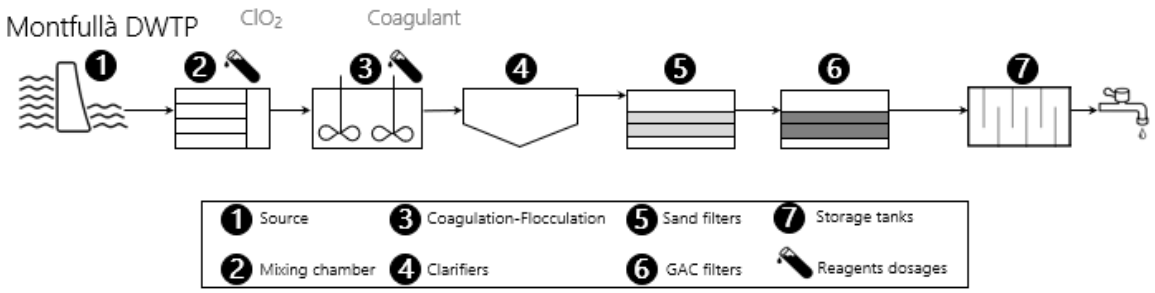

Figure 1.3: Scheme of the Drinking Water Treatment Plant of Montfullà.

Figueres

The Figueres DWTP is located in the north-east of Catalonia. The maximum treatment flow rate is 0.17 $m^{3/}s$. The plant supplies the population of the region of Figueres and its surroundings, with a total population of around 65,000 inhabitants. This plant collects water from the Darnius-Boadella reservoir located 17 km from Figueres. The reservoir has a capacity of 61.1 m3 and this is currently at 11,32% of its maximum capacity (32.65 km2). It should be noted that this ETAP consists of two treatment lines that consistently operate at an average nominal flow rate. When demand increases, the entrance of one or both pipes is opened wider, allowing more water to enter for

The DWTP Figueres treatment train is as follows: 1) capture, 2) peroxidation with ozone, 3) coagulation-flocculation, 4) sedimentation, 5) filtration with active carbon, 6) disinfection with ultraviolet light, 7) disinfection with sodium hypochlorite. The treatment train can be seen in Figure 1.4.

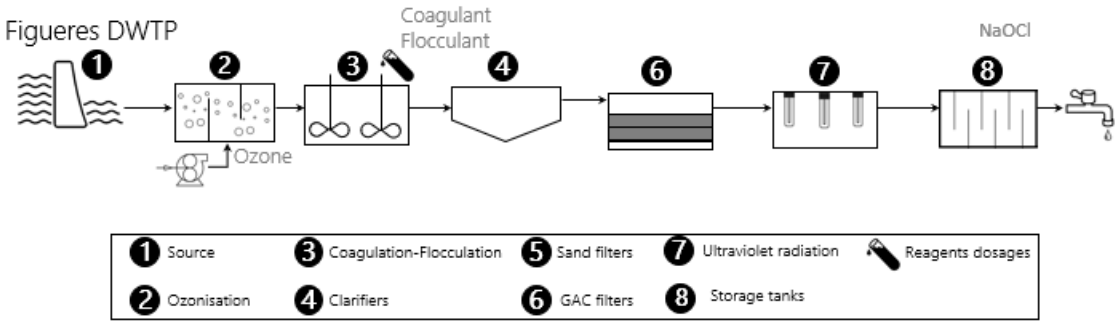

Figure 1.4: Scheme of the Drinking Water Treatment Plant of Figueres.

1.7 Problem Statement and Research Hypothesis

Optimizing drinking water treatment processes, particularly those involving ozone and chlorine, is crucial for ensuring water quality and minimizing health risks. While these processes effectively eliminate microbial contaminants and NOM, challenges arise in managing DBPs and the potential elevation of AOC levels during NOM breakdown, serving as a DBP precursor and impacting disinfection effectiveness.

Understanding the intricate relationship between AOC, NOM, and THM formation is essential for the efficient design and operation of DWTPs. This study focuses on investigating AOC levels and THM formation in two DWTPs utilizing different treatment trains.

The hypothesis posits that utilizing ozone as an efficient step, followed by chlorine disinfection, influences AOC levels and subsequently impacts THM formation in treated water. The interplay between ozone and chlorine may alter NOM composition, affecting AOC production, and influencing microbial regrowth and DBP formation in distribution systems.

Within the framework of the Sherlock Research project, funded by the Spanish Science Ministry and in collaboration with Aigües de Girona and Aigues de Figueres, LEQUIA researchers actively investigate AOC and THM dynamics to enhance overall drinking water treatment efficiency and safety.

This final degree project, part of ongoing LEQUIA projects, is based on the following hypothesis:

- Ozone efficiency followed by chlorine disinfection significantly reduces THM formation, minimizing the chemical risk of DBPs.

- Ozone efficiency alters NOM upon chlorination, increasing AOC production and posing a microbial risk for bacterial regrowth.

Achieving a delicate balance between ozone-induced DBP minimization and increased AOC levels during chlorination is crucial for optimizing drinking water treatment processes, and managing both chemical and microbial risks.

2. OBJECTIVES

This comprehensive study contributes to the optimization of DW treatment processes, the mitigation of microbial risks, and the provision of high-quality, safe water to communities. The general objectives are:

1. **To Implement the analysis protocol for the determination of AOC.**

Develop a standardized protocol for analysing Assimilable Organic Carbon (AOC) in water samples by:

- Testing acquired strains and identifying any challenges encountered in adapting the methodology to real-world water samples.
- Establishing a finalized methodology that ensures an accurate determination of AOC levels, thus contributing to the optimization of drinking water treatment processes**.**

2. **To Evaluate Treatment Efficiency on a lab scale**

Assess the effectiveness of various treatment processes in a laboratory setting by:

- Monitoring changes in Natural Organic Material (NOM) characteristics such as turbidity, UV-Vis absorption, and fluorescence at different treatment stages.
- Testing different doses of ozone to determine their efficacy in removing NOM and improving the treatability of raw water.
- Evaluating the performance of coagulation and flocculation processes in removing NOM from ozonated water samples.
- Investigating the efficiency of activated carbon (AC) adsorption in further reducing residual NOM and enhancing the quality of treated water.

3. **To Examine Chlorine Disinfection and THM Formation**

Investigate the impact of chlorine disinfection on the formation of Trihalomethanes (THMs) in water treated with various methods by:

- Analysing THM formation in water treated with ozone, coagulation/flocculation, and activated carbon filtration.
- Establishing correlations between THM formation and the efficiency of preceding treatment processes contributes to the understanding of disinfection byproduct formation and mitigation strategies.

4. **To Measure Assimilable Organic Carbon (AOC)**

Quantify the presence of Assimilable Organic Carbon (AOC) in treated water and distribution systems by:

- Implementing methods to measure AOC levels in treated water.

3. MATERIALS & METHODS

3.1 Protocol for Biological Stability Analysis

The conventional AOC analysis method is based on a bioassay that was developed by van der Kooij and co-workers (1982) and later adapted by others in the Standard Methods. The literature references for the following methodology are Van der Kooij *et al*. (1982) and LeChevallier (1993). This procedure has never been used before by the LEQUIA group, and it will be implemented and adapted with technical support from Laia Mauricio Estrada, Frederic Gich and researchers from gEMM, and UdG.

3.1.1 Preparation of organic carbon-free glassware

The glassware for the experiments was meticulously cleaned to eliminate organic components. This involved washing with detergent, rinsing with ultrapure water, soaking in 0.2 N HCl for 24 hours, and three additional rinses. To render it organic carbon-free, the glassware was baked at 550°C for at least 6 hours. PTFE-lined silicone septa used for sealing the 60 mL vials in the AOC test underwent treatment by soaking in a 10% sodium persulfate solution at 60°C for at least 1 hour, followed by three rinses with ultrapure water and air-drying. This rigorous preparation ensured the absence of organic contaminants, maintaining the integrity of the experimental setup.

3.1.2 Bacterial stain revival and preservation

The revival of freeze-dried cultures of *Pseudomonas fluorescens* strain (ATCC 49642) and *Spirillum* sp. strain (ATCC 49643) involved incubation in Nutrient broth and Tryptic Soy respectively, at room temperature following the guidelines of the American Type Culture Collection (ATCC). Post-revival, these cultures were preserved in 20% glycerol in cryovials at -70°C.

3.1.3 Preparation of stock cultures

For the preparation of stock cultures, the thawed frozen cultures underwent cultivation on R2A agar plates for 3–5 days at room temperature. Subsequently for each strain, a single colony from the agar plate was transferred into 100 mL chlorine-neutralized tap water, followed by incubation for 1 week to acclimate the organisms to oligotrophic conditions at room temperature. Then, 0.1 mL of adapted cultures were then transferred to a 2 mg/L sodium acetate-containing minimal medium solution and incubated for 1 week to attain final cell densities of $8.9 \cdot 10^6$ CFU/mL for P17 and $2 \cdot 10^7$ CFU/mL for NOX. The resultant stock cultures were stored at 4°C for up to 60 days and periodically replaced with fresh stock cultures.

3.1.4 Calibration curve

Bacterial strains were inoculated into liquid culture media and incubated under optimal conditions until they reached the exponential growth phase. The optical density (OD) of the aliquots was measured at regular intervals during the exponential growth phase at a wavelength of 550 nm using a spectrophotometer. OD readings were recorded for each sample. For each aliquot used for OD measurement, a series of dilutions was prepared to

cover a range of concentrations, and the corresponding cell density was determined using a separate method such as plate counting. For plate counting, the aliquots of P17 and NOX were plated onto Broth nutritive and Tryptic soy agar plates respectively and incubated at room temperature for 3-4 days. The resulting colonies were counted to determine the UFC/mL.

Linear regression analysis was performed to correlate OD readings with cell density for each time point. The calibration curve was validated by comparing the predicted cell densities obtained from OD readings with the actual cell counts obtained from plate counting or direct cell counting.

3.1.5 AOC Testing

In the experimental testing methodology, sterile 1L bottles were used to sample desired points. The samples were filtered through 0.45 μm filters, and 45 mL of the filtered samples were transferred to 60 mL "crimp-cap glass" vials. Pasteurization at 70°C for 30 minutes was performed to eliminate vegetative cells. Inoculation with 1 mL of each strain followed, with triplicates prepared for each condition or sample (Figure 3.1).

Additional vials were included for control purposes, addressing growth control, potential carbon pollution, and strain growth control. During the process, absorbance measurements of the inoculations at 550 nm were taken to determine the cellular density at that time using the calibration curve. To determine the initial number of organisms (No) present in the samples UFC values of the mother solution were initially assessed. By employing Equation 1, the initial No of the samples could be calculated.

$$N_o = \frac{1\,mL\ inoculum\ x \frac{UFC}{mL}\ stock\ inoculum}{60\,mL/vial} \qquad \text{Eq. 1}$$

A prolonged incubation period of 5 days at 23°C was implemented, they were followed by dilutions and plating on R2A agar plates. Manual colony counting was conducted, and the colonies were converted to, UFC values. For the identification of colonies P17 colonies appeared as whole, smooth, slightly convex, and opaque, while NOX colonies are circular, whole, slightly convex, shiny, and translucent.

