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Prediction of THMs Formation Potential in disinfection of drinking water

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DEDICATION

I want to dedicate my Master Thesis to my mother and grandmother, without whose support and love, I could have never completed this mission. We are 2000 km apart, but you supported, motivated me, and you have never left my side. I am thankful for all the time, sacrifices, and work you have made for the formation of my personality. I am happy to make you proud and to share this milestone step in my life with you.

Beyond my family, I would like to dedicate this Master thesis to my friends, who supported me and made my study life full of positiveness and inspiration.

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ABBREVIATIONS

AWWA	american water works association
BOD	biological oxygen demand
BCAA	bromochloroacetic acid
BDCAA	bromodichloroacetic acid
BDCM	bronodichloromethane
DWTP	drinking water treatment plant
DWDS	drinking water distribution system
DBCM	dibromochloromethane
DBP	disinfection by-products
CPF	cancer potency factors
EPA	environmental protection agency
HANs	haloacetonitriles
HKs	haloketones
HAs	haloaldehydes
HAAs	haloacetic acids
HNMs	halonitromethanes
NOM	natural organic matter
NH₂Cl	monochloramine
TBAA	tribromoacetic acid
TCM	chloroform
TOC	total organic carbon
THMs	trihalomethanes
UF	ultrafiltration
UV	ultraviolet radiation
USEPA	united states environmental protection agency
WHO	world health organization

ABSTRACT

Many people are exposed to disinfection by-products through centralized drinking water supplies around the world. There is a big concern about the possible relation between DBPs formation and cancer cases. THMs and HAAs are the main groups of DBPs, which in general form 80 – 84 % of total DBPs. DBPs are the result of a chemical reaction between applied disinfection reagent and naturally occurred organic matter in the water. However, the regulation of some specific compounds (NDMA, HBQs, etc.) will be strictly focused in the future, due to toxicological and cancerogenic data.

Many disinfectants are used, which have shown the drastically reduction of the DBPs compared to chlorine. Some DWTPs install additional treatment step for removal of DBPs precursors.

Finally, treatment with pre-ozonation is an option for disinfection, which may increase disinfection effectiveness and decrease DBPs formation.

This study evaluated various ozone dose and contact time in combination with chlorination under different water quality parameters. Water samples from nine lakes, which are used for drinking water supply, across Oslo region (Norway) with differing in water quality (pH, NOM, TU, color, conductivity) were collected. Each water sample was treated with ozone for times 15 min, 45 min, and the ozone doses 1.5 mg/l, 3 mg/l. In addition, control samples that were not treated with ozonation were analyzed. After the ozonation, the water samples were dosed with 2 mg/l of chlorine. Additionally, the raw water quality effect on THMs formation was investigated. The number of correlations between water parameters and THMs formation was described based on conducted experiments.

This research has shown that raw water quality plays a crucial role in further THMs formation. In turn, THMs formation has a strong correlation with TOD (93%), TOC (92%) and UV254 (91%), respectively.

Additionally, the use of ozone with a dose of 1.5 mg/l during constant contact time tends to reduce THFMFP. This reduction was ranging from 10 to 40 %, depending on the raw water quality parameters. Increasing the ozone dose helps to reduced THMs formation further.

Based on achieved results, three THMs predictive models were investigated for different water parameters and disinfection conditions.

A review of information related to DBPs regulations and an overview of disinfection processes as well as past research data presented in Chapter 2. A detailed description of the current experimental design and analytical methods used for ongoing research is presented in Chapter 3. Following the content, Chapter 4 shows the results of conducted experiments followed by conclusion, references and recommendation for further research.

Key Words: DBP precursors, DBP formation potential, THM, ozone, chlorine

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1. INTRODUCTION

Disinfection byproducts (DBPs) are compounds formed by the reaction between natural organic matter (NOM) and disinfection agents. DBPs in drinking water may cause serious health problems with reproductive functions or even cancer. The concern about DBPs appeared since the discovery of trihalomethanes (THMs) in previously chlorinated drinking waters (1970s). Many scientists and research groups were focusing on the evaluation of factors affecting the DBPs formation during drinking water treatment. There are many DBPs predictive models, which include different water qualities and treatment factors, however all of them have some limitations related to low performance or some unconsidered operational characteristics (Ross, Helm, et al., 2012). Moreover, relatively less is known about DBPs formation and exact factors affecting on their formation in DWDS.

The formation of DBPs is the highest, during the chlorination compared to other disinfection processes. While some DBPs in water are not toxic, others have been associated with cancer, reproductive problems, and developmental issues in research with laboratory animals. Thus, DBPs have an association with health risk. While some cities are replacing the chlorination as a disinfecting method due to the health hazards aspects, other cities continue to have chlorination in combination with ozonation. Even the cities which have replaced chlorination with ozonation, continue to have chlorination as a standby measure for emergency situations. Studies related to THM/HAA formation during combined chlorination and ozonation are limited. However, some research in this field showed that the symbiose of Cl and O₃ helps to eliminate the ozone dose and decrease the THM/HAA formation (Fang, Liu, et al., 2014). That is why, in this research, the one of the main focus was on ozone effect on THMs formation in DW.

The objective of this study was to evaluate THMFP after combined chlorination and ozonation and the dependency on water quality indicators (turbidity, UV254/TOD/color, temperature, TOC, pH) and water disinfection parameters (dose of O₃ & contact time) within the drinking water disinfection sequence of the study case. And THMs predictive models creation based on achieved results from the research.

Water samples were collected at nine different locations of Oslo region (Akershus and Bærum municipalities). Water from different sources has varying concentrations of natural organic matter (NOM).

In the frame of current research, the two methodic for evaluation ability of water to THMs formation were applied: 1) THM formation potential (THMFP) with different chlorine dose (2 mgCl₂/l and 6 mg Cl₂/l) and incubation period 7 days within temperature 12 °C. Current analyse demonstrate the ability to perform the worst case scenarios: when the pre-ozonation will be disconnected and only chlorination will be applied; when the chlorine dose will be accidentally increased; when the water will be stored in the special reservoir (imitates water age).

2) THMs concentrations after the treatment with pre-ozonation followed by chlorination were evaluated. The controlled ozonation parameters include ozone dose (1.5 and 3 mgO₃/l) and contact time (15 and 45 mins). This part of the research demonstrates the THMs formation within the change of disinfection parameters; and shows the reduction of THMs within different ozonation parameters.

2. LITERATURE REVIEW

2.1 DBPs problem history: monitoring, regulation etc.

Humanity in past centuries faced a huge problem related to bad sanitation with further leading to waterborne diseases and epidemics (cholera, typhoid and plague). The most significant year in disinfection history was 1854. That year, Dr. John Snow discovered that the reason of a cholera outbreak in London was Broad Street Pump, which provided the water with an admixture of sewage contaminations. After that, the chlorine was used for water disinfection in different European countries (Thompson, Gillespie, et al., 2015). Chlorination became one of the major achievements of public health in XX century, based on successful results of chlorine disinfection implementation and reducing of the waterborne diseases (Hrudey, 2008). It is undeniable, that the discovery mentioned above was crucial and helped to save the lives of thousand. Even these days we can observe some cholera outbreaks around the World.

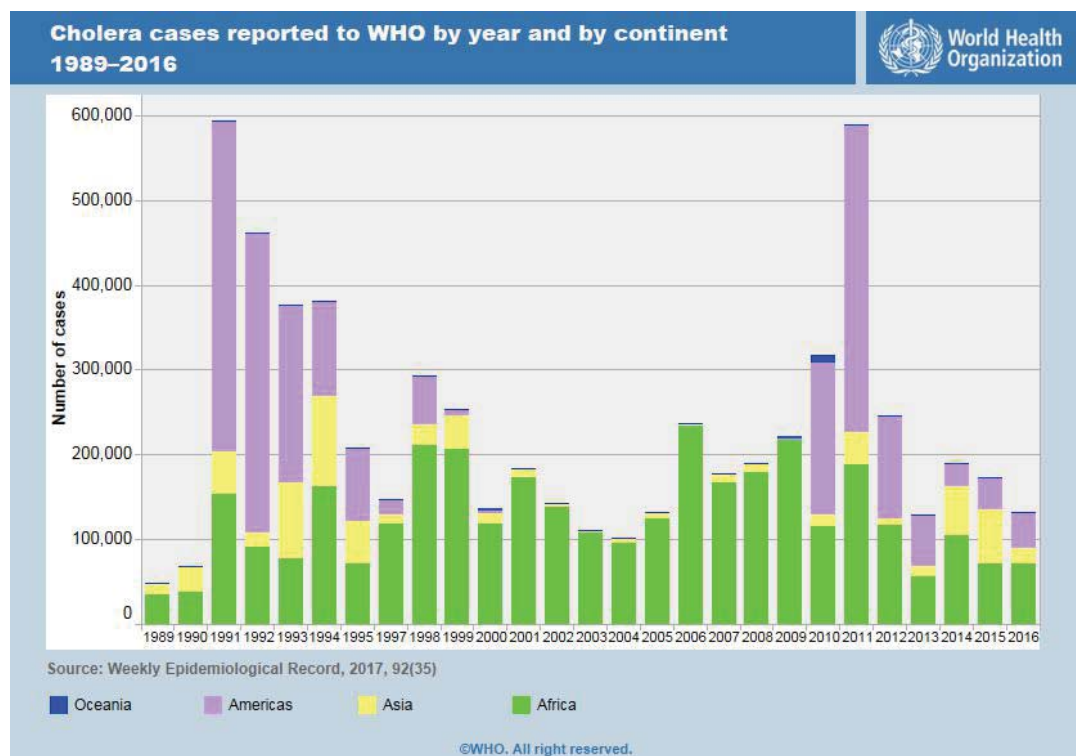


Figure 1 – Cholera outbreaks in 1989-2016 (*Guidelines for DW Quality FOURTH EDITION WHO, 2011*)

A hundred years later (1974), a group of researchers led by J.J. Rook discovered that chlorine reacts with natural organic matter (NOM) with further trihalomethanes formation in effluent drinking water (Collivignarelli, Abbà, et al., 2018). Later this year T.A. Bellar proved the organic

halides formation in chlorine water. The discoveries mentioned above triggered a research about DBPs.

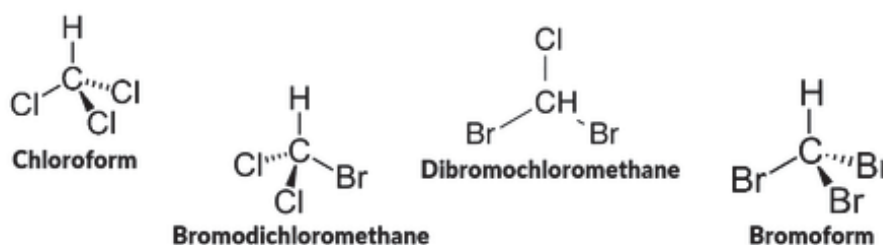
From 1974, the particular interest has been grown on the understanding the DBPs occurrence, effect on human health and possible monitoring. Nowadays, more than 600 different DBPs were identified (Thompson, Gillespie, et al., 2015). The toxicological risk is still unknown for half of the founded DBPs. THMs & HAAs are among the most commonly discussed, well-known and regulated types of disinfection by-products (STUART W. KRASNER, MARIA KOSTOPOULOU, MIREILLE B. TOLEDANO, JOHN WRIGHT, 2016). However, there are other DBPs groups which were found later in the recent years (Table 1). Many of them are not regulated but are more genotoxic in comparison to currently regulated DBPs.

Table 1 – Recently investigated DBPs groups (Thompson, Gillespie, et al., 2015), (Richardson, 2005), (Ivahnenko and Zogorski, 2006)

DBPs group	Compounds included	Year of discovery	Description/Review
Iodo-DBPs	Iodoacetaldehyde; Iodo-THMs (dichloroidomethane, bromochloroidomethane, iodoform, dibromiodomethane, bromodiiomethane, chlorodiiomethane); Iodo-acids Iodo-amides	mid 1970s - 2005	The highest concentration can be found in chloraminated water; Iodo-acids are most genotoxic & cytotoxic compounds from this group; Lower free chlorine time leads to increasing Iodo-DBPs; Ozone pretreatment (before chlorination) together with low pH of water can decrease the Iodo-DBPs formation; Iodo-THMs can be formed with applying of low Cl doses;
Nitrosamines	N-Nitrosodimethylamine (NDMA) N-nitrosopiperidine N-nitrosopyrrolidine N-nitrosodiphenylamine N-nitrosomorpholine	2002	All nitrosamines are cancerogenic; Firstly, Nitrosamines were investigated in chlorinated DW (Canada). Afterwards, the regulation about NDMA for drinking water was established at 40 ng/l; Presence of pharmaceuticals can be as a precursor for NDMA formation in DW; The information about N-Nitrosodimethylamine formation in ozonated water was occurred In the recent research. It is a big discovery in DBPs field, because previously the formation of any Nitrosamines was associated only

			with chlorination or chloramination of DW.
HALONITRO-METHANES	Chloropicrin (trichloronitromethane) Brominated nitromethane	-	The concentration of Br-nitromethane has been found up to 3 µg/L in drinking water; The ozonation treatment before chlorination step can lead to increasing of Br-nitromethane; Chloropicrin can be easily decomposed by temperature at GS or GS/MS analyzers.
HALOPYRROLES	2,3,5-Tribromopyrrole Tetra-halopyrroles	2003	Halopyrroles can be produced in DW with pre-chlorination and followed by ClO ₂ -Cl ₂ ; They are very cancerogenic.
HALOBENZO-QUINONES (HBQs)	2,6-dichlorobenzoquinone 2,6-dichloro-3-methylbenzoquinone	2005	Halobenzoquinones can be formed by applying combined disinfection: Chlorine, ozone-chloramine or UV-chloramines; Halobenzoquinones are highly toxic compounds.