To determine the "yield factor," the strains' performance in a specific carbon source (sodium acetate) was calculated. Alternatively, empirical performance factors (Eq 2), as described by Van der Kooij (1990) and referenced in Aggarwal (2015), were utilized, demonstrating the comprehensive nature of the undertaken microbial analysis.

$$\frac{\mu g}{L} AOC = \left(\frac{aver.\,UFC\ P17}{mL} \cdot \frac{\mu g\ acetate}{yield\ factor} + \frac{aver.\,UFC\ NOX}{mL} \cdot \frac{\mu g\ acetate}{yield\ factor}\right) \cdot\ 1000 \frac{mL}{L} \qquad \text{Eq. 2}$$

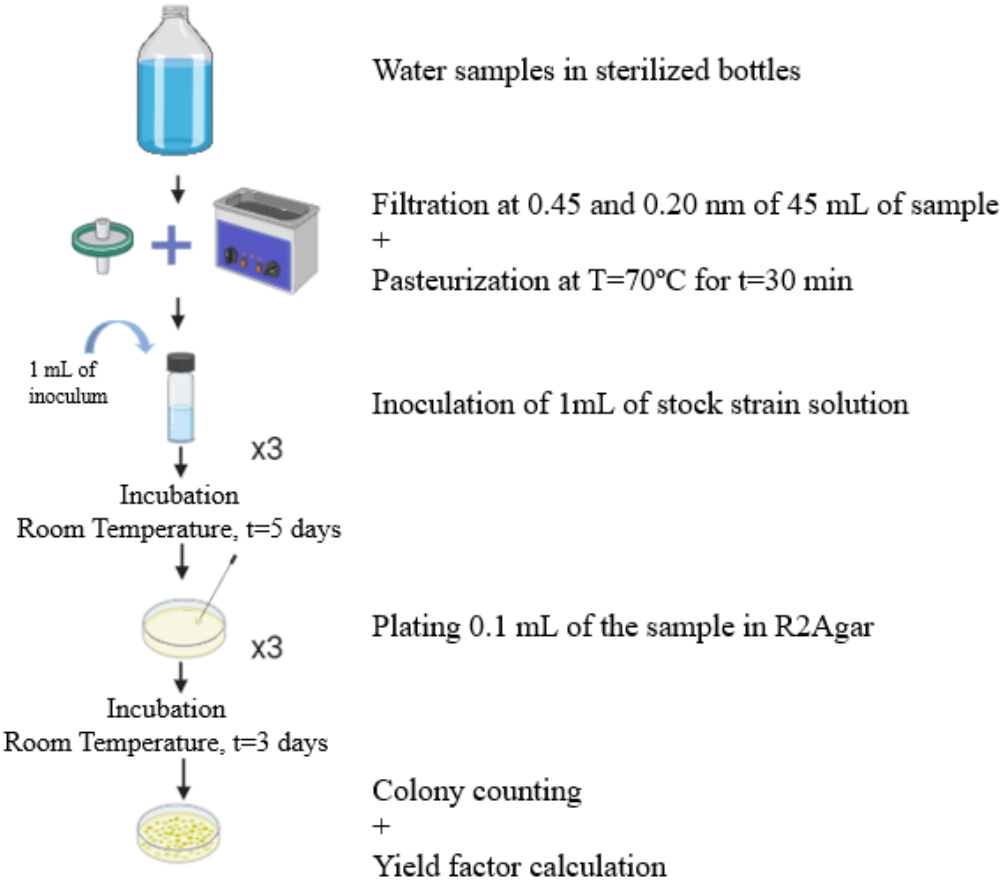

Figure 3.1: Schematic diagram of the protocol for AOC testing

3.2 Water Sampling in two DWTP

Water sampling was conducted in two DWTPs, Montfullà (Girona) and Figueres. A standard sampling system of the water from the entry point was carried out in 20L containers previously cleaned with a standard laboratory procedure to minimize contamination and preserve the integrity of the samples: (i) Rinse with soap and water, ii) Rinse with distilled water, iii) Rinse with Milli-Q water, and iv) Air dry.

The samples were kept at a temperature of approximately 10 ºC during transport until reaching the laboratory. There, they were subsequently stored in a refrigerated environment at temperatures between 4°C and 6°C. Analysis was conducted within five days of sample collection to minimize the potential for changes in the water quality. Keeping the samples at the same low temperature helped slow down biological and chemical processes that could alter the composition of the water and maintain their stability.

3.3 Lab-scale Drinking Water Treatment

3.3.1 Ozone Preoxidation Experiments

The laboratory equipment required for the pre-ozonation included an oxygen concentrator, an ozone generator and an ozone analyser. Before ozonizing the sample, to ensure the ozone generator was producing the desired ozone dose accurately, it was crucial to calibrate the system and adjust the output of the ozone generator.

The ozonation process was carried out in a contact tank that does not react with ozone, where the ozone was allowed to contact the water. Efficient stirring was employed to achieve homogenization, ensuring that all parts of the water were exposed to ozone uniformly, to maximize the effectiveness of ozone in treating the entire water volume. The use of a cabin was essential to avoid direct exposure to ozone gas as it is a powerful oxidizing agent that can be toxic if inhaled.

For each water sample under treatment, a blank and two doses of ozone were applied, which were 1.0 or 2.5 and 2.0 or 5.0 mg $O_3 \cdot L^{-1}$ of treated water. To achieve this ozone dosing, a fixed ozone gas concentration was established and the contact time of the water samples was calculated accordingly.

3.3.2 Coagulation/Flocculation Experiments

The experimental coagulation test was conducted using the Jar test method, involving the coagulation/flocculation/sedimentation stage on a laboratory scale. The equipment comprised chambers with stirrers, each with a water capacity of 2 litres. Initially, the pH of each sample was adjusted using sodium hydroxide (NaOH 0.1N) to increase it or hydrochloric acid (HCl 0.1N) to decrease it.

The coagulant used was directly extracted from each DWTP's and diluted to a concentration of 10g/L. The addition of the coagulant followed a standard process, specifying the required amount to achieve the desired concentration (Table 3.1). The experiments were conducted with a concentration of 30 ppm.

The programmed coagulation/flocculation process was executed under the following conditions: i) Coagulation: agitation at 200 rpm for 2 minutes, ii) Flocculation: agitation at 50 rpm for 10 minutes, iii) Suspension of agitation for 30 minutes to facilitate the sedimentation of flocs. Following this, the supernatant was carefully collected into pre-cleaned 1 L glass bottles for subsequent analytical testing.

Table 3.1: Coagulant volume for desired concentration in ppm

Dose (ppm)	Volume (mL)	Dose (ppm)	Volume (mL)
10	1	40	4
15	1.5	45	4.5
20	2	50	5
25	2.5	60	6
30	3	80	8
35	3.5	-	-

3.3.3 Activated Carbon Adsorption

The activated carbon adsorption undergoes an initial process of crushing and sieving to achieve a powder size. A dose of 1 g/L is then applied to the water, and the mixture is subjected to constant agitation on an orbital

shaker for an overnight contact time. After the specified duration of overnight contact time, a separation step of the water from the activated carbon is done through a vacuum filtration process, facilitated by a pump. For this purpose, 0.45 µm filters, pre-washed with MilliQ water, were utilized. This filtration approach ensures the removal of activated carbon particles, resulting in a clarified and treated water sample ready for subsequent analyses.

Two distinct types of activated carbon, BGE and AIRPEL supplied by Calgon Carbon (Belgium), were employed in the water treatment process (Figure 3.2). It is noteworthy that these variants possess varying porosity levels and specific surface areas, contributing to their diverse adsorption characteristics.

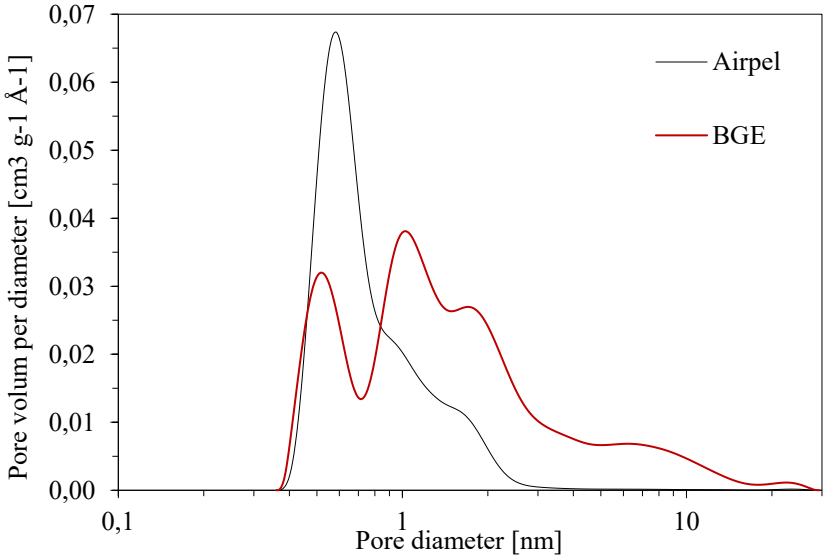

Figure 3.2: Pore size distribution of the AC used. For each pore width (x-axis) the Y-axis shows the void volume per AC mass unit and diameter length.

3.4 Physicochemical Characterization

Turbidity and PH measurements: Samples underwent laboratory analysis to characterize their physicochemical properties. Turbidity was assessed using a TU5200 turbidimeter, measuring suspended particles in Nephelometric Turbidity Units (NTU). No sample pre-processing was necessary. pH values were measured using a portable VWR pH/mV/°C pH 110 M meter, applying the potentiometric method.

UV-Vis Absorbance: Multiwavelength UV-Vis spectral analysis was performed using an Agilent Cary 3500 compact UV-Vis spectrophotometer covering a range of 190 nm to 800 nm. The samples were filtered through 0.45µm filters that had been pre-cleaned with Milli-Q water.

Fluorescence Spectroscopy: The characterization of fluorescent organic matter was conducted using a Cary Eclipse fluorescence spectrometer equipped with quartz cells. Before analysis, samples were pre-processed by filtration through 0.45µm filters cleaned with Milli-Q water. Fluorescence emission spectra were recorded between 220-450 nm, and excitation spectra were recorded between 250-580 nm, both with 5 nm increments.

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 reported by Rodríguez *et al*. (2016) (Figure 3.3).

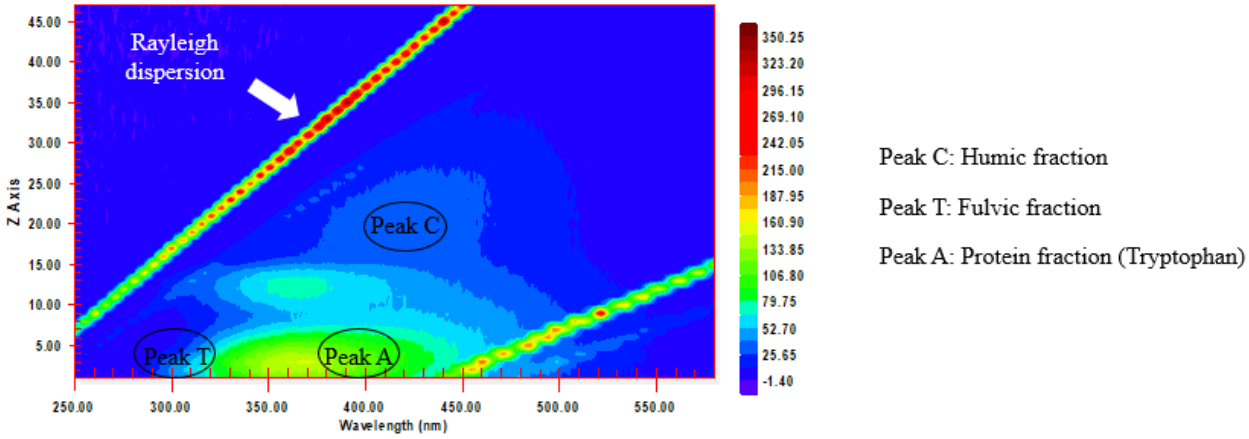

Figure 3.3: Identification of fluorescence peaks in Cary Eclipse spectrometer according to the spectra recorded.

3.5 Chlorine Disinfection and THMs Analysis

3.5.1 Samples chlorination

The chlorination procedure aimed to assess the chlorine demand in water samples and determine the formation of disinfection by-products, such as THMs.

A sodium hypochlorite solution with an initial concentration of 150000 ppm (15%) was used as a disinfectant agent. A dilution series was prepared, reaching a chlorine concentration of 200 ppm. For each water sample under treatment, three doses of chlorine were applied, resulting in three subsamples with initial chlorine concentrations ranging from 2 to 5 ppm.

After reaction periods of 24-hours period, the residual chlorine concentration was measured using a portable Hanna chlorine checker. The subsample with the chlorine level closest to 1 ppm was chosen for GC-MS analysis of THMs. Chlorination was halted using ascorbic acid as a quencher.

3.5.2 THMs analysis through Head-Space GC-MS

The analysis of Trihalomethanes (THMs) was performed using headspace gas chromatography coupled to the mass detector (GC-MS). The GC-MS employed for this study was the Agilent Technologies 7980B series. This analytical approach facilitated the separation and quantification of THMs by analysing the volatile compounds present in the gas phase above the sample. This analytical technique allowed for a comprehensive assessment of THMs based on their unique characteristics in the vapour phase. To calibrate the GC-MS, we utilized the THM calibration mix CRM48140, sourced from Supelco.

3.5.3 Statistical analysis

To relate the removal of natural organic matter and the potential for THM formation, it was necessary to apply the Pearson correlation coefficient, which is a statistical measure used to quantify if there is a significant relationship between two variables and, if so, to measure the strength and direction of that relationship.

The Pearson correlation coefficient is represented by the symbol "r", and its value varies between -1 and 1. A value of -1 indicates a perfect negative correlation, meaning that as one variable increases, the other decreases proportionally. A value of 1 indicates a perfect positive correlation, meaning that as one variable increases, the other also increases proportionally. A value of 0 indicates a lack of linear correlation between the variables.

The equation used to measure this coefficient is expressed as:

$$r = \frac{\sum(X - \bar{X})(Y - \bar{Y})}{\sqrt{\sum(X - \bar{X})^2 \cdot \sum(Y - \bar{Y})^2}} \qquad \text{Eq. 3}$$

Where X and Y are the variables for which the correlation is being calculated and $\bar{X}$ and $\bar{Y}$ are the average values of X and Y, respectively.

In this case, because the aim was to understand the relationship between more than one variable, a correlation matrix was created, showing the correlation coefficients between various combinations of variables. The Excel data analysis tool was used to create the matrix.

4. RESULTS & DISCUSSION

4.1 Modifications in the Protocol for Measuring Biological Stability for DW

The proposed protocol for measuring biological stability in DW (section 3.1) was adapted since we did not obtain the expected results. In this section, we present the modifications done aiming to establish the own protocol for the research group. In this modified protocol, the adjustments detailed are made in some critical stages: the preparation of stock cultures, the cell density determination, and the AOC testing procedure. These modifications are designed to streamline operations, minimize potential sources of error, and optimize the reliability of the results obtained.

4.1.1 Preparation of stock cultures

In the original protocol for preparing the stock cultures, there was a step involving the incubation of the frozen cultures in 100 mL chlorine-neutralized tap water for one week. This incubation period was intended to acclimate the organisms to oligotrophic conditions, a process that is believed to enhance their adaptation and viability in subsequent experimental procedures.

However, after some consideration and discussion with gEMM colleagues, we decided to remove this incubation week from the protocol motivated by several factors. Firstly, to enhance efficiency: this reduction in steps decreases the time needed for culture preparation without compromising result integrity while reducing laboratory resources such as consumables, energy, and personnel time. Additionally, we considered that the prolonged incubation period might introduce variability in experimental outcomes. Moreover, by simplifying the stock culture preparation process, we believe that reproducibility across various assays was enhanced, promoting consistency in experimental procedures, and facilitating comparisons between assays.

Regarding the step of incubation, in the original protocol, the adapted cultures were transferred to a minimal medium solution containing 2 mg/L of sodium acetate in Ringer to attain cell density. We decided to use a higher concentration of acetate, specifically 20 mg/L since the bacteria was not growing. We considered that 2 mg/L was not sufficient as a carbon source for the needed growth of the culture.

4.1.2 Cell Density Determination

The original protocol employed a calibration curve to ascertain cell density through absorption measurements. However, we could not detect absorbance in the spectrophotometer in our samples due to insufficient turbidity in the solutions tested in none of the two strains. Tables 4.1 and 4.2 show the optical density (OD) obtained for each culture dilution. We attempted to identify an alternative wavelength through wave scanning, but no viable option was found**.**

As an alternative approach, we proposed monitoring based on dilutions in the stationary phase for cell density determination of the stock cultures. We analysed the cell density of the stock cultures inoculated and during the AOC testing over three consecutive days. From the idea of the number of organisms in the stationary phase that is assumed to be the maximum number supported by the nutrients in the sample. It is considered that the

stationary phase is reached when the day-to-day variations in heterotrophic plate counts are below 20% (Zhao, X. 2013).

Table 4.1: Dilution bank of p17 strain and its OD at 550 nm

Dilution factor	OD (AU)
10^3	0.012
10^4	0.013
10^5	0.012

Table 4.2: Dilution bank of NOX strain and its OD at 550 nm

Dilution factor	OD (AU)
10^3	0.011
10^4	0.012
10^5	0.012

In future evaluations, the stationary phase colony enumeration will be conducted over three consecutive days after a week of incubation, with acceptance criteria set at a maximum variation of 20%. Samples falling within this variation range will be deemed indicative of the stationary phase. If the results on days 8 and 9 of incubation show a higher count compared to day 7 by more than 20%, day 7 results will not be considered, indicating that the strains are still in the growth phase. Conversely, if the lowest count is observed on day 9, it will not be considered, signifying the onset of the death phase. Additionally, if the variation across the three incubation days exceeds 20% but remains below 25%, the results will still be accepted as indicative of the stationary phase (Zhao, X. 2013)

4.1.3 AOC Testing

The proposed changes to the AOC testing protocol were implemented to address concerns regarding potential contamination issues arising from the presence of microorganisms. The focus was on ensuring the integrity and accuracy of the analysis by reducing the risk of contamination throughout the experimental process.

To achieve this, we employed membrane filtration using a 0.20 μm filter for further filtration of the water samples. This step ensures the removal of smaller microorganisms, such as bacteria and fungi, which could still be present after prefiltration. This pore size effectively traps most bacteria and larger particles while allowing smaller molecules and ions to pass through, thereby enhancing the purity and sterility of the samples. This change aims to eliminate these contaminants and minimize the presence of non-target microorganisms that might compromise the reliability of the experimental results (Aggarwal 2015.)

Furthermore, rinsing the membrane filters before use with ultrapure water helps minimize the potential for organic carbon leaching. This precautionary measure reduces the risk of introducing contaminants into the samples, which could affect the accuracy of the analysis (Aggarwal 2015.).

4.1.4 Final AOC Protocol Stablished

1. Unfreeze the frozen cultures according to American Type Culture Collection (ATCC) guidelines.
2. Cultivate the cultures on R2A agar plates for 3–5 days at room temperature.
3. Incubate cultures in a minimal medium solution containing 20 mg/L of sodium acetate to attain cell density.
4. Collect water samples in sterile 1L bottles and filter the samples through 0.20 μm filters.
5. Transfer 45 mL of the filtered samples to 60 mL crimp-cap glass vials.
6. Pasteurize the vials at 70°C for 30 minutes to eliminate vegetative cells.
7. Inoculate the samples with 1 mL of each strain with triplicates for each condition.
8. Include additional vials for control purposes.
9. Determine cell density in the stationary phase and calculate an initial number of microorganisms.
10. Incubate the vials for 5 days at 23°C.
11. Dilute the samples and plate on R2A agar plates for colony counting.
12. Perform manual colony counting and convert the colonies to UFC values.
13. Analyse and interpret the results based on UFC values and growth patterns of the bacterial strains**.**

4.2 Assessment of Organic Matter Removal Technologies at Lab-Scale

DWTPs use the parameters TOC, UV_{254}, and turbidity to establish quality controls and track the DOM removal along the water treatment train. In this work, for each DTWP we performed two samplings and determined the efficiency of DOM removal after each unitary unit evaluated at lab scale to assess the effectiveness of the treatment process.

The samples collected from influent water in Montfullà and Figueres from Sampling 1, were subjected to ozone treatments (section 3.3.1) of 1 ppm and 2 ppm, respectively. In contrast, samples from Sampling 2 received higher ozone concentrations of 2.5 ppm and 5 ppm O_3. Following the peroxidation, a coagulation/flocculation (C/F) process was carried out (section 3.3.2) with the same conditions for every sample. Finally, adsorption (CA) performance was evaluated for two different activated carbon materials (section 3.3.3).

4.2.1 Evaluating Turbidity Decay

Table 4.3 shows the turbidity levels for the samples treated from Montfullà water in two different samplings. The initial turbidity levels in Sampling 2 were notably higher in the influent (RW) condition compared to Sampling 1. However, despite this initial difference, Sampling 1 consistently exhibited a greater reduction in turbidity, particularly when subjected to lower ozone concentrations of 1 ppm, achieving around 35% reduction. Conversely, in Sampling 2, regardless of ozone concentration, a similar level of reduction, ranging from 2.260 to 2.545 UT was observed, indicating a consistent response to ozone treatment irrespective of its concentration.

Regarding C/F, Sampling 2 experienced a more significant total turbidity decay of 83.74% at 5 ppm ozone concentration, whereas, in Sampling 1, the turbidity decay was lower overall around 33-35%. Generally, higher ozone concentrations led to approximately 85% total.

Table 4.3: Turbidity determined in the Influent (RW) and after each operation unit. Reductions of turbidity were calculated concerning the previous treatment (-% previous) and concerning the raw water (-%RW) for the two samplings in Montfullà DWTP.