The regulations were developed by The US Environmental Protection Agency (US EPA) and World Health Organization (WHO) after conducted research about DBPs potential cancerogenic health effect by International Agency for Research of Cancer (IARC) (US EPA). IARC classification highlights four of THMs main compounds (*chloroform*, *bromodichloromethane*, *dibromochloromethane*, *bromoform*) and five of HAAs compounds (*chloroacetic acid*, *dichloroacetic acid*, *trichloroacetic acid*, *bromoacetic acid*, *dibromoacetic acid*) (Figure 2); assign them possible human carcinogenic effect (Group 2B).



(a)

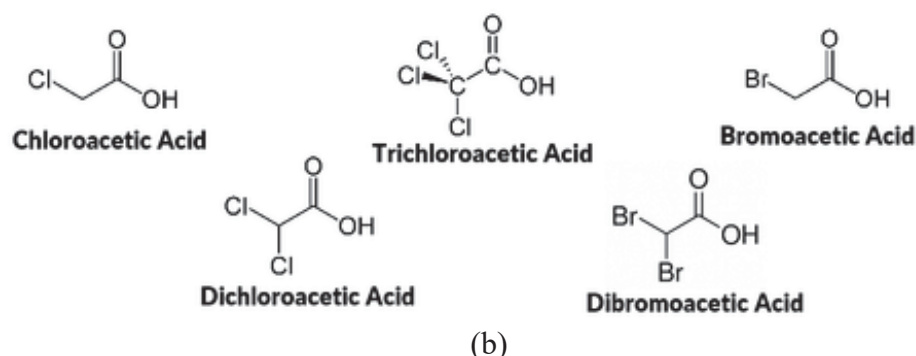


Figure 2 - a) Chemical structures of regulated trihalomethanes; b) - haloacetic acids (DBP in Public Water Systems - TCEQ)

WHO also considers potential health hazards of four THMs compounds. For this case, they have created a guideline for treated drinking water with a state, that the sum of concentration for each trihalomethane compound (THM) divided by its guidelines value cannot be higher than 1 (Equation 1)(*Guidelines for DW Quality FOURTH EDITION WHO*, 2011).

$$\frac{\text{Chloroform}}{\text{Chloroform GV}} + \frac{\text{BDCM}}{\text{BDCM GV}} + \frac{\text{DBCM}}{\text{DBCM GV}} + \frac{\text{Bromoform}}{\text{Bromoform GV}} < 1 \quad \text{Equation 1}$$

Where, Chloroform GV – 200 µg/L
 Bromodichloromethane (BDCM) GV - 60 µg/L
 Dibromochloromethane (DBCM) GV – 100 µg/L
 Bromoform GV – 100 µg/L (7,8)

US EPA designed the DBP's regulation in three steps (Table 2).

Table 2 – DBPs regulation by US EPA (US EPA)

Stage	TTHM	HAA standard
Initial	100 µg/L	-
Stage 1	80 µg/L	60 µg/L
Stage 2	80 µg/L	60 µg/L

In comparison to WHO DBPs regulation, US EPA does not regulate THMs or HAAs individually. All guidelines rules are applicable for total THM and HAA values. Besides implementation of guidelines, US EPA has calculated cancer potency factors (CPF) for chloroform, BDCM, DBCM, Bromoform. From all trihalomethanes, DBCM has the highest CPF value; chloroform has insufficient/ low data.

CPF factor can be used for calculation of cancer probability in drinking water with different DBPs concentration (Rahman, Driscoll, et al.). Most countries follow US EPA and WHO guidelines regarding DBPs concentration in the drinking water after the disinfection steps.

In 1980 The EEC Drinking directive has suggested DBPs concentration should be as low as it can be but have not set any special regulations for European countries. However, some of them have established own standards for DBPs, especially for TTHM (Figure 3).

There is a hypothesis that decrease concentration THMs by proper treatment steps can provoke the decrease concentration of other DBPs in DW. The main explanation for it is that minimization of THMs requires additional approach for natural organic matter (NOM) removal which has strong association with DBPs formation. Most countries have set a standard for total THMs.

Many countries made a step forward to DBPs regulation and started regulating individual Disinfection By-products(Goslan, Krasner, et al., 2014). Canada is one of the advanced countries regarding DBPs standards. Canada has established regulation for chlorophenols together with Australia and New Zealand; NDMA together with some states in USA; halocetontrile together with Japan (Jeong, Wagner, et al., 2012). Norway follows US EPA standard for THMs together with Canada, Japan, Korea and UK. Ukraine also has a standard 100 ppb for TTHM, however other DBPs are not regulated at all.

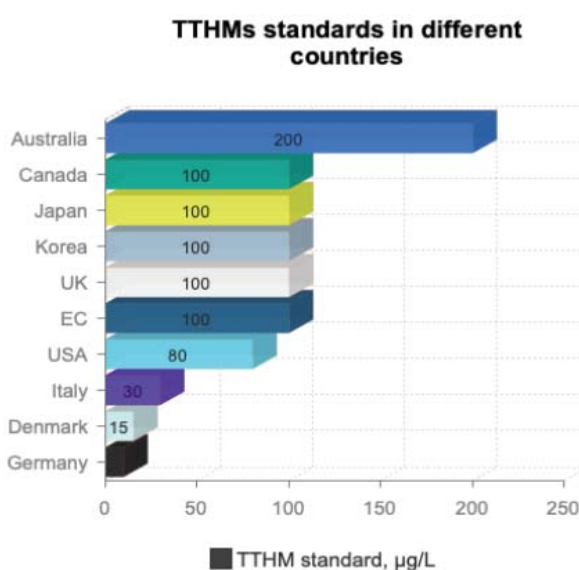


Figure 3 – TTHMs regulations in different countries

Monitoring of disinfection by-products formation is a complex task for DWTPs. The characteristics of DBPs formation are not well understood. It depends on many factors: temperature, dose of disinfectant, contact time, NOM concentration, pH, Bromide and other (Bond, Goslan, et al., 2012).

Most Drinking Water Treatment Plants have special points of the distribution networks where water samples can be taken after the treatment with a disinfection step; then water samples can be analyzed by GS or GS/MS apparatus at the laboratory. After this procedure, DWTPs achieve results about DBPs concentration in the effluent/treated water, which goes to the suppliers. Usually, DWTPs can analyze water for DBPs recognition from 4 to 8 times in a year. Based on them, the tendency of DBPs formation can be seen and the average concentration can be calculated (Chen and Westerhoff, 2010a). Additionally, the achieved results with the visible DBPs increasing may indicate the changes in water quality or effectiveness of treatment process. Nowadays, the analytical analysis is crucial in DBPs monitoring effectiveness.

Presently, the online monitoring for DBPs prediction does not exist and all DWTPs need to use external services of specially equipped laboratories. Such statement can be summed up based on literature review and real experience of DWTPs. Few studies have shown real time monitoring of disinfection by-products. Some preliminary work related to this topic was carried out in the early 2000s. Initial work in this field focused primarily on relation between differential UV spectroscopy and disinfection by-products formation in the water (DBP in Public Water Systems - TCEQ). In current research, we are going to use UV-spectroscopy due to simplicity of the method and successful application in the previous research. This aspect will be dealt with in more detail in Results and Discussion part.

2.2 Occurrence of DBPs in drinking water and their impact on human health

Today, disinfection of drinking water can be performed by most common disinfectants: ozone, UV irradiation, Cl_2 , NH_4Cl or ClO_2 (RICHARDSON, PLEWA, et al., 2007). Occurrence of DBPs in water from the tap directly depends on the initial water quality, disinfection practices at DWTP and condition of distribution system (Goslan, Krasner, et al., 2014). A few studies have been done in EU countries about the occurrence of different DBPs classes in drinking water (Goslan, Krasner, et al., 2014)(Wang, Ruan, et al., 2014). These research found that the THMs & HAAs are the most common compounds in the treated waters among all DBPs classes. The foremost factors of DBPs occurrence are pH, temperature, contact time, and stay time in distribution system. If the water contains high Br- concentration, during the disinfection treatment, it will form and contain highly-toxic brominated compounds (Saidan, Meric, et al., 2016).



Figure 4 - Ways of DBPs exposure on human health

There is an association between DBPs and health risk. DBPs can be trapped to the body and exposure on health by showering, drinking, eating or breathing (Figure 4)(Benson, Akintokun, et al., 2017). Preliminary study indicate that the inhalation and dermal contact are more harmful to human health in comparison to ingestion (Yao, Sun, et al., 2019).

Many studies have reported about the association of DBPs in chlorinated water (mainly THM & HAA) and the possibility of human cancer (Rahman, Driscoll, et al.), (King and Marrett, 1996). Moreover, there are some studies about abortion, low weight of infants or some reproductive anomalies caused by DBPs (Kogevinas, Villanueva, et al., 2010), (Grellier, Bennett, et al., 2010).

The (King and Marrett, 1996) has proved the association between DBPs and the risk of bladder cancer in some regions of Spain. In his study, he has explained the possible mechanism and classes of DBPs. Recent developments in health risk assessment have shown that chloro-DBPs have irrefutable impact on human health; however, the bromo-DBPs cause the greatest concern based on their toxicology. More than half of earlier identified DBPs (600 DBPs) have unknown toxicological risk to human health.

The Table 3 represents a brief summary of DBPs classes and their link to the health effects (Lee, Kim, et al., 2013).

Table 3 – DBPs classes

Class of DBPs	Abbreviation	Health effect
Trihalomethanes	THMs	Cancer, liver, reproductive effects (LBW, BD, SAB), kidney, nervous system (mainly Dibromochloromethane)
Haloacetic acid	HAAs	Cancer, reproductive effects (LBW, BD, SAB), developmental effects, liver, kidney, spleen.
Haloacetonitrile	HAN	Cancer and mutagenic effect
Nitrosodimethylamine		Liver, internal bleeding, cancer, infants' death

Reproductive studies:

Other observations in North Carolina indicate that women who drank water with THMs concentration higher than 100 ppb had evidence of low birth weight and miscarriages (Luben, Olshan, et al., 2007).

Waller et al (1998) found same observations. He noticed that pregnant women who drank >5 glasses per day of drinking water with more than 70-80 ppb of THMs have more cases of spontaneous miscarriages. Additionally, the study has shown that bromodichloromethane (BDCM) can provoke spontaneous abortion at concentration lower than 18 ppb. In Waller's study more than 5 100 pregnant women were participated, also he has used THMs values from 8 DWTPs.

Besides the DBPs formation in a drinking/tap water, they can be formed in swimming pool water (Thompson, Gillespie, et al., 2015). Some of DBPs found in swimming pool relate to same DBPs classes as those found in DW. However, in swimming pool water there are supplement human precursors (sweat, lotions, PSP, hair & urine). One of the brightest examples is trichloramine (NCl_3) formation. It is formed, by the reaction of chlorine together with sweat/urine. Trichloramine has high Henry's Law constant and can be transported easily from water to the air above. Many professional swimmers have asthma problems caused by trichloramine (De Vera, Stalter, et al., 2015).

(Kogevinas, Villanueva, et al., 2010) have shown increasing of bladder cancer caused by swimming pool water.

The skin rashes, respiratory issues, digestive issues can be resulted of exposure to chloraminated DW. On another hand, chloramination is a popular processes in many countries due to reduction of regulated DBPs (THMs&HAAs) and longer residual effect of disinfection in distribution system.

Cancer studies:

A growing body of literature has studied the DBPs exposure on human health and its relation to cancer.

One of the main and long study was conducted in Canada (Ontario city) by (King and Marrett, 1996) research group. They investigated the association between bladder cancer and DBPs

presence in drinking water. They were getting data of THMs concentration from DW utilities for 40 years period. Around 1500 people were participated in this research for at least 30 years. This study has investigated that the risk of bladder cancer can be increased with higher concentration and duration of THMs in DW. Study by (Lee, Kim, et al., 2013) came to the same conclusion. Additionally, he has found increasing of brain and kidney cancer in people who drank chlorinated water all the time.

At this time, many researchers try to understand the human health effects of DBPs exposure, but it is still not well known.

In the middle of 2000th, the European Commission implemented new project – Health Impacts of Long-Term Exposure to Disinfection By-products in Drinking Water (HIWATE) (Jeong, Wagner, et al., 2012). This project was made for the identification of long-term exposure to DBPs. This study has covered different regions of European countries (Italy, France, UK, Spain, Lithuania & Greece) from 2007 to 2009. The THMs concentrations tends to be higher for surface water than for the groundwater. Also, the seasonal variation have less effect on DBPs formed in DW from groundwater source. In Spain, many cities have higher evidence of bromo-DBPs formation due to presence of bromide and Br⁻/TOC ratio. Finally, the study found that the HAAs are more sensitive to different period of the year in comparison to THMs.

2.3 Factors influencing formation of DBPs

The changing of different factors can cause greater formation of DBPs in the water. All factors can influence directly or indirectly on disinfection by-products formation (Liang and Singer, 2003). Generally, the DBPs investigations consider two large categories of factors:

- 1) **The water quality** is the main and complex factor, which refer to pH, temperature, turbidity, color, natural organic compounds (NOM) concentration, nutrients, dissolved oxygen, and the presence of other species, which can potentially increase DBPs formation (Br, I & corrosion products).
- *Temperature* has an irrefutable influence on DBPs formation. The temperature increasing causes higher DBPs formation. Increasing water temperature accelerates the formation of dichloropropanol, trichloropropanol, THMs, HAAs, HANs, Br-THMs (Zhang, et al., 2012) Some conducted studies show the increasing of DBPs concentration in 15 - 25 % higher during the temperature changing from 10 to 30 °C. Another example of temperature effect on DBPs formation was demonstrated in research completed by (Kovacs, Ristoiu, et al., 2013). The TTHM concentration has risen from 89 µg/L to 105 µg/L, when temperature increased by 2°C.