Sampling 1	Turbidity [NTU]	-% previous	-% RW
RW	1.880	-	
O3 1 ppm	1.220	35.1	-
C/F	0.806	33.9	57.1
AC AIRPEL	0.106	86.8	94.3
AC BGE	0.068	91.6	96.4
O3 2 ppm	1.575	16.2	-
C/F	0.739	53.0	60.6
AC AIRPEL	0.099	86.6	94.7
CA BGE	0.051	93.1	97.3
Sampling 2	Turbidity [NTU]	-% previous	-% RW
RW	2.950	-	
O3 2.5 ppm	2.545	13.7	-
C/F	0.501	80.3	83.0
AC AIRPEL	0.112	77.7	96.2
AC BGE	0.181	63.9	93.8
O3 5 ppm	2.260	23.3	-
C/F	0.390	82.7	86.7
AC AIRPEL	0.165	62.8	95.0
AC BGE	0.145	57.6	94.4

In terms of treatment effectiveness, Sampling 1 demonstrated slightly better performance with BGE CA treatment, achieving a 10% higher turbidity decay compared to AIRPEL CA treatment. However, when considering total decay, both treatments resulted in the same 95% reduction. Conversely, in Sampling 2, AIRPEL AC treatment showed a 10% higher turbidity reduction compared to BGE CA treatment regardless of the O3 concentration, yet again yielding the same 95% total decay. Overall, both treatment processes consistently achieved a 95% turbidity decay across various conditions and samplings, emphasizing their effectiveness in reducing turbidity levels in water samples.

In Figueres (Table 4.4), there was a noticeable discrepancy in initial turbidity levels between Samplings, with Sampling 1 registering higher turbidity at 2,665 TU compared to 1,301 TU in Sampling 2. Despite this difference, both samplings exhibited a consistent turbidity reduction ranging from 15% to 25% across various ozone concentrations, suggesting that the effectiveness of the treatment was independent of ozone concentration.

Interestingly, despite Sampling 1 having lower ozone concentrations, it consistently displayed a higher reduction in turbidity compared to Sampling 2. This suggests that factors beyond ozone concentration may have influenced the observed turbidity reduction. It is plausible that the higher initial turbidity in Sampling 1 prompted a more pronounced response to treatment, leading to a higher reduction percentage.

Further analysis reveals that both treatment methods, regardless of the ozone concentration, yielded similar results, with no significant differences observed between AIRPEL and BGE treatments. Both treatments

achieved a comparable final decay of 95%. However, it is worth noting that while the initial turbidity levels were higher in Sampling 1, the final turbidity values were considerably lower compared to Sampling 2. This indicates that despite the initial turbidity disparity, Sampling 1 achieved a more substantial overall reduction in turbidity, with final turbidity values ranging between 0.060 and 0.090 TU, compared to higher values around 120 TU in Sampling 2.

Table 4.4: Turbidity determined in the Influent (RW) and after each operation unit. Reductions of turbidity were calculated concerning the previous treatment (-% previous) and concerning the raw water (-%RW) for the two samplings in Figueres DWTP.

Sampling 1	Turbidity [NTU]	-% previous	-% RW
RW	2.665	-	
O3 1 ppm	2.265	15.0	-
C/F	0.790	65.1	70.3
AC AIRPEL	0.096	87.8	96.3
AC BGE	0.065	91.7	97.5
O3 2 ppm	2.130	20.0	20.0
C/F	0.708	66.7	73.4
AC AIRPEL	0.092	87.0	96.5
AC BGE	0.059	91.6	97.7
Sampling 2	Turbidity [NTU]	-% previous	-% RW
RW	1.301	-	
O3 2.5ppm	0.973	25.1	-
C/F	0.647	33.5	50.2
AC AIRPEL	0.134	79.2	89.7
AC BGE	0.152	76.5	88.3
O3 5 ppm	1.095	15.8	15.8
C/F	0.464	57.6	64.3
AC AIRPEL	0.081	82.5	93.7
AC BGE	0.125	73.0	90.3

4.2.2 Analysis of reductions in UV254

Table 4.5 shows the results of the reduction of UV absorbance at 254 nm for the samples corresponding to Montfullà water treatment at lab-scale. For the influent water (RW) Sampling 1 had a higher UV_{254} value of 0.127 cm^{-1} compared to Sampling 2, which had a UV254 value of 0.102 cm^{-1}. This fact can be influential when comparing the two samplings.

Taking into account the variations in the O_3 concentration applied across samples or scenarios, there's a consistent reduction in UV radiation of around 30% in Sampling 1, with lower concentrations of O_3 comparing Sampling 2 even starting from higher initial absorbance. In contrast, in Sampling 1 at higher concentrations of O3, the absorbance reduction doubles up to 20%. This suggests that factors other than ozone concentration might be influencing UV levels, or that the interaction between ozone and UV is complex and not directly proportional.

The presence of a clear trend in the worsening of the reduction of UV values up to half in the Coagulation/Flocculation (C/F) process due to increased ozone levels implies that the relationship between ozone and UV reduction efficiency is negatively correlated. It suggests that higher concentrations of ozone may

interfere with the effectiveness of the C/F process. Ozone, being a powerful oxidizing agent might affect the ability of coagulants to form flocs effectively, leading to a decrease in C/F efficiency.

While the AC treatment AIRPEL demonstrates slightly more effectiveness compared to BGE,' it's remarkable that the UV254 levels are already at very low levels. This suggests that both AIRPEL and BGE are highly efficient. Despite this, AIPEL might outperform BGE, indicating its potential for even further improvement or optimization in treatment processes.

Table 4.5: UV Absorbance at 254 nm determined in the Influent (RW) and after each operation unit. Reductions were calculated concerning the previous treatment (-% previous) and concerning the raw water (-%RW) for the two samplings in Montfullà DWTP.

Sampling 1	UV_{254}Absorbance	-% previous	-% RW
RW	0.127	-	
O3 1 ppm	0.092	27.5	-
C/F	0.075	18.4	40.9
AC AIRPEL	0.051	32.0	59.8
AC BGE	0.057	24.0	55.1
O3 2 ppm	0.089	30.3	-
C/F	0.082	7.91	35.8
AC AIRPEL	0.053	34.9	58.2
AC BGE	0.055	32.5	56.6
Sampling 2	UV_{254}Absorbance	-% previous	-% RW
RW	0.102	-	
O3 2.5 ppm	0.092	10.2	-
C/F	0.082	10.3	19.6
AC AIRPEL	0.045	45.7	56.3
AC BGE	0.055	33.5	46.5
O3 5 ppm	0.080	21.5	-
C/F	0.079	1.87	23.0
AC AIRPEL	0.044	43.9	56.8
AC BGE	0.053	32.4	48.0

The significant reduction of 56,693 % in UV254 levels from Sampling 1 underscores the effectiveness of the process being studied, regardless of the process. However, it is needed to take into account that in Montfullà, Sampling 1 had a higher UV254 value of 0.127 compared to Sampling 2, which had a UV254 value of 0.102, as it was previously mentioned.

In the Figueres assay (Table 4.6), both samplings exhibit similar initial UV254 absorbance levels in the RW condition, with Sampling 1 at 0.075 and Sampling 2 at 0.083, indicating comparable starting points for the treatments. This difference in initial absorbance levels between the two samplings is crucial to consider when evaluating the effectiveness of subsequent treatments.

Throughout the treatments despite variations in ozone concentration, there is a consistent UV reduction of 12-20% observed in both samplings, regardless of the ozone concentration applied. This suggests a uniform response to treatment across different conditions and may be influenced by other factors. For example, in Sampling 1, increasing ozone concentration from 1 ppm to 2 ppm resulted in a reduction in UV absorbance from 0.066 to 0.062, representing a decrease of approximately 16.78%. However, in Sampling 2, a similar

increase in ozone concentration from 2.5 ppm to 5 ppm led to a smaller reduction in UV absorbance from 0.066 to 0.066, indicating a decrease of around 20.10%.

Despite variations in ozone concentration, there is no clear relation in UV reduction observed because of the C/F process. It's noteworthy that in Sampling 1, the C/F process doubles the reduction in UV when ozone concentration increases. Conversely, in Sampling 2, the C/F process generates more absorbance with the opposite effect, indicating contrasting responses to ozone concentration in the two samplings. This suggests that the interaction between ozone concentration, C/F process, and UV reduction efficiency is complex and may not follow a consistent pattern across different conditions.

Table 4.6: UV Absorbance at 254 nm determined in the Influent (RW) and after each operation unit. Reductions were calculated concerning the previous treatment (-% previous) and concerning the raw water(-%RW) for the two samplings in Figueres DWTP.

Sampling 1	UV_{254}Absorbance	-% previous	-% RW
RW	0.075	-	
O3 1 ppm	0.066	12.0	-
C/F	0.056	14.5	24.8
AC AIRPEL	0.041	27.6	45.6
AC BGE	0.046	18.7	38.9
O3 2 ppm	0.062	16.7	16.7
C/F	0.043	30.3	42.0
AC AIRPEL	0.042	2.7	43.6
AC BGE	0.047	-7.6	37.5
Sampling 2	UV_{254}Absorbance	-% previous	-% RW
RW	0.083	-	
O3 2.5ppm	0.073	12.0	-
C/F	0.074	-1.3	10.8
AC AIRPEL	0.043	41.5	47.8
AC BGE	0.051	30.7	38.2
O3 5 ppm	0.066	20.0	20.0
C/F	0.076	-14.5	8.4
AC AIRPEL	0.043	43.6	48.4
AC BGE	0.051	32.8	38.5

Comparing the effectiveness of treatments, particularly between CA AIRPEL and CA BGE, indicates that both treatments contribute to reducing UV absorbance effectively. In Sampling 1, for instance, both AIRPEL and BGE treatments at 1 ppm ozone concentration resulted in UV absorbance levels below 0.05 cm^{-1}, indicating high efficiency. However, the AIRPEL treatment showed slightly better performance with lower UV absorbance levels. This suggests that while both treatments are effective, AIRPEL might offer slightly better performance, indicating potential for further optimization. Remarkably, the UV254 levels are already at very low levels.

Regardless of the treatment or process applied, there is a significant reduction in UV254 levels, as evidenced by the substantial percentage reductions of about 37-47% across various conditions.

4.2.3 Examining EEM Fluorescence Patterns

Lastly, the organic matter reduction in the treated samples was evaluated by EEM fluorescence (section 3.4). Table 4.7 shows the results for Montfullà samples, with notable differences in the initial fluorescence levels between samplings, particularly evident in Peak T and Peak A. Sampling 1 exhibits higher initial values for

Peak T and Peak A compared to Sampling 2. This discrepancy suggests variations in the initial conditions between the samplings.

Ozone application appears to have varying effects on the reduction of fluorescence intensity across different peaks and samplings. While reductions are observed in Peaks C, A, and T in both samplings when comparing different ozone concentrations, the magnitude of reduction varies. Peak C shows a similar reduction of around 35% across both samplings, indicating a consistent response in comparison to Peaks T and A

Table 4.7: Intensity of the fluorescence peaks determined in the Influent (RW) and after each operation unit. Reductions are calculated concerning the previous treatment (-% prev.s) and concerning the raw water(-%RW) for the two samplings in Montfullà DWTP.

Sampling 1	Peak C	-% prev	-% RW	Peak A	-% prev.	-% RW	Peak T	-% prev.	-% RW
RW	32.170	-	-	97.158	-	-	132.143	-	-
O3 1 ppm	29.212	9.2	-	53.594	44.8	-	25.844	80.4	-
C/F	23.474	19.6	27.0	84.341	-57.4	13.2	142.199	-450.2	-7.6
AC AIRPEL	7.786	79.1	84.8	13.196	90.7	91.9	5.914	96.7	96.4
AC BGE	4.901	66.8	75.8	7.863	84.3	86.4	4.736	95.8	95.5
O3 2 ppm	31.605	1.8	-	57.395	40.9	-	31.535	76.1	-
C/F	26.181	17.2	18.6	53.253	7.2	45.2	27.545	12.7	79.2
AC AIRPEL	5.597	78.6	82.6	13.773	74.1	85.8	8.945	67.5	93.2
AC BGE	5.355	79.5	83.4	10.240	80.8	89.5	6.680	75.7	94.9
Sampling 2	Peak C	-% prev.	-% RW	Peak A	-% prev.	-% RW	Peak T	-% prev.	-% RW
RW	37.678	-	-	72.903	-	-	55.940	-	-
O3 2.5 ppm	26.157	30.6	-	55.757	23.5	-	22.410	59.9	-
C/F	47.512	-81.6	-26.1	23.514	57.8	67.7	25.801	-15.1	53.9
AC AIRPEL	4.436	90.7	88.2	0.353	98.5	99.5	13.191	-84.8	76.4
AC BGE	34.124	28.2	9.4	11.802	49.8	83.8	47.676	-261.4	14.8
O3 5 ppm	14.959	60.3	-	24.755	66.0	-	16.587	70.3	-
C/F	13.236	11.5	64.9	26.907	-8.7	63.1	19.992	-20.5	64.3
AC AIRPEL	1.303	90.2	96.5	0.589	97.8	99.2	4.322	78.4	92.3
AC BGE	3.126	76.4	91.7	1.653	93.9	97.7	4.812	75.9	91.4

The Coagulation/Flocculation process demonstrates different behaviours in reducing fluorescence intensity across different ozone concentrations and samplings. The C/F process leads to a reduction in fluorescence intensity, while in other cases, it increases. This variability suggests that the responsiveness of the C/F process may depend on factors such as initial conditions and ozone concentration.

Both BGE and AIRPEL treatments contribute to the reduction of fluorescence intensity across all peaks and ozone concentrations. The effectiveness of each treatment method varies across different peaks and ozone concentrations, with some variations observed between samplings. In Sampling 1, both AC treatments exhibit similar effectiveness, with reductions of around 70-90% across all peaks. However, in Sampling 2, AIRPEL demonstrates higher effectiveness, achieving approximately a 90% reduction in fluorescence intensity. Notably, at 2.5 PPM ozone concentration, BGE treatment leads to an increase in the intensity of Peak C and Peak T, suggesting a different treatment response under certain conditions.

In Figueres DWTP (Table 4.8), the fluorescence values in the initial RW sample show a similar intensity on each peak, indicating uniformity in the composition of the samples at the outset. Furthermore, regardless of the

ozone concentration applied, there is a consistent trend in fluorescence reduction, suggesting that ozone treatment affects all peaks similarly. However, there is an increased intensity observed on peak C. Regarding the C/F ratio, there is a tendency for reduction to approximately half of the initial value, except in peak A when subjected to high ozone concentrations in each sampling. This deviation in peak A could be due to specific interactions between ozone and components present in that peak.

Table 4.8: Intensity of the fluorescence peaks determined in the Influent (RW) and after each operation unit. Reductions of calculated respect to the previous treatment (-% prev.) and respect to the RW raw water (-%RW) for the two samplings in Figueres DWTP.

Sampling 1	Peak C	-% ant.	-% RW	Peak A	-% ant.	-% RW	Peak T	-% ant.	-% RW
RW	15.860	-	-	33.680	-	-	15.685	-	-
O3 1 ppm	10.620	33.0	-	28.560	15.2	-	21.760	-38.7	-
C/F	7.980	24.9	49.7	14.784	48.2	56.1	6.627	69.5	57.8
AC AIRPEL	0.930	88.4	94.1	2.690	81.8	92.0	1.450	78.1	90.8
AC BGE	2.885	63.9	81.8	5.195	64.9	84.6	2.780	58.1	82.3
O3 2 ppm	10.170	35.9	-	20.980	37.7	-	9.170	41.5	-
C/F	6.980	31.4	56.0	41.032	-95.6	-21.8	70.284	-666.5	-348.1
AC AIRPEL	1.900	72.8	88.0	5.460	86.7	83.8	1.340	98.1	91.5
AC BGE	1.780	74.5	88.8	4.040	90.2	88.0	4.700	93.3	70.0
Sampling 2	Peak C	-% ant.	-% RW	Peak A	-% ant.	-% RW	Peak T	-% ant.	-% RW
RW	16.951	-	-	33.761	-	-	19.396	-	-
O3 2.5ppm	8.231	51.4	-	30.637	9.3	-	43.107	-122.3	-
C/F	7.414	9.9	56.3	16.654	45.6	50.7	10.825	74.9	44.2
AC AIRPEL	1.864	74.9	89.0	4.130	75.2	87.8	2.638	75.6	86.4
AC BGE	1.588	78.6	90.6	4.452	73.3	86.8	3.898	64.0	79.9
O3 5 ppm	8.231	51.4	-	30.637	9.3	-	43.107	-122.3	-
C/F	7.414	9.9	56.3	16.654	45.6	50.7	10.825	74.9	44.2
AC AIRPEL	1.864	74.9	89.0	4.130	75.2	87.8	2.638	75.6	86.4
AC BGE	1.588	78.6	90.6	4.452	73.3	86.8	3.898	64.0	79.9

Both AC treatments demonstrate high efficiency, with no specific AC showing superior performance over the other. They consistently achieve relative reductions of about 60-80%, contributing to an overall reduction of 80-90% regardless of the sampling or treatment method employed at the end. This underscores the effectiveness of both AC treatments in reducing fluorescence levels in the samples

4.2.4 Comparative Evaluation of Treatment Technologies

Ozone treatment stands out as a pivotal process in enhancing water quality in both Montfullà and Figueres DWTPs although different degrees of effectiveness across the sampling periods and treatment stages were observed. In Montfullà DWTP, ozone treatment demonstrates notable effectiveness, particularly during Sampling 1, where reductions in turbidity, UV_{254} and fluorescence peak intensity are evident. For instance, ozone treatment at 1 ppm achieves a 9.2% reduction in turbidity, an 80.4% reduction in fluorescence peak intensity and 27.6% in UV_{254}, higher reductions compared to posterior treatments. However, the efficacy of ozone treatment appears to decrease in certain instances, such as during Sampling 2, where the reduction in turbidity is less pronounced. These fluctuations suggest potential challenges in consistently achieving effectiveness and may need further optimization of ozone treatment processes. For instance, the oxidation of organic molecules by ozone can lead to the formation of smaller molecules that cause higher turbidity.

In Figueres DWTP, ozone treatment similarly exhibits variable effectiveness across different sampling periods and treatment stages. During Sampling 1, ozone treatment at 1 ppm results in moderate reductions in turbidity and fluorescence peak intensity, with reductions of 33.0% and 38.7%, respectively, compared to anterior treatments. However, ozone treatment at higher concentrations, such as 2.5 ppm and 5 ppm, shows more significant reductions in turbidity, highlighting the dose-dependent nature of ozone treatment efficacy, and fluctuations in treatment effectiveness between samplings.

Analytically, the variability in ozone treatment effectiveness observed in both DWTPs underscores the complexity of water treatment processes and the influence of factors such as water quality characteristics, treatment methodologies, and operational parameters. While ozone treatment shows promise in enhancing water quality by effectively reducing turbidity and organic matter, achieving consistent and optimal treatment outcomes may require continuous monitoring and adjustment of treatment processes.

C/F is also a crucial treatment in both Montfullà and Figueres samples, playing a significant role in enhancing water quality. Across different sampling periods and treatment stages, C/F consistently demonstrates effectiveness in reducing turbidity, UV254 absorbance, and fluorescence peak intensity. In Montfullà DWTP, C/F achieves notable reductions in turbidity, with percentages ranging from 26.1% to 27.0% compared to the previous treatment. Moreover, UV254 absorbance reductions by C/F reach up to 35.827%, indicating substantial removal of organic matter. However, the performance in reducing fluorescence peak intensity exhibits some variability, suggesting potential challenges in consistently addressing specific contaminants.

In contrast, Figueres DWTP showcases remarkable performance by C/F, with higher reduction percentages observed across all parameters and samplings. For instance, during Sampling 1, C/F achieved a 49.7% reduction in turbidity and a 24.8% reduction in UV254 absorbance compared to the previous treatment. Moreover, fluorescence peak intensity reductions in Figueres DWTP are consistently substantial, with percentages ranging from 45.6% to 75.6%. These results underscore the robustness C/F process in Figueres DWTP, contributing significantly to overall water quality improvement.

Activated carbon treatment, using different materials such as AIRPEL and BGE, plays a vital role in improving water quality in both Montfullà and Figures. In Montfullà DWTP, both AIRPEL and BGE exhibit substantial effectiveness in reducing contaminants, with some variations in performance. During Sampling 1, AIRPEL demonstrated superior efficiency, achieving impressive reductions in turbidity (84.8%) and fluorescence peak intensity (96.4%) compared to BGE. However, BGE still proves to be highly effective, particularly in reducing turbidity (75.8%) and fluorescence (86.4%). These results indicate that both materials contribute significantly to water quality improvement, with AIRPEL showcasing slightly superior performance during certain sampling periods.

In Figueres DWTP, the effectiveness of activated carbon treatment with AIRPEL and BGE materials is also evident, albeit with differences in performance between the two materials. During Sampling 1, both materials achieve substantial reductions in turbidity and fluorescence peak intensity, with AIRPEL generally exhibiting

slightly higher efficiency. For instance, AIRPEL achieves reductions of 94.1% in turbidity and 90.8% in fluorescence peak intensity, while BGE achieves reductions of 81.8% and 82.3%, respectively. However, during Sampling 2, BGE showcases notable improvements, particularly in reducing turbidity, with a reduction percentage of 93.88% compared to AIRPEL's 89.70%. These findings suggest that while both materials are effective in enhancing water quality, their performance may vary depending on the specific sampling period and treatment conditions.

The comparison between AIRPEL and BGE activated carbon materials highlights the importance of material selection and optimization in achieving desired treatment outcomes. Both materials demonstrate significant effectiveness in removing contaminants from water, with slight variations in performance observed between the two. Factors such as material properties, pore structure, and surface chemistry may influence the adsorption capacity and efficiency of activated carbon materials. Therefore, ongoing research and evaluation of different materials, coupled with process optimization, are essential for maximizing the efficacy of activated carbon treatment and ensuring the delivery of safe and high-quality drinking water to consumers.

4.3 Chemical Risk: Chlorination and Disinfection By-Products

Following the assessment of organic matter reduction in terms of turbidity, UV-Vis, and fluorescence, the treated samples underwent chlorination to evaluate the formation potential of trihalomethanes (THM-FP) after 24 hours (section 3.5). From the results obtained in the four samplings, the distribution of the four most frequent types of THM found in the different operating points of the treatment plant can be observed in Figures 4.1-4.4. It is highlighted that CHCl3 is the compound found in the highest proportion in all the samples analysed. Likewise, in general, it is highlighted that CHBr3 was the compound with the lowest concentration in the samples with a percentage of approximately 1%. This may be largely because the samples come from waters with relatively low bromine content.