- *pH* can change the DBPs formation greatly. The TTHM formation in the water at pH=8 is higher in comparison to water with pH=6. (Liang and Singer, 2003) has conducted several experiments and concluded that DBPs concentration rises with increasing of water pH. Moreover, DBPs stability is highly depended on pH values (Hung, Waters, et al., 2017).
- *NOM* (*natural organic matters*) is the organic precursors which can react with chlorine to form DBPs (Grunwald, Nikolaou, et al., 2002). Many scientist use *TOC and UV₂₅₄* parameters for the determination of NOM in the water, however, the NOM character and class play an crucial role (Reckhow, 2009). For example, humic acids (HA) react faster and can create higher numbers of DBPs in comparison to fluvic acids (FA)(M.A. Zazouli, S. Nasser, et al., 2007). Humic substances are hydrophobic and polyfunctional polymers that can be formed by decomposition of organisms and different chemical & biological reactions in the nature. Humic substances have complex polymeric structure, which is difficult to characterize (Golea, Upton, et al., 2017).

The water with higher values of TOC and UV₂₅₄ tends to have bigger values of DBPs concentration.

One of the studies (Zhang et al., 2010) on relation between TOC and DBPs connection found that TTHM formation increased from 6 µg/L to 8 µg/L when the TOC concentration was risen in 7 mg/L.

- An increasing number of studies have found that the *presence of bromides and iodides* precursors have dramatical influence on DBPs formation and tend to form more cancerogenic and hazardous species.

Both iodide and bromide occur naturally in waters and the react in a different way with different disinfectants. After the injection of chlorine to the water Br tend to react with free chlorine (FC) and produce HOBr (hypobromous acid). HOBr, in turn, reacts with NOM and form Br-DBPs.

Ozone can oxidize hypobromous acid to bromate. Due to US EPA the bromate is cancerogenic for the human health. Many WTPs try to lower the ozone application or reduce the applied dose in the water with a high bromide concentration.

Same with Br, the iodide reacts with NOM with further forming of hypoidous acid (HOI). HOI reacts with NOM and form I-DBPs, which are toxic.

However, the hypobromous acid and hypoidous acid react differently in a presence of ozone or excessive amount of chlorine (Good and Vanbriesen, 2017).

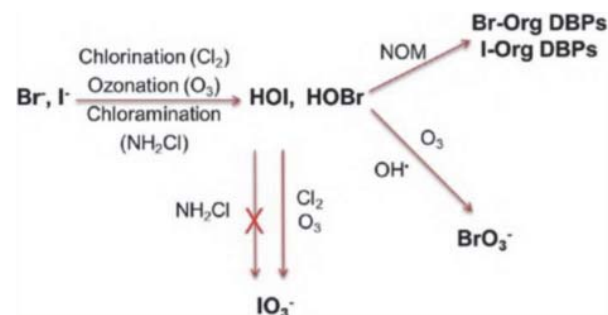


Figure 5 - The Br and I oxidation processes at disinfection treatment steps

Recent findings regarding iodide have led to conclusion that free chlorine and ozone help to oxidize HOI to iodate, which is not toxic (De Vera, Stalter, et al., 2015), (Xia, Lin, et al., 2017).

2) **The operating parameters at DWTPs** which mostly related the disinfection step and distribution system. The hydraulic condition of water distribution, pipe materials, applied disinfectant, contact time of disinfectant with water and water age are the main factors in the current category (Li, McDonald, et al., 2019).

- *Water age* is a very complicated factor, because during the DWT steps the water with different ages mixed together. This is common practice if DWTPs have water from multiple sources or if drinking water distribution system has a pipe network with interconnected units. Moreover, water age influenced by seasonal demand, especially during the dry period people use more water compared to the rainy period. Many scientists express the water age as an average value a specific system (Blokke, Furnass, et al., 2016). The water age factor does not influence directly on DBPs formation. However, it contributes to the reducing of disinfectant residuals, and at once increasing of DBPs formation due to a longer contact time (Zhang, Yang, et al., 2012)

If DWTP has a long-distance distribution system, the water will have prolonged water age. The increase in contact time tend to influence in higher Br-DBPs concentration, compared to Cl-DBPs.

- *Pipe material & hydraulic condition.* Recent research have shown the lower THM formation rate under the turbulent flow by installing new PVC pipes (Whittaker, Beylot-barry, et al., 2017). Besides the higher DBPs formation, iron-pipes can be affected by corrosion, which also form precursors for DBPs (Idornigie, Templeton, et al., 2010).

(Sharifan, 2010) has applied different worst scenarios in the hydraulic operations (pumping conditions and levels of storage reservoir) with further measurement of THMs and HAAs

concentrations. Their research summarized that the DBPs concentration varies significantly due to hydraulic operations parameters, and DWTPs should consider the hydraulic conditions of DWDS in the model of DBPs prediction.

(Zhang, et al., 2012) have reported that NDMA increases with prolonged retention time.

In addition, the formed biofilm in DWDS worsens the water quality and promotes DBPs formation (Lemus Pérez and Rodríguez Susa, 2017).

- *Chlorine dose* is one of the factors that has a major part in the THM formation. THM concentrations directly increase with increase of applied chlorine doses (Rodríguez, Rosal, et al., 2008). The significance of chlorine dose can be evaluated effect for different type of THM; for example, it is more significant for dibromochloromethane formation, compared to other THMs.

2.4 Strategies for DBPs reduction in drinking water

Nowadays, there are a plenty number of strategies that can be used to decrease DBPs formation. Most of them focus on TOC removal, use of alternative disinfectants, pH adjustment & control, reducing of contact (exposure) time, and optimizing of chlorine and ozone residual, removing sediment after the chlorination, removing biofilm that converts some inorganic compounds to organic (Collins, Malley, et al.).

Many DWTPs try to remove organic concentration in the water by implementing of granular activated carbon filters (GAC), coagulation or membrane treatment (Ding, Deng, et al., 2019). However, decreasing of chlorine residual and exposure time can have negative effects– potential health risk by micro-biological contamination (Martínez, Gómez, et al., 2014).

Every strategy for DBPs reduction has to be evaluated for the specific treatment facility, water quality and hydraulic conditions (Government of Newfoundland and Labrador, 2009).

Many literature sources pointed different strategies, but there are some of them which are effective:

- Watershed protection and minimization of tourism activity;
- Chancing the location of the water intake;
- Recovery and renovation of water reservoir;
- Changing of disinfectant dose and relocation of injection point;
- Online monitoring of residual chlorine in treated water;
- Reducing storage capacity & water age;

- Controlling of stagnant zones in DWDS;
- Implementing of aeration in the storage reservoir;
- Regular system flashing for preventing of biofilm formation;
- Changing old iron-pipes to new PVC pipes;
- Applying of alternative disinfectants.

The successes of pointed above strategies and practices, directly depends on the final aim of DBPs reduction; seasonal and quality variances have to be considered (Crepeau, Fram, et al., 2003).

2.5 Models predicting DBPs formation

After the DBPs discovery in 1974, many predictive models have been created for various purposes. There are two prior aims for DBPs predictive models developing:

- 1) To study the kinetics for different DBPs classes formation.
- 2) To identify the effect of different operational (treatment) conditions and raw water quality on the DBPs formation.

In fact, the concentration of DBPs in drinking water requires a specific analyze – gas chromatography (GS) or Gas chromatography–mass spectrometry (GC-MS). Both analysis are time consuming and relatively expensive.

The predictive model developing is a process of establishing empirical relationships between water quality and operational conditions together with values of DBPs concentrations at different disinfection stages (Sadiq and Rodriguez, 2004).

Most scientists linked DBPs concentration with TOC/DOC, pH, temperature UV^{254} , specific UV-absorbance (SUVA), chlorine dose, Br^- and contact time.

Classically, predictive models are implemented to identify the connection between water quality and operational variables. There are potential benefits of using DBPs predictive models in drinking water:

Benefits for water utility managers

DBPs predictive model can be applied to assist decision-making for parameters control, which can help reduce DBPs formation during the all treatment steps at DWTP.

Additionally, they can serve as an addition to the residual disinfectant models for the sampling point selection.

Benefits for environmental epidemiologists

They can use for the exposure and health risk assessment. Moreover, the human exposure to various classes of DBPs can be estimated at different locations.

Benefits for the agencies with perspective on upgrading

The DBPs predictive models help regulatory agencies in risk reduction programs, calculation of economic impacts if the DWTP upgrading is required or if water source has to be changed.

The creation of good predictive model requires data from laboratory experiments, due to ability of conditions controlling (Bond, Goslan, et al., 2012).

There are two type of DBPs predictive models:

1) Laboratory- scaled models

Due to advantages, this type of model is easy applicable, can provide good statistical data, ability to control within different variables, easy in development, less – time consuming and cost effective. These models are developed and evaluated with a higher number of observations. However, lab-scale models do not include effect of water distribution system. Additionally, in some cases, laboratory - scaled models do not consider the different water temperatures, and the changes of applied chlorine doses, which can be much higher and vary during the season of the year.

2) Field-scaled models

Field-scaled models provide less informative statistical data, applicability of such models is low, due to specific treatment process and water type. In comparison to laboratory-scaled models, they have lower ability to control different variables, because of treatment process and guidelines. However, field-scaled models include information and data about distribution system (pipe, material, biofilm formation, the distance from the DWTP to the suppliers).

Generally, laboratory-scaled models represent more explanatory variables, compared to the field-scaled studies.

Moreover, most DBPs predictive models are developed based on data, which were used for their calibration and do not include external database from other research. The model creation with a high predictability and applicability can be achieved only by combination laboratory results and field results from DWTP (Sadiq and Rodriguez, 2004).

To date, there are around 30 predictive models for various DBPs. All of them have some advantages and limitations. The most common limitations relate to the absence of reaction time, temperature, pH, as well as many models do not represent conditions of real water utilities.

Non-linear regression together with multiple-linear regression are the most commonly used methods in creation new DBPs predictive models (Sadiq and Rodriguez, 2004).

(Chen and Westerhoff, 2010b) in their research developed a predictive model for five different water sources within four types of DBPs precursors (DOC, UVA_{254} , Br⁻). In result of their work, two predictive models were gotten. The first (Equation 1) represents DBPFP prediction based on precursors pointed above, the second (Equation 2) model has same factors, but additionally, the nitrogen species were involved.

$$DBPFP = a \times DOC^b \times UVA_{254}^c \times (Br + 1)^d \quad \text{Equation 2}$$

$$DBPFP = a \times DOC^b \times UVA_{254}^c \times (Br + 1)^d (N + 1)^e \quad \text{Equation 3}$$

(Abokifa, Yang, et al., 2016) have demonstrated mathematical model which combined predictive DBPs model together with bacterial growth dynamics model in DWDS.

Every DBPs predictive model requires empirical verification. Any developed predictive model needs to have a remarkable linear correlation based on predictive parameters.

2.6 Formation of DBPs at different disinfections steps/processes of drinking water treatment

To date, there are three main type of disinfection: ozonation, chlorination or chloroamination and UV-radiation. All of them have some advantages and disadvantages; and can be selected according to the special case or water qualities. Besides, three main water disinfection treatments, there is another promising disinfection process – sonication (disinfection by ultrasound).

Ozonation:

In the past 20 years, the ozone application has arisen significantly. From a hygienic point of view, the method of water ozonation has significant advantages due to the high redox potential. Water ozonation is based on the property of ozone to decompose itself in the water with further formation of atomic oxygen, which can oxidize some organic and inorganic compounds that give an unpleasant odor (for example, humic acids)(Eagleton, 2000). The dose of ozone varies depending on the content of natural organic matter (NOM) concentration. The ozonation process in the water can be performed by two main reactions illustrated on Figure 6.

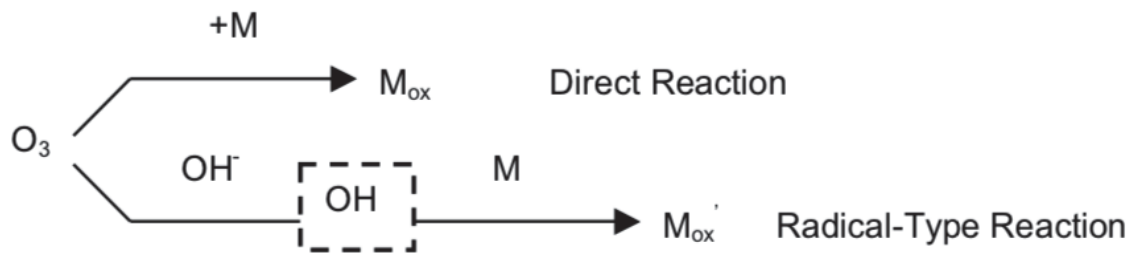
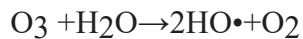
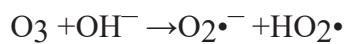


Figure 6 - Two main reactions of ozone in the water

The ozone dose needed to disinfect drinking water depends on the degree of water pollution and its amount. Usually it varies in a range 1 – 6 mg O₃ /l at contact for 8–15 minutes; the amount of residual ozone should be less than 0.3 – 0.5 mg / l, because a higher dose gives the water a specific smell and can be a cause of corrosion in DWDS (de Vera, Keller, et al., 2016). The main reaction, which can be occurred in aqueous environment:



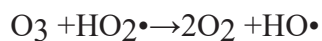
Equation 4



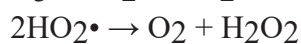
Equation 5



Equation 6



Equation 7



Equation 8

DBPs produced by ozonation:

Ozone has very high reactive ability and tends to oxidase some organic/inorganic compounds and create new. However, ozone can produce less amount of DBPs in comparison to chlorine. During the ozonation disinfection *Trihalomethanes (THM, bromoform)*, *Haloketones (HAA)*, *Haloacetonitrile (HAN)*, *Bromate*, *Aldehydes (formaldehyde)*, *Ketones (acetone)*, *Aromatic acid (Benzoic acid)*, *Cyano bromine*, *Ketoacids*, *Carboxylic acids* can be produced.

Chlorination:

Chlorine is a widely used reagent for water disinfection. In comparison to other disinfectants, chlorine is relevantly cheap and effective in minimizing microorganisms in the water. Many operators at DWTPs use a special chlorine dose, which will provide residual chlorine in water for further passing of DWDS. Chlorination has helped to eliminate many waterborne diseases, at the same time reduced mortality (Telford, 2018).

Proper calculated chlorine dose, for a special water source, will produce water-free from bacteria and eliminate algae, taste, and odour.