In the analysis of Sampling 1 in Montfullà, as illustrated in Figure 4.1, a notable decrease in the potential for THM formation is observed in the AC filters for the two doses of O3. This treatment exhibits higher reduction percentages compared to the other treatments, achieving reductions of up to half the initial THM value. Importantly, the efficiency of organic matter elimination appears to be independent of the ozone dose and instead reliant on the treatment method utilized.

In Sampling 2 in Montfullà, Figure 4.2, it is evident that the potential for THM formation decreases across the treatment for the two doses of O3 evaluated. Notably, the coagulation/flocculation and the active carbon filter treatments exhibit higher reduction percentages compared to the ozone treatments, reaching approximately 10-20 ppb THM values. The efficiency of organic matter elimination does not depend on the dose of ozone but on the treatment.

In Sampling 1 in Figueres, as illustrated in Figure 4.3, there appears to be a discrepancy in the doses of O3 applied in different treatments. Specifically, while there is a significant and stable reduction in all treatments at a dose of 1.5 ppm O3, with THM values of 30 ppb or less, representing more than half the initial THM value, at a dose of 1 ppm O3, the total THM slightly decreases but with higher values observed. The efficiency of organic matter elimination appears to depend on the dose of ozone used.

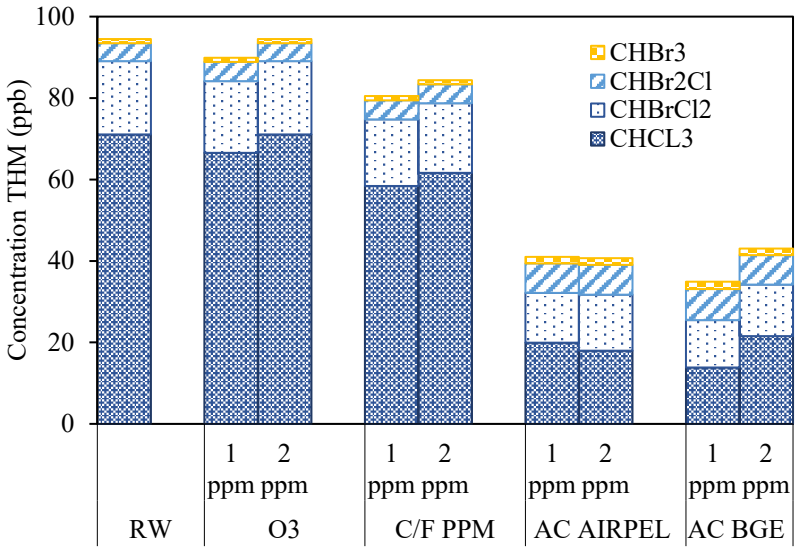

Figure 4.1: Potential for THM formation 24 hours after the different treatment stages of Montfullà Sampling 1. In the x-axis, it represents the different stages of treatment in the two applied doses of ozone. While the y-axis represents the concentrations of the 4 different types of trihalomethanes.

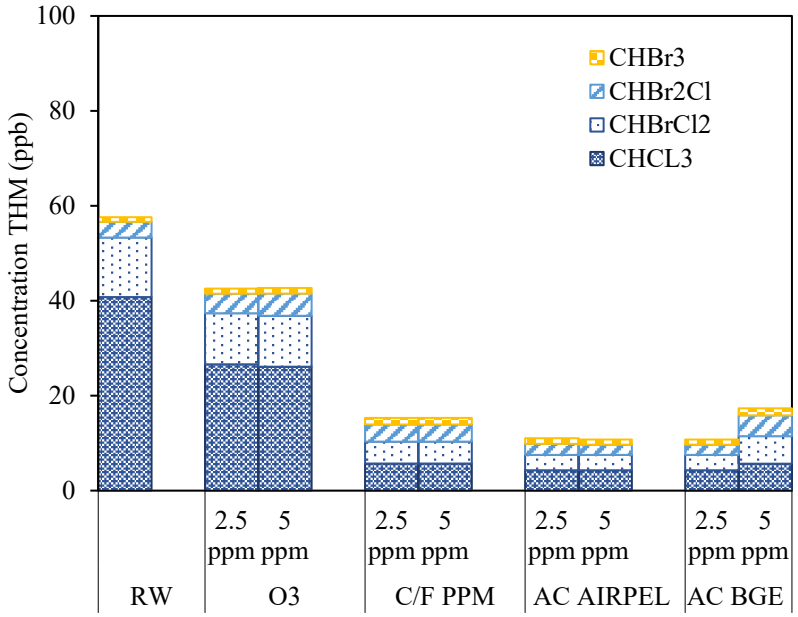

Figure 4.2: Potential for THM formation 24 hours after the different treatment stages of Montfullà Sampling 2. In the x-axis, it represents the different stages of treatment in the two applied doses of ozone. While the y-axis represents the concentrations of the 4 different types of trihalomethanes.

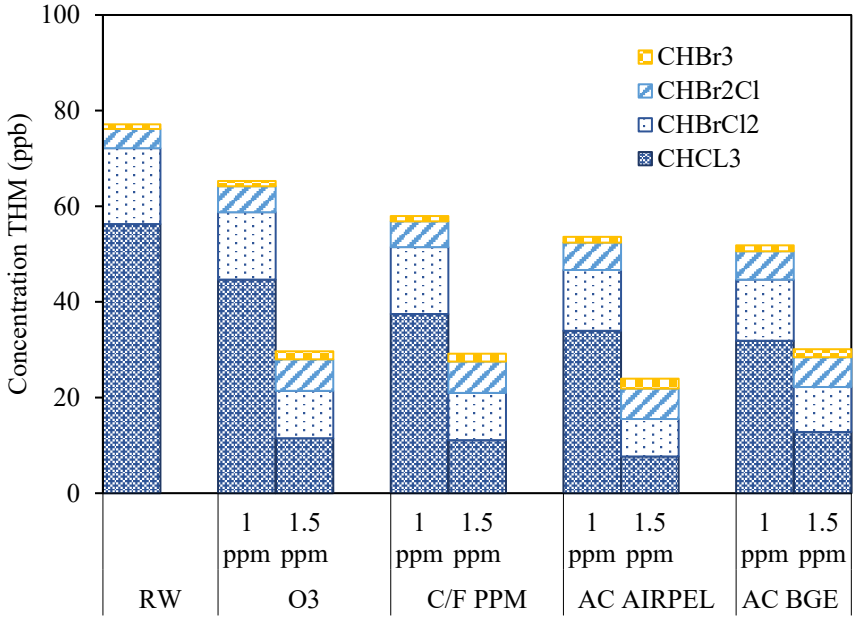

Figure 4.3: Potential for THM formation 24 hours after the different treatment stages of Figueres Sampling 1. In the x-axis, it represents the different stages of treatment in the two applied doses of ozone. While the y-axis represents the concentrations of the 4 different types of trihalomethanes.

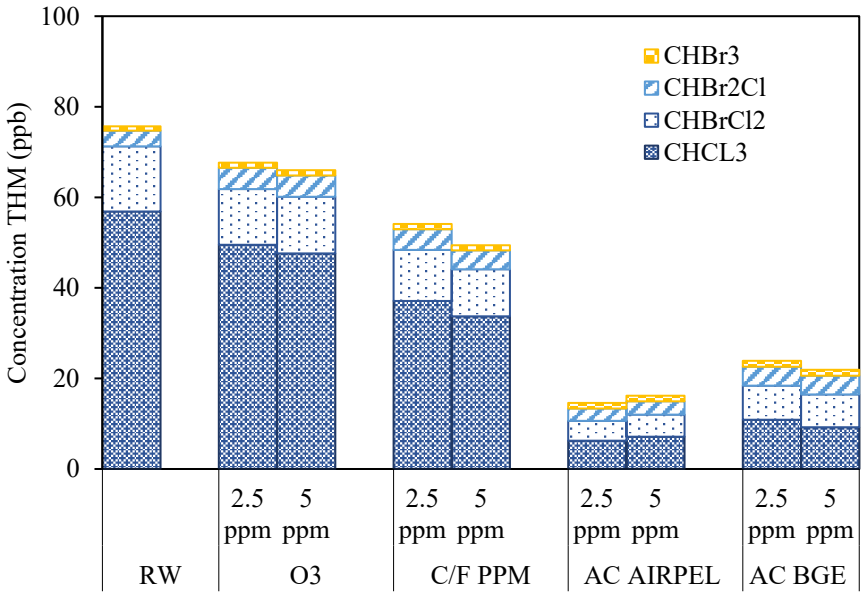

Figure 4.4: Potential for THM formation 24 hours after the different treatment stages of Figueres Sampling 2. In the x-axis, it represents the different stages of treatment in the two applied doses of ozone. While the y-axis represents the concentrations of the 4 different types of trihalomethanes.

In the analysis of Sampling 2 in Figueres, as depicted in Figure 4.4, it is apparent that the potential for THM formation decreases notably in the AC filters for the two doses of O3. This treatment demonstrates higher

reduction percentages compared to the other treatments, achieving up to a 20 ppb reduction in THM levels. It appears that the AIRPEL AC is more efficient than the BGE AC. Moreover, the efficiency of organic matter elimination does not seem to rely on the dose of ozone but rather on the treatment method employed over the CHCl3 compound.

After determining the THM-FP after the sequential organic matter removal of the DW samples, THM-FP was correlated with the chemical parameters. Tables 4.9 and 4.10 show the r coefficients (Eq. 3) obtained from the study of the formation potential of the total and each THM species compared to turbidity, fluorescence peaks, UV_{254}, and the UV ratios identified in Table 1.1.

In examining water samples from Montfullà (Table 4.9) and Figueres (Table 4.10) DWTPs it can be observed that they have several similarities. CHCl3 exhibits noteworthy correlations with the absorbance at 254nm and various ratios, with exceptions noted in the 465/665 ratio. The lack of significant correlation with the 254/203 ratio indicates a potential limitation in discerning information from this ratio regarding CHCl3 concentration. Similarly, CHCl2Br demonstrates a similar correlation profile to CHCl3, although with lower correlation coefficients for UV254 and the ratios, except for a comparatively higher correlation with the 254/203 ratio. This implies a similar relationship with organic matter as CHCl3 but with some variations in correlation strengths. In contrast, both CHClBr2 and CHBr3 exhibit generally poor correlations with the mentioned parameters, suggesting a weaker association with the absorbance at 254nm and the derived ratios.

Peak C and Peak A display robust correlations with CHCl3 and CHCl2Br but notably poor correlations with the less abundant CHClBr2 and CHBr3. This suggests a close relationship between these peaks and the presence of CHCl3 and CHCl2Br, possibly indicating their involvement in the formation or composition of these peaks. Peak T, on the other hand, fails to provide meaningful information regarding CHCl3 and CHCl2Br and exhibits an inverse relationship with CHClBr2 and CHBr3. This implies that Peak T may not be indicative of the presence of CHCl3 and CHCl2Br but rather inversely related to CHClBr2 and CHBr3 concentrations.

Turbidity has similar characteristics observed in Peak C and Peak A, showcasing strong correlations with CHCl3 and CHCl2Br but weak correlations with CHClBr2 and CHBr3, which are produced in very low concentration. This suggests a shared influence of these compounds on the turbidity of the water, possibly due to their interactions with particulate matter or other components affecting turbidity.