A number of studies have found that chlorine application for surface water (lakes, rivers, springs) are more difficult and complex process, compared to groundwater (Lamsal, Walsh, et al., 2011). In most cases, it required combined method of chlorination, or combination with other disinfectants.

The chlorine can be injected to the water in one of the three forms (Table 4).

Table 4 – The chlorine forms in drinking water treatment

Sodium hypochlorite NaOCl	Calcium hypochlorite Ca(ClO)₂	Liquid chlorine Cl₂
Physical properties: Molar mass: 74.44 g /mol Density: 1.11 g / cm ³ Melting point: 18 ° C Boiling point: 101 ° C Another common name is “ <i>liquid bleach</i> ”. It is a chemical with strengths - 15 %. Always, operators add sodium hypochlorite to the water by different methods: 1) Injecting directly to the stream by gravity; 2) Dosing by the use of metering pump. NaOCl + H₂O = OCl⁻ + OH⁻	Physical properties: Molar mass: 142.98 g /mol Density: 2.35 g / cm ³ Another common name is “ <i>powder chlorine</i> ”. Calcium hypochlorite contains around 70% available chlorine. Always, operators add calcium hypochlorite to the water by different methods: 1) Injecting directly to the stream by gravity; 2) Using of special pellets; 3) Mixing a solution with a water and calcium hypochlorite, after that water need to sediment in a sedimentation tank. Ca(ClO)₂ + 2H₂O = 2 HClO + Ca(OH)₂	Another common name is “ <i>chlorine gas</i> ”. The liquid chlorine can be achieved by a compression of a chlorine gas under 7.4 bar at the room temperature. Liquid chlorine has 100% strength. The most common practice of adding it to a water is to feed gas with a special system, or to feed the liquid gas directly to the stream . Cl₂ + H₂O = HOCl + HCl

The chlorine forms tend to produce hypochlorous acid (HOCl), under the reaction with water. The hypochlorous acid acts like disinfectant in the water, moreover, its effectivity depends on the pH. The increasing of disinfection efficiency and eliminating of DBPs formation can be achieved by combination with other disinfectant agents.

Some research demonstrated that the use of pre-ozonation helps to reduce THMs formation up to 65% (Deeudomwongsa, Phattarapattamawong, et al., 2017).

DBPs produced by chlorination:

Chlorine has less reactive ability, compared to ozone, however can form the biggest amount of DBPs among all disinfectants. During the chlorination *Trihalomethanes (THM)*, *Halogenic acetic acids (HAA)*, *Halofuranones*, *Haloacetonnitrils (HAN)*, *Chlorine hydrates*, *Benzene*, *Chloropicrin*, *Chlorophenols*, *N-chloramines*, *bromohydrins* and *Carboxylic acids*

Chloramination

Chloramine is a chemical produced by reaction between chlorine and ammonia.

Chloramination is a relatively new disinfection step in DWT. In comparison to chlorination, it is more stable, which helps to have chloramine residuals longer in water. Some research reported, that the half-life of chloramine can vary from few minutes to 20 days, depending on water quality and conditions.

Many operators use chloramine in water with high DBPs formation in the distribution system. Chloramination produced less DBPs, compared to conventional chlorination, but more DBPs, compared to ozonation (Nieuwenhuijsen, Martinez, et al., 2009).



DBPs produced by chloramination :

Applying chloramination has some advantages about DBPs formation, over using chlorination. *Haloacetonnitrils*, *Chloramino acids*, *Cyano chlorine*, *Haloketons*, *Nitrate*, *Nitrite* and *chlorate*, *hydrazine aldehydes* are formed.

Ozonation in combination with UV

This combined method has many benefits both in economic sector and treatment performance. The symbiose of UV and O₃ helps to eliminate the ozone dose for water treatment, while the UV exposure time can also be reduced.

$\text{O}_3 + \text{H}_2\text{O} + h\nu \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$ (Where $h\nu$ represents UV irradiation) with high redox potential. These radicals are able to make more effective disinfection processes than applying ozone only. Fang et al., 2014 have conducted research with implementation of combined UV/O₃ disinfection. Results of the study showed the positive effect on E.coli reduction at ozone concentration 0.05 mg O₃/l. The main explanation is a multiple barrier for bacteria, which are created by combination of two disinfection processes. More recent evidence (Fang, Liu, et al., 2014) highlights that UV and ozone (low doses) can enhance disinfection efficiency.

UV-irradiation and Sonication

The disinfection efficiency by ultraviolet irradiation (UV) was investigated recently. UV disinfection can effectively inactivate bacteria and microorganisms by breaking up the carbon bonds of DNA 1 (Cheema, Kaarsholm, et al., 2017) . For the drinking water disinfection, the applied UV range is between 250 and 285 nm. The UV dose can be calculated by next equation:

$$D = I \bullet t \quad \text{Equation 9}$$

Where D - ultraviolet dose (mW•s/cm²)

I – intensity (mW/cm²)

t – exposure time (s) (US EPA 1999 e)

Sonication is an alternative method for drinking water treatment, which helps to inactivate bacteria and protozoa, by breaking their structure with a high frequency sound wave. Sonication can be installed alone or with other disinfection processes such as chlorination or ozonation. Both UV-irradiation and sonication don not produce disinfection by-products. They may some influence on DBPs formation in combination with ozonation, chlorination or chloroamination; however, this influence is insignificant (Carter and Joll, 2017).

Advantages and disadvantages of commonly used disinfection practises.

All disinfection practises have some advantages and disadvantages Table 5. Their application depends on water quality, treatment conditions and regulations (Collivignarelli, Abbà, et al., 2018).

Table 5 - Advantages and disadvantages of disinfection practices

Disinfectant	Advantages	Disadvantages
Ozone	• Reduction of DBPs. • Odor and taste elimination. • The minimal influence on pH. • Effectively remove DBPs precursors. • Ozone is more effective in inactivating viruses and bacteria, compared to chlorine. • Ozonation has a short contact time and varies from 10 to 20 min. • Does not produce harmful residual in water, because it can be decomposed rapidly.	• The cost of ozonation is relatively higher, compared to other disinfectants. • There is no measurable residual value, as chlorine residual (CR). • Ozone is a toxic gas, so it requires special monitoring, ventilation and alarm system. • Ozonation is not economical for wastewater treatment. Because of high suspended solids concentration (SS) and

		biochemical oxygen demand (BOD). • Ozone is a very reactive and lead to corrosion, thus requires special materials resistant to corrosion and ozone. • Ozonation requires special and more complex equipment. • Application of low doses can be non-effective for some bacteria and viruses groups.
Chlorine	• The most cost-effective densification method. • The chlorine residual can prolong disinfection affect in DWDS. • Chlorine is the most widely-used disinfectant, thus the chlorination process is well-developed.	• Some waterborne pathogens are highly resistant to chlorine. • Chlorine reacts with NOM and bromide to form DBPs, such as THMs and HAAs. • Chlorine is a toxic compound. • In some cases, the additional dichlorination is required. • Chlorine gas requires additional alarm sensors for leak alerts. • Can cause the pipe corrosion. • $\text{Ca}(\text{ClO})_2$ is sensitive to heat and light, thus should be stored in cold and dry place. • Can be a reason of specific taste and odour.
Chloramine	• Forms lower amount of DBPs, compared to chlorine. • The residual is more stable and can stay in water during long time. • Can prevent biofilm growing in DWDS. • Can produce water with less chlorinous odour and taste.	• It has lower disinfection efficiency compared to other disinfectants. • It cannot oxidize iron and manganese. • Can be a cause of nitrification in distribution system.
UV	• Does not require additional chemicals. • Can inactivate many viruses, bacteria and spores. • Does not produce hazardous residuals. • The UV equipment has small footprint. • UV process requires a short contact time.	• Low doses may be not effective for some groups of viruses and pathogens. • Require proper maintenance to prevent fouling of tubes. • There is no measurable residual value, as chlorine residual (CR). • The presents of particles and high turbidity can reduce the UV treatment efficiency.

- Requires more investments, in comparison to cost-effective chlorination.

2.7 Prediction of DBPs applying online control methods

The high quality of drinking water is the main task for operators and engineers at DWTPs. It is well-known fact that disinfection step is the key process which helps to inactivate pathogens, bacteria, viruses in water, in order to make it potable. Many researchers were trying to find different solutions which can help to eliminated DBPs formation and predict possible concentrations due to existing regulations. The information about WHO and USEPA guidelines are presented in more detail in Section 2.1.

The DBPs concentration can be assumed by water quality (NOM, pH, temperature, color and etc.) and residual chlorine data. However, a special instrument for online monitoring of DBPs formation is not created yet.

In 2008 (Korshin, Chow, et al., 2008) has proposed a possibility for DBPs measurement by using differential UV spectroscopy. Current method based on the difference in UV-spectrum for pre-chlorinated and post-chlorinated water. Additionally, the linear correlation between A_{272} and chloroform formation was proved.

The most important advantages of the current method are rapid measurement, simplicity and ability to make online instrument for DBPs monitoring and process optimization.

The conceptual scheme of the instrument for differential UV spectroscopy measurement in DWDS was proposed in the article (Figure 7).

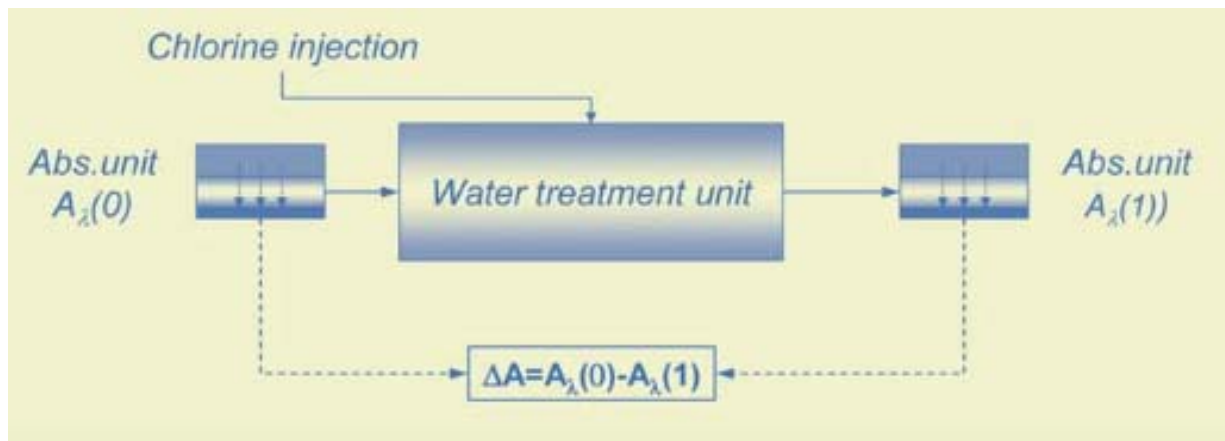


Figure 7 – The conceptual scheme for DBPs monitoring by UV spectroscopy (Korshin, Chow, et al., 2008)

In 2015, another scientific work about real time monitoring of DBPs by using absorbance and fluorescence indices was published (Lavonen, Kothawala, et al., 2015).

The research group achieved spectroscopic indexes which refer to NOM change in the water. Spectroscopic indexes were achieved based on fluorescence and absorbance data. The correlation between these indexes and concentration of DBPs (TCM, DCM, DCAN, TCAA & BCAA). Current research shows promising results, which can be applied for DBPs online monitoring in the upcoming future.

2.8 Coquitlam water treatment plant

Metro Vancouver Company has three main DWTPs:

- Coquitlam DWTP
- Seymour DWTP
- Capilano DWTP

In the frame of our research we took a Coquitlam drinking Water Treatment scheme like a study case. The Coquitlam DWTP is located north of the Coquitlam City in British Columbia region (Canada). The Coquitlam DWTP has water intake at Coquitlam watershed and supplies water to Vancouver city. The treatment capacity of the plant is about 380 million liters per day. The Coquitlam watershed is closed for the public in order to protect water quality and avoid unwanted pollutions.

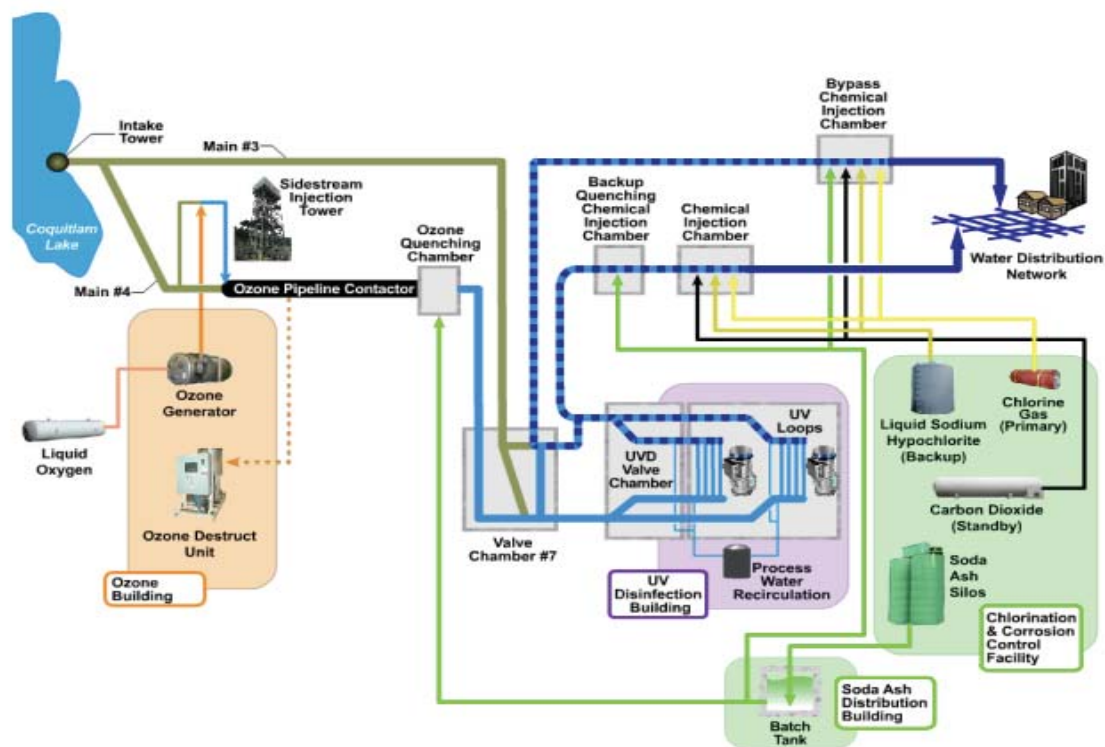


Figure 8 – Drinking Water Treatment Process Flow Diagram at Coquitlam DWTP

The Ozonation was put into operation in 2000 and it places the main part of the current Drinking Water Treatment System. The ozonation step provides the pre-disinfection of water and prevents the bacteria growth in distribution system.

The pre-ozonation helps to eliminate microorganisms and tends to reduce the DBPs formation. The main advantage and aim of pre-ozonation is improving of water transparency, which leads to a significant efficiency increases of the subsequent UV- disinfection.

UV treatment was designed and implemented in 2014. In the Coquitlam DWTP, the UV treatment uses 30 % less energy, compared to conventional water treatment, due to meeting the Leadership in Energy and Environmental Design (LEED) target. The UV provides possibility of primary disinfection – (3-log).

Together ozonation and UV treatment are the main drinking water processes at Coquitlam DWTP.

Chlorination is the final stage of the treatment scheme and creates the additional barrier for bacteria inactivation. In 2017, the technicians were starting the strategy about modernization of chlorination and change from gas chlorine to sodium hypochlorite.

Ozonation together with chlorination provide viruses and bacteria inactivation – (4-log). The datils regarding contact time and applied dose are presented in Appendix.

Coquitlam DWTP has proper treatment system with high removal efficiency of color, turbidity and bacteria inactivation. The formed concentration of DBPs meet WHO and US EPA regulations. The Table 6 shows the results for untreated and treated water from Coquitlam watershed.

Table 6 – Raw and treated water quality at Coquitlam watershed (Quality Control Annual Report 2014-17)

Year / Parameter	2014		2015		2016		2017	
	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
pH	6.3	7.5	6.3	7.5	6.3	7.3	6.3	7.5
TOC (mg/l)	1.6	1.5	1.79	1.7	1.62	1.52	1.5	1.4
Color true (mg-Pt/l)	9	1	11	1	9	<1	9	<1
Color apparent (mg-Pt/l)	13	2	17	2	15	2	14	<2

Turbidity (NTU)	0.49	0.42	0.56	0.54	0.33	0.28	0.45	0.38
DBPs	TTHM 33 µg/l THAA 40 µg/l	TTHM 33 µg/l THAA 38 µg/l	TTHM 24 µg/l THAA 25 µg/l	TTHM 20.4 µg/l THAA 20.9 µg/l				

* - All values are mean and taken from Metro Vancouver Water Quality reports 2014-2017

There were few main reasons, why we have taken the Coquitlam DWTP as a study case with applying pre-ozonation with followed chlorination for our research. First reason is a common using of a chlorination step as an additional barrier for preventing waterborne outbreaks both in Canada and Norway. Second reason is the similarity of water quality in water sources for further DW purpose in Canada and Norway. It is a known fact, that the majority of lakes in Canada and Norway, which are using for drinking water have a high raw quality and mostly belong to the Oligotrophic group of lakes. The third reason was the interest to study the combined treatment – ozonation & chlorination. In the experiments, we have applied one of the ozone doses (1.5 mg/l), which is used at Coquitlam DWTP, another one (3 mg/l) can be considered as an exception or specific case.

2.9 Procedures of this Study

The main objectives of this study are as follows:

1. Determine the effect of ozone dose and contact time on the trihalomethanes (THMs) formation.
2. Evaluate the impact of turbidity, pH, color, NOM, conductivity, TOC, TOD, UV254 on the THMs formation.
3. Evaluate the impact of incubation conditions under direct chlorination of raw water on the THMFP concentrations.
4. To investigate the different THMs predictive models based on achieved results.

3. EXPERIMENTAL METHODS AND MATERIALS

The nine raw water samples were taken in February 2019, then they were transported and refrigerated for being used and analyzed for THMs formation potential. The location of sampling sites for current research were taken based on past research conducted in 1999 (Gjessing E. T, Egeberg P. K, Hakedal. J. 1999). Referred research was focused on investigation of NOM and basic characteristics of drinking water. The research was involved nine water sources in Norway. We have taken mentioned research as a reference for our research. The goal of this research was to evaluate the impact of raw water quality and disinfection parameters on DBPs formation.

Figure 9 shows the location of the water sources in Oslo region which were main focus of this study. All water sources are used to produce drinking water for people. Generally, each treatment plant consists of pre-treatment with combined disinfection step.

All water sources have different origin and that is why their quality differs considerably. There are few known facts about some of the investigated waters.

Farris water source was created by rainwater falling on the hill close to the Bøkeskogen. After hitting the ground, water slowly filtered through deposit of glacial marine materials. The water entering to the spring after slow filtration, which takes approximately from 15 to 20 years and characterized by strong mineralization.

Vannsjø has poor water quality status due to the high input of nutrients (mainly P) from the surrounded fertilized agricultural soils and sediment release (Skarbøvik and Bechmann, 2010).

Aurevann has high concentration of iron and manganese, which can be a cause of yellow color of water.

Glitenvann has high oxygen content in the water and depth ≈ 90 m. The Røysjø has artificial aeration inside the lake together with good watershed protection.

This chapter provides detailed information about the methods used to quantify THMs concentrations; methods for water quality description; methods for ozone determination and dosing.



Figure 9 – Location of sampling sites in Oslo region, Norway

3.1 Experimental design

A series of experiments were conducted to evaluate the resulting THMFP after the treatment with ozonation (different contact time and ozone dose) and followed by chlorination (one applied concentration), compared to control samples that were not ozonated.

In brief, the existing treatment system at Coquitlam DWTP in Canada was considered like a study case for current master thesis research. The water from nine Norwegian water sources was taken with different quality (TU, pH, conductivity, TOC, TOD, SUVA, color) and was ozonated with followed by chlorination. The THMs were formed by reaction with natural organic matter (differ from the water origin), under room temperature. Additionally, the THMFP method was applied to raw waters for the worst scenario creation without ozonation treatment. The schematic presentation of the experimental design is shown in Figure 10.

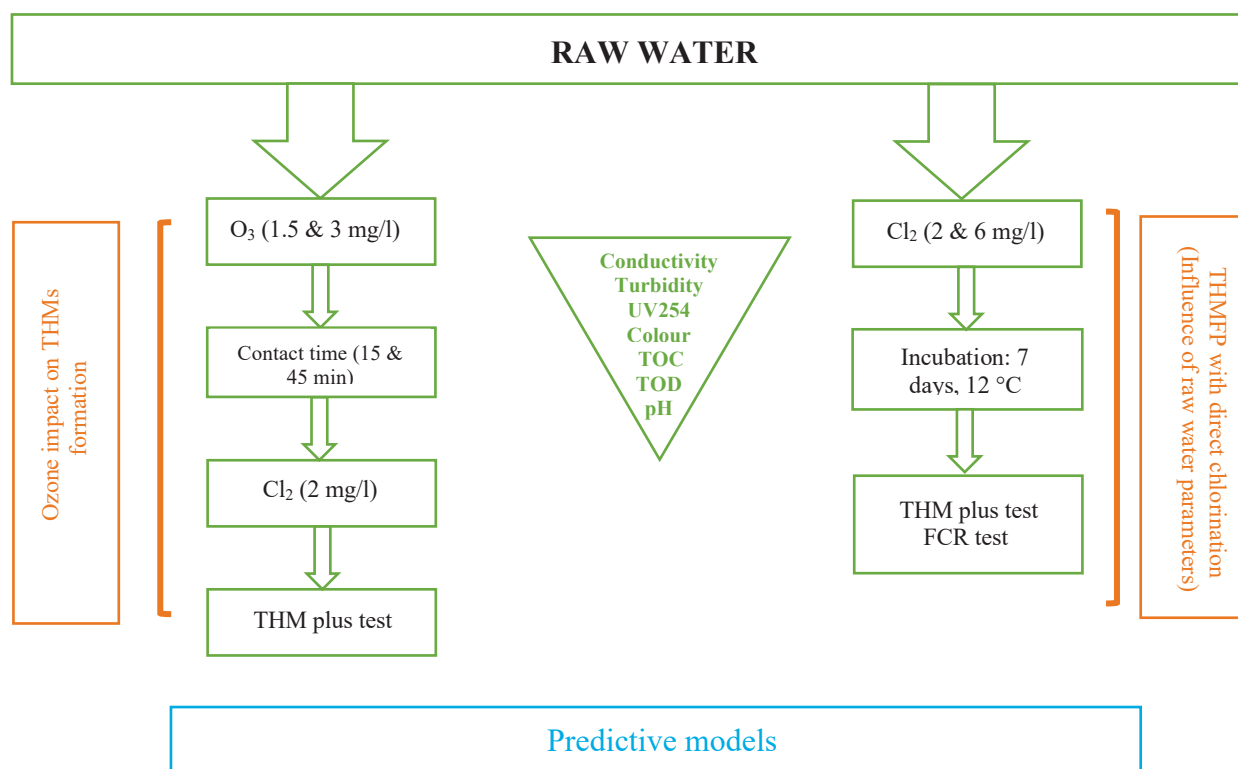


Figure 10 – Research approach (Experimental design)

Each water sample had four experiments with variation of ozone dose and contact time during ozonation, additionally each experiment was done in duplicate for the achieving average data. All experiments were conducted under stable temperature - 12 °C. The illustrated experiments matrix summary is shown in Appendix.

3.2 Experimental procedures

All water experiments were done following the described procedures in Standard methods for the examination of water and wastewater (Rice, Bridgewater, et al., 2012).

3.2.1 pH

The pH was measured based on Electrometric Method. The standard solutions were used to standardize the pH meter before the measurement. Also, the temperature was noted for each data. The *WTW ProfiLine pH meter 3110* was used for current analyze.

3.2.2 Color measuring

Color of solution was measured according to the Norwegian standard and *Hach-Lange DR 3900* spectrophotometer was used for analyses. Color measuring is based on measurement of absorbance at 410 nm and results are presented in mg-Pt/l.

3.2.3 Turbidity

One of the main parameters, which has to be defined for drinking water treatment process, is turbidity. It is an indication of the number of colloidal particles in source water. The higher content of particles leads to the higher value of turbidity. The method of measurement based on the amount of light which is diffuse when it passes through the water sample. *Hach 2100Q Portable Turbidimeter* was used for turbidity measurement. The procedure based on the untreated source water is filled into the special glass tube, where all air bubbles should be removed. After this step, the tube was placed into turbidimeter. All results are presented in Formazin Nephelometric Units (FNU). Turbidity was measured for all nine waters for further comparison. Moreover, the second turbidity measurement was done by *Hach 2100N Turbidity Meter* for the comparison and increased accuracy.

3.2.4 Electrical conductivity

Taken water samples were taken from the cooling room (4 °C) and kept at room temperature to be stable for the measurements. Electrical conductivity (EC) measurement was performed by *WTW™ Cond 3210™ Portable Conductivity Meter*. This analyze was done by taking a water aliquot of approximately 30 ml into a glass cylinder and measured for EC reading, when the value was stabilized.

3.2.5 TOD measuring

TOD analyze does not require any chemicals and based on the oxidation by the heat. This analyze was developed 40 years ago. For the TOD measuring, the *Quick COD lab by LAR company* was used.

The analyze for one sample takes 3-5 minutes. Water sample analyzed by a combusting aliquot at high temperatures (1.200°C) in the reactor with further measuring the amount of realized oxygen.

3.2.6 TOC

TOC measurement determines organic content in water sample. The principle based on catalytic oxidation at high temperature (680°C) and the generated CO₂ is detected.

The analyses were carried out with a TOC analyzer (*Shimadzu TO-5000A*) at MINA faculty according ISO 8245 (1985) method.

3.2.7 UV-Absorbance (full spectrum)

UV-absorbance demonstrates the aromatic groups presence in water. Higher UV absorbance value means bigger number of aromatic groups in the organic molecule.

Absorbance of each water samples at full spectrum with wavelengths 190 – 840 nm were determined for all samples. Special quartz cuvettes were used for this measurement. After the measurements UV254 and UV272 data were extracted for further data processing. Ultraviolet absorbance at 254 nm (UV254) was used to quantify the concentration of organics in the water. Ultraviolet absorbance at 272 nm (UV 272) was used to observe correlation with THM formation. Absorbance was measured using a *UV-5800(PC) UV/VIS Spectrophotometer* (China) with a 5-cm quartz cell. Spectral data were acquired at wavelengths of 190 - 840 nm at 0.5-nm resolution.

3.3 Ozonation methods and materials

3.3.1 Ozone stock solution

For the preparing ozone stock solution, the distill water was trained for one hour ozonation with the constant ozone input for the better ozone solubility in the liquid phase.

Ozone stock solution was prepared at 17 – 20 mg- O_3 /l residual by bubbling one gas into already trained distilled water for 1 hour. Such methodology helps to slow down the decays of ozone residual, however the ozone residual was determined for each experiment for the concentration controlling and applied dose calculation.



Figure 11 - The Ozonation set-up

New stock solution should be prepared when the ozone residual is too low.



Figure 12 – Ozone determination by Indigo method

For the ozonation disinfection ozone generator Ozone UM-80 was used. Maximum produced concentration of ozone is 150 mg- O_3 /l; power consumption up to 80W; Gas flow speed ranging from 0.5 to 2.0 l/min. The experimental set-up includes ozone generator connected to the ozone bubbler (500 ml). The ozone was fed to the bottom of the bubbler for better mixing and bubbling. The experimental cell for ozonation is shown on the Figure 11.