Overall, the correlation coefficients provide concrete evidence of the relationship between water quality parameters and THM formation potential. UV254 absorbance, UV ratios, turbidity, and EEM fluorescence peaks serve as reliable indicators for monitoring and predicting THM formation, enabling water treatment plant operators to implement targeted strategies to minimize disinfection byproduct formation and ensure the delivery of safe drinking water to consumers.

Table 4.9: Correlation coefficients of THM Formation Potential at 24 h with UV at different wavelengths, turbidity, and fluorescence intensity of Montfullà DWTP samples.

Montfullà	PF-THM 24h					Parameter			
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	T-THM	Turbidity	Peak C	Peak A	Peak T
UV254	0.757	0.630	-0.093	-0.615	0.724	0.804	0.658	0.912	0.623
254/203	0.878	0.899	0.353	-0.334	0.901	0.499	0.402	0.692	0.292
465/665	0.798	0.810	0.415	-0.152	0.824	0.291	0.284	0.556	0.412
265/465	0.916	0.826	0.099	-0.554	0.902	0.637	0.507	0.948	0.781
254/436	0.880	0.788	0.080	-0.544	0.865	0.639	0.509	0.947	0.818
280/350	0.687	0.677	0.234	-0.254	0.698	0.459	0.465	0.768	0.720
250/365	0.798	0.708	0.078	-0.473	0.783	0.549	0.458	0.893	0.884
270/400	0.885	0.800	0.104	-0.531	0.872	0.613	0.482	0.942	0.822
254/210	0.871	0.934	0.441	-0.278	0.908	0.507	0.419	0.792	0.504
Turbidity	0.554	0.444	-0.139	-0.554	0.522	-	0.464	0.677	0.380
Peak C	0.366	0.191	-0.318	-0.485	0.312	-	-	0.624	0.473
Peak A	0.831	0.711	-0.060	-0.648	0.801	-	-	-	0.811
Peak	0.608	0.459	-0.135	-0.505	0.570	-	-	-	-

Table 4.10: Correlation coefficients of THM Formation Potential at 24 h with UV at different wavelengths, turbidity, and fluorescence intensity of Figueres DWTP samples.

Figueres	PF-THM 24h					Parameter			
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	T-THM	Turbidity	Peak C	Peak A	Peak T
UV254	0.850	0.678	-0.294	-0.725	0.822	0.494	0.791	0.951	0.783
254/203	0.441	0.643	0.454	0.042	0.511	0.665	0.499	0.169	-0.200
465/665	-0.363	-0.445	-0.186	0.069	-0.395	-0.385	-0.373	-0.110	0.130
265/465	0.855	0.755	-0.220	-0.716	0.843	0.602	0.848	0.957	0.733
254/436	0.803	0.684	-0.190	-0.679	0.788	0.514	0.737	0.960	0.831
280/350	0.698	0.575	-0.175	-0.584	0.682	0.390	0.624	0.951	0.916
250/365	0.692	0.579	-0.131	-0.574	0.680	0.383	0.587	0.934	0.919
270/400	0.825	0.723	-0.199	-0.683	0.813	0.558	0.800	0.974	0.800
254/210	0.566	0.768	0.545	0.024	0.644	0.644	0.574	0.392	0.076
Turbidity	0.755	0.732	-0.031	-0.540	0.764	-	0.741	0.529	0.133
Peak C	0.910	0.832	-0.263	-0.709	0.900	-	-	0.791	0.365
Peak A	0.821	0.683	-0.238	-0.642	0.801	-	-	-	0.854
Peak	0.471	0.333	-0.163	-0.378	0.449	-	-	-	-

In both Montfullà and Figueres DWTPs, UV254 absorbance showed strong positive correlations with several THM species with coefficients ranging from 0.757 to 0.822. This indicates that higher UV254 absorbance levels are associated with increased THM formation potential, highlighting UV254 as a robust predictor of THM precursor concentration. UV ratios, such as 254/203 and 265/465, also exhibited significant correlations with THM species, with coefficients ranging from 0.878 to 0.916. These ratios serve as useful surrogates for assessing THM formation potential, with higher values indicating elevated THM precursor concentrations.

Turbidity demonstrated notable correlations ranging from 0.522 to 0.764 in both DWTPs, underscoring the role of turbidity as an indicator of organic matter content and THM precursor concentration in water. EEM fluorescence spectroscopy revealed strong correlations, emphasizing the utility of fluorescence analysis in

assessing THM formation potential. In Montfullà, Peak A and Peak T showed correlations ranging from 0.624 to 0.948, while in Figueres, correlations ranged from 0.529 to 0.854. These findings underscore the potential of EEM fluorescence spectroscopy as a tool for characterizing organic matter and predicting THM formation in water treatment processes.

4.4 Biological Risk: Assimilable Organic Carbon

The analysis of assimilable organic carbon (AOC) provides insights into the biostability of water samples, indicating the potential for microbial growth and the need for further chlorination. AOC levels were measured for water samples collected at the Figueres DWTP. The sampling points included the influent water (RW), post-ozonation (O3), and after AC filtration (F4).

Table 4.11 presents the average UFC (unit forming colonies) per millilitre for samples collected at different points in the water treatment process. At the RW, the average UFC/mL is 477, indicating a relatively high level of microorganisms present in the untreated water. After ozonation, there is a reduction in the average UFC/mL to 312, suggesting that ozonation effectively reduces microbial populations in the water. Following F4, there is a substantial further reduction in the average UFC/mL to 92, indicating that AC filtration is effective in removing remaining microorganisms from the water.

Table 4.11: Essay of 20 ppm sodium acetate stock solution with p17 strain

Sample	Average UFC/mL
RW	477
O3	312
F4	92

Regarding NOX cultures, the presence of colonies with differing morphologies on some plates indicated contamination issues. Thus, conclusive numerical results could not be obtained. Nevertheless, the qualitative analysis suggests a consistent trend of decrease in the colony growth after ozonation compared to the influent, with a subsequent reduction in colonies observed after filtration with activated carbon filters.

These results constitute an initial phase of testing that will be continued during the next months. Time constraints for the final degree project presentation limited the acquisition of further data, as the re-establishing of the protocol took longer than anticipated. Moreover, out of the four assays performed, only this one could be used for results extraction due to contamination issues and experimental difficulties in quantifying yield factors.

As a potential solution, the use of the flow cytometer has been proposed, which enables the rapid and automated quantification of UFC. This implementation aims to enhance efficiency by processing a significantly larger volume of samples in a shorter timeframe. Recently, Flow cytometry coupled with fluorescent staining has emerged as the leading tool for single-cell analysis in microbiology. Multiple examples already exist of the application of flow cytometry for the enumeration of either total bacteria or specific bacterial groups using either total nucleic acid or selective RNA stains (Porter, J., & Pickup, R. W. 2000). Probably the biggest advantage of

flow cytometry is that it allows for rapid and accurate enumeration of all cells, including those which are unculturable or inactive. An obvious offspring of this is the ability to quantify a natural microbial consortium consisting largely of microbial cells that cannot be cultured on conventional media (Hammes, F. A., & Egli, T. 2005).

5. CONCLUSIONS

The general conclusions of this work can be classified according to the different objectives proposed.

1. Implementation of Protocol for AOC Analysis

- The modifications made to the protocol for measuring biological stability in DW aimed at its adaptation to LEQUIA experimental capabilities. The established protocol outlines clear steps for sample collection, preparation, inoculation, and analysis, ensuring consistency and accuracy in measuring AOC levels in treated water samples.
- The removal of the one-week incubation period in chlorine-neutralized tap water streamlined the culture preparation process, reducing time and resource consumption while improving reproducibility across assays. Additionally, increasing the acetate concentration to 20 mg/L enhanced bacterial growth, addressing previous challenges.
- Despite initial difficulties with absorption measurements, an alternative approach based on monitoring cell density in the stationary phase was proposed. This method ensures more reliable results, with acceptance criteria established for interpreting colony enumeration over consecutive days of incubation.
- Changes to the AOC testing protocol, such as membrane filtration and rinsing with ultrapure water, were implemented to minimize contamination issues and improve the accuracy of analysis.

2. Evaluation of Treatment Efficiency on Lab-Scale

- The effectiveness of ozone. C/F and reducing turbidity levels were analysed. Overall, both treatment processes consistently achieved a 95% turbidity decay across various conditions and samplings, highlighting their effectiveness in reducing turbidity levels in water samples.
- Ozone treatment and C/F processes were observed to influence the reduction of UV254 absorbance, with varying degrees of effectiveness across different concentrations and samplings.
- Both AIRPEL and BGE activated carbon treatments contributed to reducing UV absorbance effectively, with slight differences observed in their performance, indicating the potential for further optimization.
- EEM fluorescence analysis revealed notable differences in initial fluorescence levels between samplings, influencing treatment effectiveness. Both BGE and AIRPEL activated carbon treatments demonstrated high efficiency in reducing fluorescence intensity across all peaks and ozone concentrations, contributing to an overall reduction of 80-90%.
- Ozone treatment, C/F processes, and activated carbon treatments were identified as pivotal processes in enhancing water quality, with varying degrees of effectiveness observed across different samplings and treatment stages.

3. Examination of THM Formation Potential upon Chlorine Disinfection

- The evaluation of THM-FP after different treatments for Montfullà and samples showed varying efficiencies. While ozone treatments showed some reduction in THM-FP, significant decreases were observed in AC treatments. The efficiency of organic matter elimination was found to be crucial in THM-FP.
- The correlation analysis provided valuable insights into the relationship between water quality parameters and THM-FP. UV254 absorbance emerged as a robust predictor of THM precursor concentration, with strong positive correlations observed across different treatment scenarios. Additionally, UV ratios and turbidity demonstrated significant correlations, further emphasizing their utility in assessing THM-FP.
- EEM fluorescence spectroscopy proved to be a valuable tool for characterizing organic matter and predicting THM-FP in water treatment processes. Peaks A and T exhibited strong correlations with THM-FP, highlighting the potential of fluorescence analysis in optimizing water treatment strategies.
- The findings of this study have practical implications for water treatment plant operators. By understanding the relationships between water quality parameters and THM-FP, operators can implement targeted strategies to minimize disinfection byproduct formation and ensure the delivery of safe drinking water to consumers.

4. Measurement of Assimilable Organic Carbona

- The study demonstrates the effectiveness of ozonation and AC filtration in reducing microbial populations in water samples. Ozonation led to a significant reduction in microbial counts, while AC filtration further lowered microbial levels, highlighting the importance of these treatment steps in ensuring water safety.
- Challenges such as contamination issues and experimental difficulties were encountered, affecting the quantification of microbial growth. These limitations underscore the need for careful consideration and potentially alternative methods in future research to mitigate such challenges.

Future Research Directions

The study acknowledges the need for continued research beyond the initial phase to gather more comprehensive data. Future research should focus on developing robust protocols and procedures to minimize contamination risks in biological assays, ensuring the reliability of results. Advanced techniques such as flow cytometry may be explored for rapid and automated quantification of AOC, enhancing efficiency and accuracy.

Long-term monitoring studies should be conducted to assess the dynamics of THM formation and biological risks over extended periods, providing insights into seasonal variations and treatment efficacy. Comparative studies between different water treatment plants and processes should be undertaken to evaluate the

effectiveness of various treatment methods in mitigating THM formation and biological risks. Optimization strategies for water treatment processes should be investigated to minimize THM formation potential and biological risks while maintaining water quality standards.