The chemical analysis was applied for the determination of ozone residual in the water. The gas was passed through the special bubbling vessel containing 100-200 ml of distilled water.

After the complete ozonation, the certain volume of ozonized solution was acidified with 20 ml 1M sulfuric acid, then 10 ml of 2% potassium iodide was added to the solution together with 1-2 drops of starch (for the visibility of reaction) and titrated with standardized 0.1 N sodium thiosulfate. The presence of ozone can be visually determined by intensity of blue color.

The determination of the correction coefficient for sodium sulphate solution was done in advance to titration experiments with ozone stock solution.

Procedure for the determination of the correction coefficient:

0.5 g of dry potassium iodide was poured into a flask and dissolved in a small volume of distilled water. Then the solution needed to stand in a dark place for 6 - 8 minutes. After that, the formed iodine was titrated by $\text{Na}_2\text{S}_2\text{O}_2$ solution of with a corresponding normality in the presence of starch. The correction factor (K) is determined by the formula:

$$K = \frac{10}{a} \quad \text{Equation 10}$$

Where a – the amount of $\text{Na}_2\text{S}_2\text{O}_2$ used by titration, ml

3.3.2.1 KI solution

20 g of potassium iodide (KI) is dissolved in distilled water and the volume is adjusted up to the mark 1L. The solution has to be stored in a dark and dry place.

3.3.2.2 H_2SO_4 solution 1N

28 ml of concentrated sulfuric acid is carefully added to the distilled water by small portions. The volume is adjusted up to the mark 1L. The H_2SO_4 solution 1N needs to cool down before the use.

3.3.2.3 $\text{Na}_2\text{S}_2\text{O}_2$ solution 0.005 N

50 ml of 0.1 N sodium sulphate solution was transferred to a 1L volumetric flask and diluted with a distilled water, after that the 0.2 g of sodium carbonate was added and the volume is adjusted up to the mark.

3.3.2.4 Starch 0.5 %

5 g of soluble starch is mixed with 50 ml of cold distilled water and poured into 950 ml of boiling distilled water. The solution can be preserved by the addition 1.25 g of salicylic acid.

3.3.3 Processing results of iodometric method for ozone determination

$$X = \frac{(a-b)K \times N \times 24 \times 1000}{V} \quad \text{Equation 11}$$

Where,

X – ozone concentration, mg-O₃/l

a – the amount of Na₂S₂O₂ spent on the sample titration, ml

b - the amount of Na₂S₂O₂ spent for the blank titration, ml

K – the correction factor

N – the normality of Na₂S₂O₂

24 – the ozone content corresponding to 1 ml 1 N Na₂S₂O₂ solution

V - the sample volume, ml

3.3.4 Ozone dosing

The ozone dosing was done by adding predefined volume of prepared stock solution (2.3.1) to a known volume of source water sample. The achieved solution (stock solution/water sample) was well mixed and starting time of ozonation was recorded.

The dose calculation was done based on (Rakness, 2005)

Calculations (example):

Concentration of ozone stock solution – 40.7 mg-O₃/l

Sample volume – 200 ml

Stock solution volume - 30 ml

Ozone mass (mg) = (40.7 (mg-O₃/l) *30 (ml))/1000 ml/l) = 1.221

Ozone dose = ((1.221 (mg) /230 (ml)) *1000 (ml/l)) = 5.3 mg-O₃/l

3.4 Chlorination

3.4.1 Chlorine doses and concentrations

Chlorination was done by dosing Chlorine Standard Solution with concentration 1250 mg-Cl₂/l. (HACH company). The concentration of added chlorine was calculated by following formula:

mg-Cl₂/l = (Volume of standard added * ampule certificate value) / volume of water sample or

mg-Cl₂/l=(0.08 mL *1250 mg-Cl₂/l) / 50 ml = 2 mg-Cl₂/l

Table 7 shows the injected dose of a 1250-mg/L Chlorine Dosing Solution

Table 7 – Injected chlorine dose

Number	Cl ₂ Dosing solution (mL)	Cl ₂ concentration (mg/l)
1.	0.08	2 mg/l
2.	0.24	6 mg/l

The chlorine concentrations presented in the table above were applied for both THMFP test and THM after combined disinfection by ozonation and chlorination.

3.4.2 Residual Free Chlorine Measurements

For testing free chlorine in water the HACH method 8021 was applied. The FRC in water samples were measured on a spectrophotometer HACH DR 2800™ with program 80 and measured wavelength 520 nm. In advance to FRC measurements, the accuracy test for the methodic was performed.



Figure 13 – Presence of FRC in the water

After the chlorine dosing to the water, the formed hypochlorite ion directly reacts with N,N-diethyl-p-phenylenediamine indicator (Chlorine Reagent Powder 2105569) followed by a pink color formation. The intensity of the color is proportional to the FRC in the water. Water with low chlorine concentration has more transparent color.

3.5 Analytical methods for THMs

3.5.1 Trihalomethane measurements by Hach method

EPA Method 551, 552, 524 are the most widely used techniques to quantify DBPs concentration in the water. These methods based on gas chromatographic separation (GS) and detection by mass spectrometry (MS) or by electron capture detection (ECD). Most DWTPs do not have the equipment to perform the highlighted methods for DBPs analyzing. Additionally, the time for these tests can vary from one to four weeks. That is why the new method THM Plus by Hach Company was used for all THMs determination experiments in this research. The accuracy and equivalency of new method were determined by detailed comparison THM Plus method results with three US EPA methods (Lord, T., 2004). This method includes in the results several DBPs compounds (Table 8) and can be sensitive in a range 10 to 600 ppb as Chloroform.

Table 8 - Disinfection by-products (DBPs) included in the THM Plus method results

Compound	DBPs group	Effect
1,1,1-trichloro-2-propanone	HKs	Interferes positively
1,1,1-trichloroacetonitrile	HAN (Haloacetonitriles)	Interferes positively
Chloral hydrate	HALs (Haloacetaldehydes)	Interferes positively
Dibromochloroacetic acid	HAA	Interferes positively
Dichlorobromoacetic acid	HAA	Interferes positively
Tribromoacetic acid	HAA	Interferes positively
Trichloroacetic acid	HAA	Interferes positively

The THM Plus represents the trihalogenated disinfection by-products that can be formed due to the reaction between NOM and chlorination agent.

THM Plus method (10132) (Trihalomethanes Method) has 30 steps before the final measuring absorbance by HACH DR 2800™ spectrophotometer. The water samples were pre-ozonated with followed by chlorination. The summary of the procedure for one water sample:

1. The cell was filled with 10 ml of water sample.
2. The 3 drops of sodium tiosulphate (Reagent 1) was added to the sample to raise the pH and dechlorinate water.
3. 3 ml of N,N –diethyl nicotinamide (Reagent 2) was added to the sample.
4. After the proper mixing sample cell were placed in a boiling water for the next 5 minutes.
5. After the boiling, sample cell was cooled down by placing to cold water for 3 minutes.
6. After the cooling, 1 ml of Reagent 3 (acid) was added to lower the pH 2.5.
7. The sample cell was cooled again to the room temperature.
8. The G-amino powder (Reagent 4) was added to the sample cell.
9. For the next 15 minutes the color was developed (yellow/orange) at the room temperature.
10. The absorbance was read at 515 nm.



Figure 14 – The THMs formation by THM Plus method (10132)

Generally, in this method the THM compounds present in a water sample reacts with N,N –diethyl nicotinamide under heated alkaline conditions by followed transitional dialdehyde formation. In turn, the transitional dialdehyde ($C_{21}H_{24}N_2O_4$) reacts with 7-amino-1,3 naphthalene disulfonic acid to form a $R_2C=NR$ or Schiff base. The detailed mechanism is shown on Figure 15.

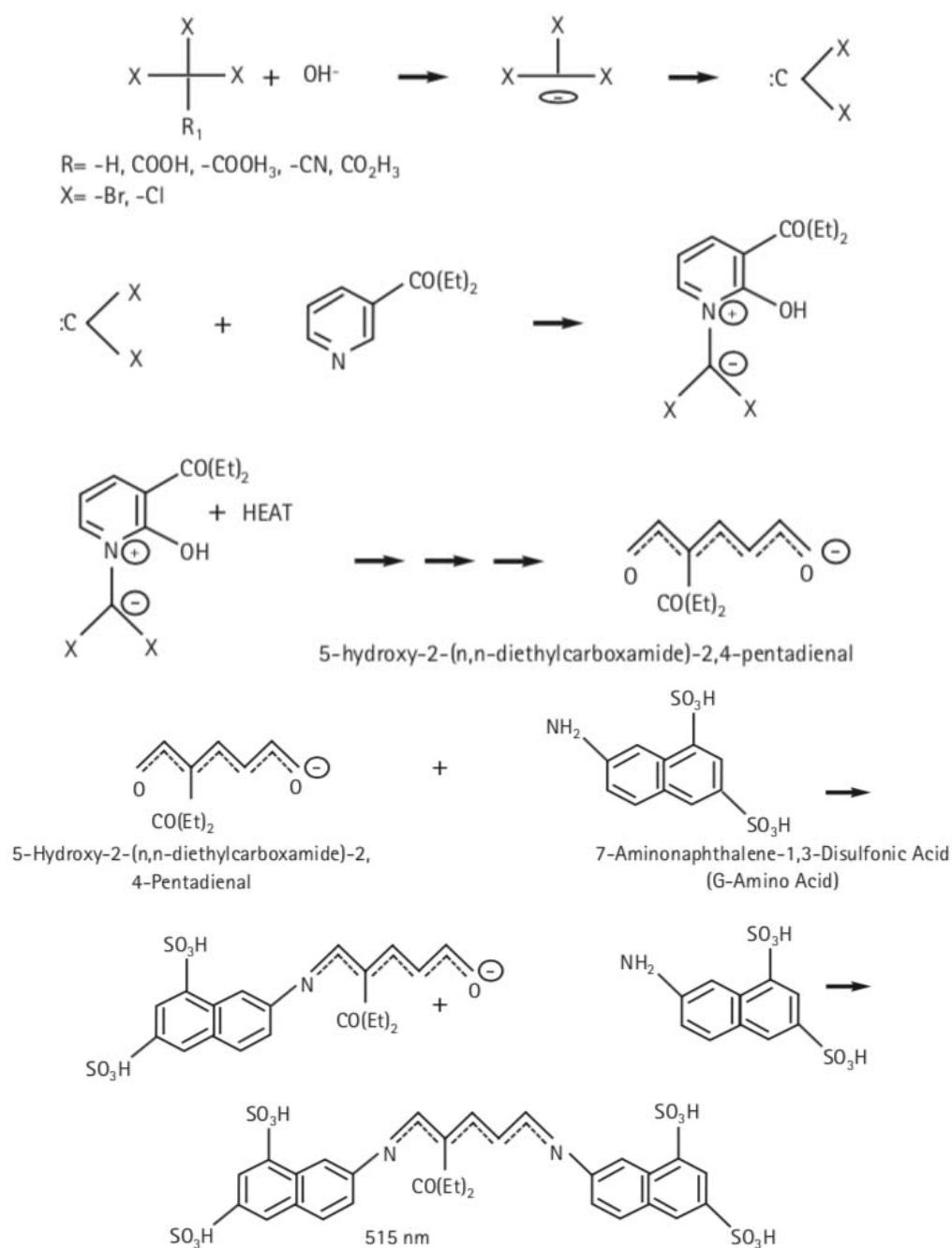


Figure 15 - Mechanism of DBPs determination by THM Plus method

THMFP method (10224) (Trihalomethane Formation Potential Method) also based on THM Plus method, however it determines the potential of source water to form DBPs under the influence of direct chlorination (without pre-ozonation), incubation time and constant temperature.

3.5.2 THMs stock solution (accuracy test)

The accuracy test by preparing 99 ppb chloroform standard. The procedure based on adding 0.1 ml of the chloroform standard to 10 ml of organic-free water. After that the step from 6 to 30 in THM Plus (10132) method was performed.

4. RESULTS AND DISCUSSION

4.1 Quality of raw water

The raw water samples were directly taken from nine water resources in Norway in the winter season. All water samples have specific water quality due to different location (agriculture facilities, forest, nearest roads, slope and etc.), depth, weather condition, and feeding. The visual estimation of water qualities can be gotten based on Figure 16.



Figure 16 – Visual water comparison

The obvious colour difference between waters can be observed on figure above even without proper measurements. The Farris, Vannsjø, Aurevan and Sjunken have more yellowish color which may indicate a greater NOM concentration. In turn, the Glitrenvann, Hurdalsjøen, Eikervann, Røysjø and Holsfjærd are almost transparent which indicate the lower NOM content. It can be explained by known factors about some water sources presented in Chapter 3.

Based on Figure 16, the quality and organic content estimation can me made preliminary, however requires additional laboratory analyses to characterize the waters.

For the water samples characterization, turbidity, color, TOD, TOC, pH, UV absorbance and conductivity were measured. The detailed methods description is described in Chapter 3. The Table 9 includes all measurements data of raw water characteristics.

Table 9 – Raw water characteristics

Water Source	pH*	TU (NTU)*	Color (mg- Pt/l)*	TOD (mg/l)**	TOC (mg/l)**	UV 254 (cm ⁻¹)*	SUVA (L m mg ⁻¹)*	Conductivity (μS/cm)*
Aurevann	6.56	1.13	50.50	11.4	6.10	0.301	4.93	46.50
Eikerenvann	7.09	1.77	16.00	4.20	2.60	0.102	3.92	26.70
Farris	6.73	2.54	54.50	6.80	3.90	0.235	6.03	75.60
Glitre	6.48	0.98	14.50	3.63	2.60	0.105	4.04	33.30
Holsfjord	6.89	0.45	15.50	5.83	3.40	0.121	3.56	42.00
Hurdalsjøen	6.74	0.48	19.00	4.40	3.80	0.131	3.45	31.30
Røysjå	6.35	0.35	5.00	0.90	2.30	0.031	1.35	43.30
Sjunken	5.97	1.57	44.00	10.70	5.50	0.271	4.93	85.70
Vannsjø	6.78	5.37	68.50	16.27	6.30	0.441	7.00	127.40

* - This table includes average data from triplicate results ** - This table includes average data from duplicate results

As stated in introduction, one of our goals was to evaluate the impacts of quality indicators of source water (turbidity, UV254, TOD, color, TOC, pH, conductivity) on THMs formation. Table 9 highlights that Røysjå has the lowest turbidity, TOD, TOC, UV 254 and color; In turn, Vannsjø has the highest values of turbidity, color, conductivity, UV 254, TOC and TOD; The highest pH belongs to Eikerenvann, the lowest - Sjunken source. However, most of the pH values were within range from 6.5 to 7.5 – neutral pH range.

The TOC levels in raw water samples were ranging from 2.3 to 6.3 mg/l, which is not so high and can be explained by low organic concentration in waters during winter time.

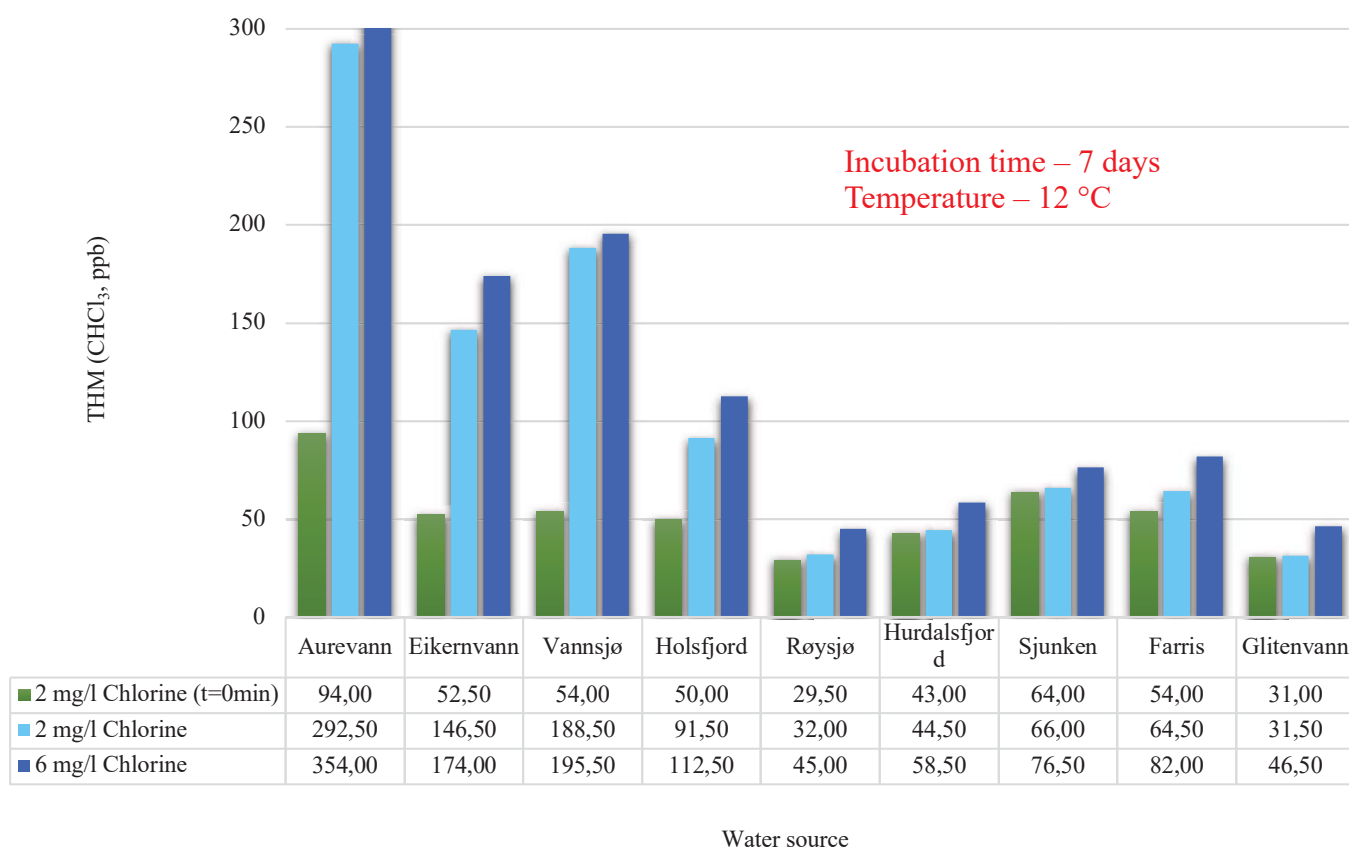
Taken together, these data would seem to suggest that Vannsjø has the worst water quality among other investigated water sources. At the same time, Røysjå source has the clearest water with promising data.

Characteristics of Raw water samples has direct correlation with THMs formation refer to (Thompson, Gillespie, et al., 2015).

The TOC, UV254 and colour are the main parameters for organic content indication. The detailed results and explanation of THMs formation due to raw water quality will be discussed in Section 4.2.

4.2. THMFP results under the direct chlorination.

As described in Chapter 2, each water sample was directly chlorinated with applied two chlorine doses 2 & 6 mg/l and kept in a dark place with constant temperature for 7 days. Current method helps to simulate the possible worst scenario with operational mistake of chlorine dose increasing and DWDS conditions (water age). Additionally, the chlorine demand within a long period (7 days) can be observed. Moreover, the mean concentration of THMs (as CH₃Cl) for raw water at 0 time under 2 mg-Cl₂/l injection was detected.



* - This table includes average data from duplicate experiments

Figure 17 – THMFP data for raw waters under different chlorine doses and time

Figure 17 shows significant results for DBPs formation estimation. The achieved data examined the different chlorine doses effect on THMs formation over the time.

The results obtained from Norwegian water resources showed that the level of THMFP in raw water was high in the case of surface water with higher TOC, TOD, color, TU and after incubation period it increased by 34 - 73%. The THMFP at 0 time is the highest for Aurevann (94 ppb), the lowest – for the Røysjø. However, it can be seen that within the incubation time and applied chlorine doses (2 & 6 mg/l) this tendency is greatly changed.

Refer to Figure 17, all raw water samples tend to form THMs concentrations at zero time, which are lower of the existing guidelines. However, within the time the THMs concentrations increases in 3 - 5 times for some waters. Such great increase can be explained by presence of some THMs precursors, which can easily react with chlorine and continue the formation of THMs species.

Nevertheless, there is no significant difference in THMs formation between THMFP at zero time and THHFP after 7 days with same chlorine dose 2 mg/l for Røysjø, Hurdalsfjord, Sjunken, Glitten and Farris waters. The possible explanation for this maybe that Røysjø, Hurdalsfjord and Glitten waters have low contamination level, which clearly presented in Table 9. In turn, Sjunken and Farris have high color and turbidity and small shifts in THMs formation after 7 days under chlorination. This may have occurred because of chlorine consumption for the other DBPs species formation.

On account of the fact that the difference in THMs formation at chlorine dose 2 mg/l and chlorine dose 6 mg/l is low, the chlorine overdosing can be concluded with applying 6 mg/l.

Significantly, the Eikerenvann source tends to form high THM concentration (64 % higher compared to THM₀) within the time despite low color and TOC values. This exception can be refer to the highest pH values, which has direct effect on THMs formation, or possible presence of some DBPs precursors of organic chemicals (pesticides, pharmaceuticals, herbicides and etc.)

It should be noted that Auevann, Eikernvann and Vansjø waters after the treatment utility (disinfection) need to be strictly regulated though DWDS due to the high THMFP under the time. The supplemental method which can help to clarify the chlorine consumption and THMFP is Free residual chlorine (FRC).

The chlorine residuals help to prevent unpredicted pollutions in the distribution lines, however recent studies show the chlorine can cause allergic symptoms (Grellier, Bennett, et al., 2010).

In our research, we have analysed the water samples after incubation period for FRC by HACH method 8021. According to the WHO the FRC values should be in range 0.2 – 0.5 mg/l. The Figure 18 represents achieved data of FRC for all water sources.

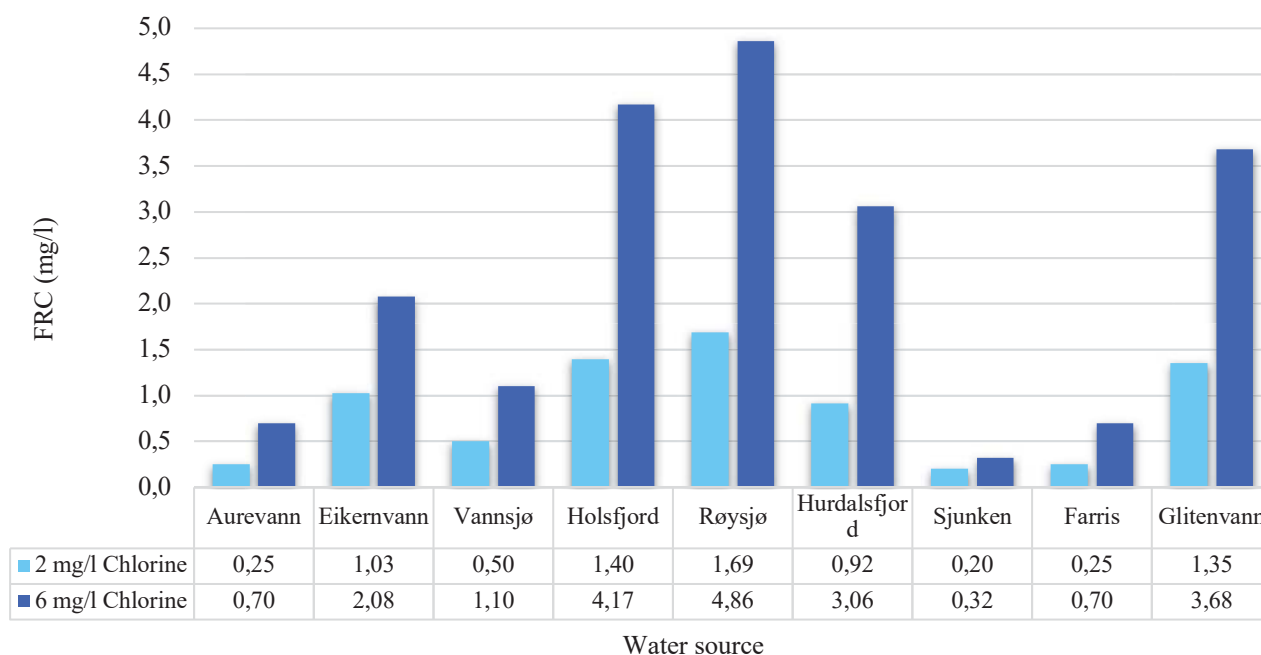


Figure 18 – FRC data after applying different chlorine doses

Based on presented data on Figure 18, Aurevann, Sjunken, Vannsjø and Farris under the chlorine 2 mg/l are compliance the WHO guidelines. In this case, FRC data ranging between 0.2 – 0.25 mg/l. However, Eikervann, Holsfjord, Røysjø, Hurdalsfjord and Glitenvann have very high FRC data. It means that the applied dose 2 mg/l is high for them and the dichlorination step should be implemented due to possible human health effect.

However, the FRC concentration gradually decreases over the time. It can be seen based on results for Aurevann, Sjunken, Vannsjø and Farris. From the applied chlorine dose 6 mg/l over the time it decreased to 0.32 – 1.10 mg/l.

On the other hand, if compare Figure 17 and Figure 18, some interesting observations can be highlighted. For example, Sjunken and Farris have great decay in chlorine, however the THMFP does not change significantly. Such finding can be explained by possible presence of other organic and inorganic compounds, which react with chlorine and consume it (Wang, Ruan, et al., 2014).

Our research focuses on THMs formation within the disinfection, however other DBPs should also be identified for the more complete understanding of chlorine behaviour in water.

Based on THMFP experiments and FRC identification, can be concluded that Røysjø water has the lowest THMFP₀ (29.5 ± 0.5 ppb) and the highest FRC values , which characterize it like the

clearest water with low contaminations content. The highest THMFP₀ refer to Aurevann (94 ± 0 ppb).

Taken together, these findings and results highlight the influence of raw water indicators on THMFP. The results presented in this section are essential for further prediction modelling creation described in section 4.5.

4.3 THMFP vs raw water quality indicators

Water quality parameters can help to indicate the presence of DBPs precursors in water. Generally, DBPs precursors are a combination of organic and inorganic compounds that can form DBPs under different disinfection conditions. In many literature sources (Blokker, Furnass, et al., 2016), (Bond, Goslan, et al., 2012), (Ding, Deng, et al., 2019) described some trends between water quality parameters (TU, TOC, pH, UV₂₅₄ & etc.) and DBPFP. One of the purpose of this research was to evaluate the impact of water quality parameters on THMFP, and create a mathematical prediction from achieved data.

4.3.1 TOC

Total organic carbon (TOC) describes the total amount of carbon in water or organic content. It is imperative that disinfectants are able to react rapidly with TOC present with followed DBPs formation.

The NOM can be characterized by TOC and UV₂₅₄ parameters. Greater value of these parameters means higher organic concentration in water. Generally, TOC and THMFP has a strong correlation, which can be observed on the Figure 19.