It is important to note that this undergraduate thesis serves as a foundation for further research, which will continue as a Master's degree project. The continuation of this work allows for a more in-depth exploration of the topic, with a focus on addressing the identified limitations and implementing innovative methodologies to enhance the accuracy and efficiency of microbial analysis in water treatment systems.

6. REFERENCES

Aggarwal, S., Jeon, Y., & Hozalski, R. M. (2015). Feasibility of using a particle counter or flow-cytometer for bacterial enumeration in the assimilable organic carbon (AOC) analysis method. Biodegradation, 26, 387-397.

Beckett, R., & Ranville, J. (2006). Natural organic matter. Interface Science in Drinking Water Treatment, Theory and Applications, 10, 299-315.

Bieroza, M., Baker, A., & Bridgeman, J. (2009). Relating freshwater organic matter fluorescence to organic carbon removal efficiency in drinking water treatment. Science of the Total Environment, 407(5), 1765-1774.

Bridgeman, J. Bieroza, M. & Baker, A. (2011). The application of fluorescence spectroscopy to organic matter characterisation in drinking water treatment. Reviews in Environmental Science and Bio/Technology 10, 277–290.

Cabral, J. P. (2010). Water microbiology. Bacterial pathogens and water. International journal of environmental research and public health, 7(10), 3657-3703.

Camper, A. K. (2004). Involvement of humic substances in regrowth. International Journal of Food Microbiology, 92(3), 355-364.

Chen, W., & Yu, H. Q. (2021). Advances in the characterization and monitoring of natural organic matter using spectroscopic approaches. Water Research, 190, 116759.

Chen, Y., Senesi, N., & Schnitzer, M. (1977). Information provided on humic substances by E4/E6 ratios. Soil science society of America journal, 41(2), 352-358.

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine chemistry, 51(4), 325-346.

De Haan, H., & De Boer, T. (1987). Applicability of light absorbance and fluorescence as measures of concentration and molecular size of dissolved organic carbon in humic Lake Tjeukemeer. Water research, 21(6), 731-734.

Dietrich, A. M. (2006). Aesthetic issues for drinking water. Journal of water and health, 4(S1), 11-16.

Ding, S., Deng, Y., Bond, T., Fang, C., Cao, Z., & Chu, W. (2019). Disinfection byproduct formation during drinking water treatment and distribution: A review of unintended effects of engineering agents and materials. Water Research, 160, 313–329.

EPA, U. (2002). Health risks from microbial growth and biofilms in drinking water distribution systems. Distribution System White Paper. Office of Water. Washington, DC.

Escobar, I. C., & Randall, A. A. (2001). Case study: ozonation and distribution system biostability. Journal-American Water Works Association, 93(10), 77-89.

Escobar, I. C., Randall, A. A., & Taylor, J. S. (2001). Bacterial growth in distribution systems: effect of assimilable organic carbon and biodegradable dissolved organic carbon. Environmental Science & Technology, 35(17), 3442-3447.

Hambsch, B., & Werner, P. (1993). Control of bacterial regrowth in drinking-water treatment plants and distribution system. Water Supply, 11(3-4), 299-308.

Hammes, F. A., & Egli, T. (2005). A new method for assimilable organic carbon determination using flow-cytometric enumeration and a natural microbial consortium as inoculum. Environmental Science & Technology, 39(9), 3289-3294.

Her, N., Amy, G., McKnight, D., Sohn, J., & Yoon, Y. (2003). Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. Water Reseach 37(17) 4295-4303

Hua, G., & Reckhow, D. A. (2007). Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. Water Research, 41(8), 1667–1678.

Hua, G., Reckhow, D. A., & Abusallout, I. (2015). Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. Chemosphere, 130, 82-89.

Hur, J., Williams, M. A., & Schlautman, M. A. (2006). Evaluating spectroscopic and chromatographic techniques to resolve dissolved organic matter via end member mixing analysis. Chemosphere, 63(3), 387-402.

Jacangelo, J. G., DeMarco, J., Owen, D. M., & Randtke, S. J. (1995). Selected processes for removing NOM: an overview. Journal-American Water Works Association, 87(1), 64-77.

Jaffé, R., Boyer, J. N., Lu, X., Maie, N., Yang, C., Scully, N. M., & Mock, S. (2004). Source characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by fluorescence analysis. Marine chemistry, 84(3-4), 195-210.

Koley, S., Dash, S., Khwairakpam, M., & Kalamdhad, A. S. (2024). Perspectives and understanding on the occurrence, toxicity and abatement technologies of disinfection by-products in drinking water. Journal of environmental management, 351, 119770.

Korshin, G., Chow, C. W. K., Fabris, R., & Drikas, M. (2009). Absorbance spectroscopy-based examination of effects of coagulation on the reactivity of fractions of natural organic matter with varying apparent molecular weights. Water Research, 43(6), 1541–1548.

Krasner, S. W., Croué, J. P., Buffle, J., & Perdue, E. M. (1996). Three approaches for characterizing NOM. Journal-American Water Works Association, 88(6), 66-79.

LeChevallier, M. W., Shaw, N. E., Kaplan, L. A., & Bott, T. L. (1993). Development of a rapid assimilable

LEQUIA. (2024.). Retrieved from http://www.lequia.udg.edu/presentation/who-we-are.html

Levchuk, I., Màrquez, J. J. R., & Sillanpää, M. (2018). Removal of natural organic matter (NOM) from water by ion exchange–a review. Chemosphere, 192, 90-104.

Li, A., Zhao, X., Mao, R., Liu, H., & Qu, J. (2014). Characterization of dissolved organic matter from surface waters with low to high dissolved organic carbon and the related disinfection byproduct formation potential. Journal of Hazardous Materials, 271, 228-235.

Lin, Y., Lou, Y., Li, A., Wei, Y., Li, H., Zhou, M., & Li, Y. (2022). Effects of pre-oxidation by ozone, permanganate and ferrate on generation and toxicities of disinfection byproducts. International Journal of Environmental Science and Technology, 19(7), 5969–5984.

Maqbool, T., Qin, Y., Ly, Q. V., Zhang, J., Li, C., Asif, M. B., & Zhang, Z. (2020). Exploring the relative changes in dissolved organic matter for assessing the water quality of full-scale drinking water treatment plants using a fluorescence ratio approach. Water research, 183, 116125.

Mazhar, M. A., Khan, N. A., Ahmed, S., Khan, A. H., Hussain, A., Changani, F., ... & Vambol, V. (2020). Chlorination disinfection by-products in municipal drinking water–a review. Journal of Cleaner Production, 273, 123159.

Mustapha, S., Tijani, J. O., Ndamitso, M. M., Abdulkareem, A. S., Shuaib, D. T., & Mohammed, A. K. (2021). A critical review on geosmin and 2-methylisoborneol in water: sources, effects, detection, and removal techniques. Environmental Monitoring and Assessment, 193, 1-34.

Nescerecka, A., Rubulis, J., Vital, M., Juhna, T., & Hammes, F. (2014). Biological instability in a chlorinated drinking water distribution network. PloS one, 9(5), e96354.

Pan, Y., Li, H., Zhang, X., & Li, A. (2016). Characterization of natural organic matter in drinking water: Sample preparation and analytical approaches. Trends in Environmental Analytical Chemistry, 12, 23-30

Porter, J., & Pickup, R. W. (2000). Nucleic acid-based fluorescent probes in microbial ecology: application of flow cytometry. Journal of microbiological methods, 42(1), 75-79.

Rodríguez, F. J., Schlenger, P., & García-Valverde, M. (2016). Monitoring changes in the structure and properties of humic substances following ozonation using UV–Vis, FTIR and 1H NMR techniques. Science of the Total Environment, 541, 623-637.

Sandaa, K. (2019). Monitoring of the formation of disinfection by-products (DBPs) in a large drinking water distribution system (Master's thesis, Norwegian University of Life Sciences, Ås).

Sommer R, Cabaj A, Hirschmann G, Haider T (2008) Disinfection of drinking water by UV irradiation: basic principles - speci fi c requirements – International implementations. Ozone Sci Eng 30(1):43–48

Spanish Ministry of Science and Innovation. (2021.). Científicas en cifras 2021: Resumen ejecutivo [PDF]. Retrieved from https://www.ciencia.gob.es/dam/jcr:75ad4b3e-6cfc-4506-93df-089174e69425/CientificasenCifras2021_ResumenEjecutivo_EN.pdf

Srinivasan, R., & Sorial, G. A. (2011). Treatment of taste and odor causing compounds 2-methyl isoborneol and geosmin in drinking water: A critical review. Journal of Environmental Sciences, 23(1), 1-13

Standard Methods Committee of the American Public Health Association, American Water Works Association, and Water Environment Federation. 9217 biodegradable organic matter In: Standard Methods For the Examination of Water and Wastewater. Lipps WC, Baxter TE, Braun-Howland E, editors. Washington DC: APHA Press

Tian, C., Liu, R., Liu, H., & Qu, J. (2013). Disinfection by-products formation and precursors transformation during chlorination and chloramination of highly-polluted source water: significance of ammonia. Water Research, 47(15), 5901-5910.

Van Der Kooij D (1990) Assimilable organic carbon (AOC) in drinking water. Drinking water microbiology. Springer, New York, pp 57–87
Van der Kooij D, Hijnen WA (1984) Substrate utilization by an oxalate-consuming spirillum species about its growth in ozonated water. Appl Environ Microbiol 47:551–559
Van Der Kooij D, Visser A, Hijnen W (1982) Determining the concentration of easily assimilable organic carbon in drinking water. J Am Water Works Assoc 74:540
Van der Kooij, D., Hijnen, W. A. M., & Kruithof, J. C. (1989). The effects of ozonation, biological filtration and distribution on the concentration of easily assimilable organic carbon (AOC) in drinking water. Ozone: science & engineering, 11(3), 297-311.
Vital, M., Stucki, D., Egli, T., & Hammes, F. (2010). Evaluating the growth potential of pathogenic bacteria in water. Applied and Environmental Microbiology, 76(19), 6477-6484.
WHO (2011) World health organisation guidelines for drinking water quality, 4th edn. WHO, Geneva. ISBN 978 924 154815 1
Wingender J, Flemming HC. Biofilms in drinking water and their role as reservoirs for pathogens. International journal of hygiene and environmental health. 2011; 214(6): 417–423.
Xin, C., Wang, J., Zhang, Y., Liu, Y., Jia, H., & Li, L. (2021). Application of UV-vis absorption spectrum to test the membrane integrity of Membrane bioreactor (MBR). Water Research, 198, 117153.
Yang, P., Li, H., Zhang, X., & Li, A. (2016). Characterization of natural organic matter in drinking water: Sample preparation and analytical approaches. Trends in Enviromental Analytical Chemistry, 12(2016), 23-30
Zhang, T., Tao, Y. Z., Yang, H. W., Chen, Z., Wang, X. M., & Xie, Y. F. (2020). Study on the removal of aesthetic indicators by ozone during advanced treatment of water reuse. Journal of Water Process Engineering, 36, 101381.
Zhao, X., Hu, H., Liu, S., Jiang, F., Shi, X., Li, M., & Xu, X. (2013). Improvement of the assimilable organic carbon (AOC) analytical method for reclaimed water. Frontiers of Environmental Science & Engineering, 7, 483-491.