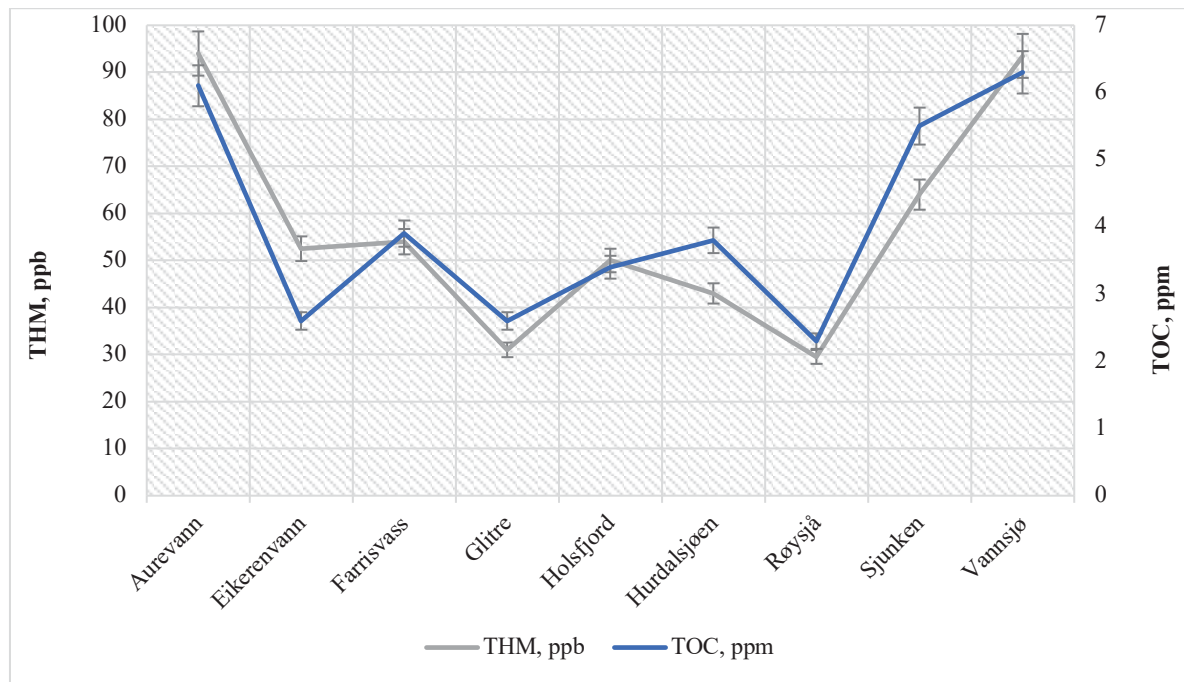


Figure 19 – TOC concentration in raw water VS THMFP results

The TOC levels for investigated water samples was ranging from 2.3 – 6.3 mg/l, which is quite low for open water sources.

Results on Figure19 show that TOC concentrations in Aurevann and Vannsjø were significantly higher with followed higher THMFP compared to other water samples. These observations indicate that the higher TOC concentration leads to higher THMFP after the chlorination.

(Assmann, Scott, et al., 2017) reaches the conclusion that TOC analysis is a useful tool that can help operators to effectively perform treatment process, in order to meet DBPs regulations.

4.3.2 TOD

TOD is relatively new analysis and was investigated 40 years ago. In comparison to the widely applicable TOC analyze which based on thermal oxidation with CO₂ formation and measuring; TOD based on the same principle, but the detector measures the formed O₂. In the literature sources there is rare information about TOD correlation with other parameters. However, some articles pointed that TOD and COD has the highest correlation. On the Figure 20, the correlation between TOD and THMFP are presented.

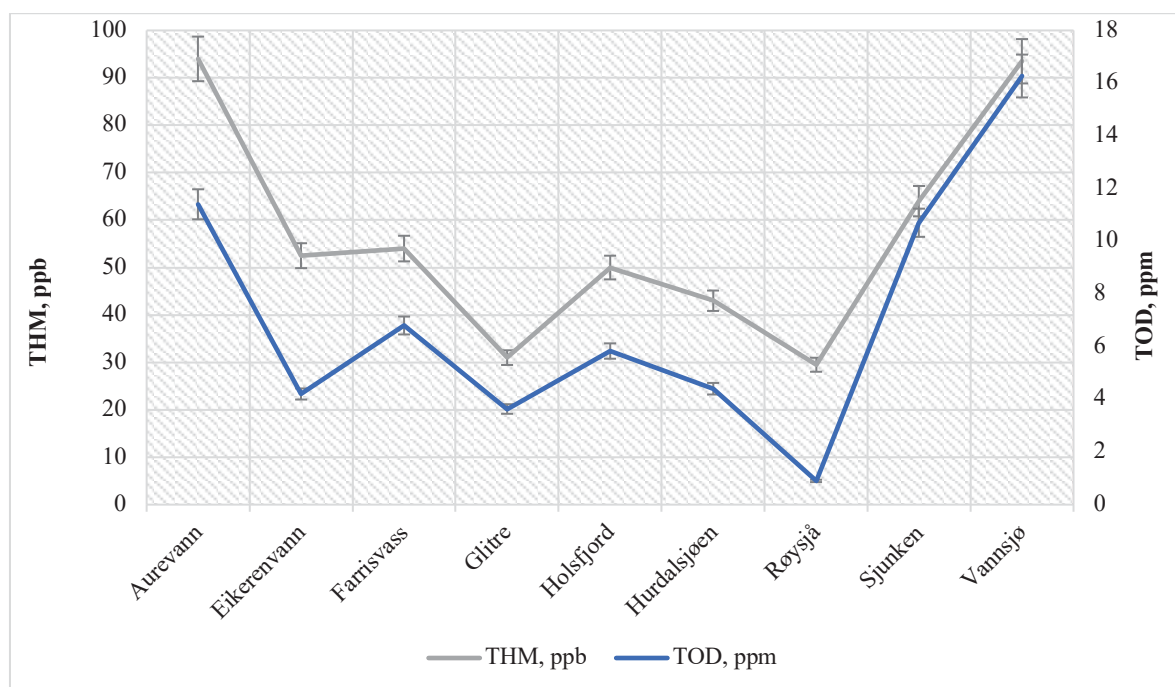


Figure 20 – TOD concentration in raw water VS THMFP results

The clear correlation between TOD and THMFP can be observed on figure 20. The achieved result show that TOD increasing leads to THMFP increase. The Vannsjø with the high TOD concentration has higher DBPs formation. Røysjø source has the lowest TOD level. Taken together, these findings highlight a role of TOD for DBPs prediction and controlling. Our investigations into TOD vs THMFP relation has confirmed our hypothesis, that TOC measurement can be replaced by TOD for DBPs research. Remarkably, we have achieved slightly better TOD/THMFP correlation (93%) in comparison to TOC/THMFP (92%).

4.3.3 Color

Color is one of the quality factors which can be used for NOM characterization. It is known fact, that color highly correlate with UV_{254} and TOC (Bancroft, 2011). Figure 21 represents results of correlation between colour and THFMP.

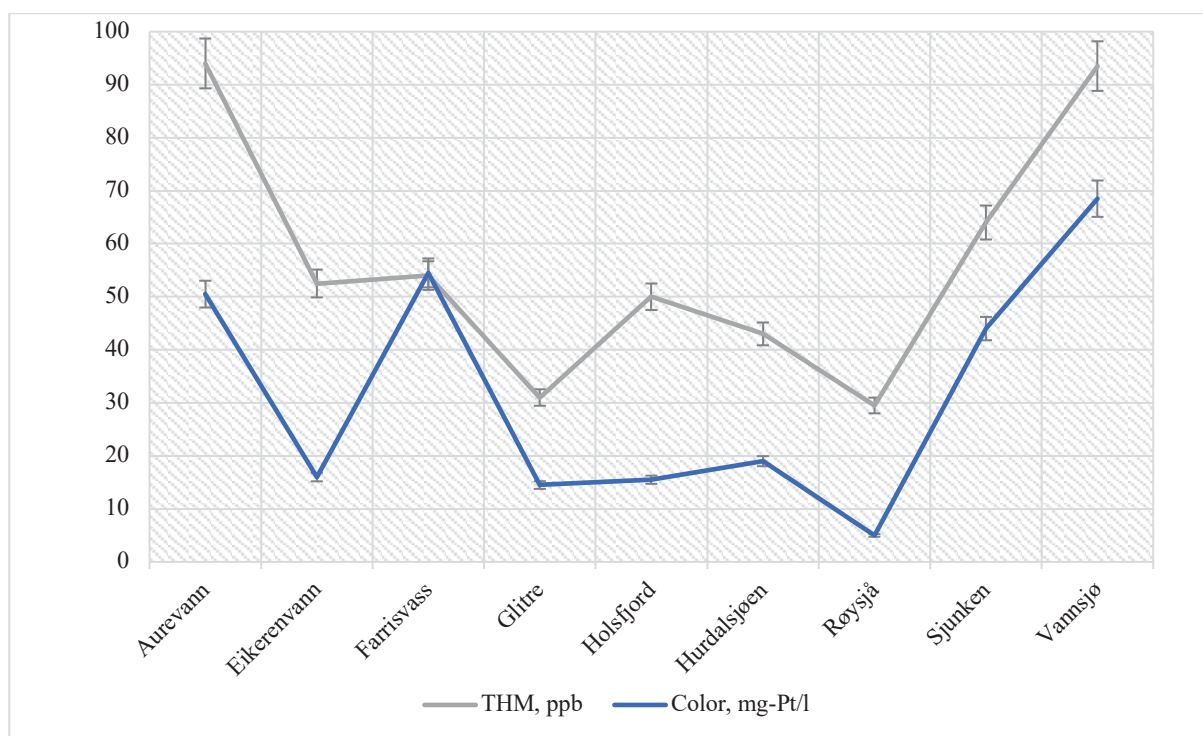


Figure 21 – Color VS THMFP results

The color for raw water samples varied from 5.0 NTU to 68.5 NTU . From figure 21, we can conclude, that color and THMFP curves have same tendencies. Vannsjø has the highest THMFP and colour data. The color curve is zig-zagged in the interval between Eikerenvann and Glitre. This happened due to high color in Farris sample, caused by the presence of inorganic compounds and high mineralization. In between Glitre and Hurdalsjøen, the color curve gently changes. Røysjø reached the lowest point of the color curve.

4.3.4 Conductivity

Conductivity is a physical parameter of water. The measurement of conductivity based on water ability to conduct electricity. The electrical current can be transported in the water by presence of ions (caused by alkalis, chlorides, sulfides or carbonate). Thus, conductivity increases as ionic concentration increases. In this research, the conductivity was measured for all samples to study the possible correlation between conductivity and THMFP (Figure 22).

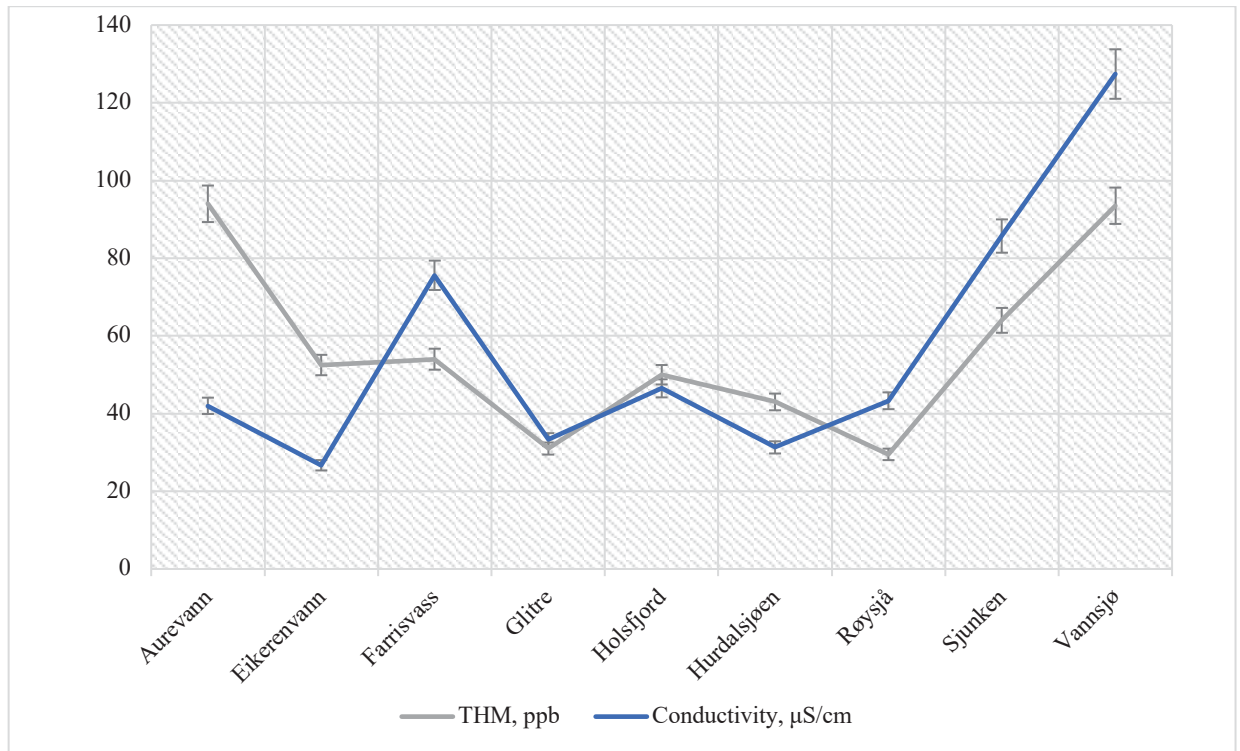


Figure 22 – Conductivity VS THMFP results

The conductivity, for water samples, was in range between 26.7 to 127.4 µS/cm, which pertains to conductivity between melted snow and tap water. As would be expected, the highest conductivity together with THMFP belong to Vamsjø source (127.4 µS/cm), which means the high ion concentration in the water. The conductivity of Farris went up due to high mineralization caused by infiltration through marine deposit (74.5 µS/cm). The lowest conductivity belongs to Eikerenvann (26.7 µS/cm). Thus, the highest water conductivity can lead to higher THMFP.

4.3.5 SUVA and Absorbance

Specific UV Absorbance (SUVA) is another drinking water quality parameter that is becoming increasingly referenced especially for disinfectants applications. SUVA includes two other parameters: TOC or DOC and UV₂₅₄. The Equation 12 Represents the SUVA calculation.

$$SUVA = \frac{UV_{254}}{TOC} \times 100 \quad \text{Equation 12}$$

Basically, SUVA characterizes the number of aromatic compounds in the water independently from the general level of organics. Figure 23 shows the SUVA/ THMFP correlation within performed experiments (Hua, Reckhow, et al., 2015).

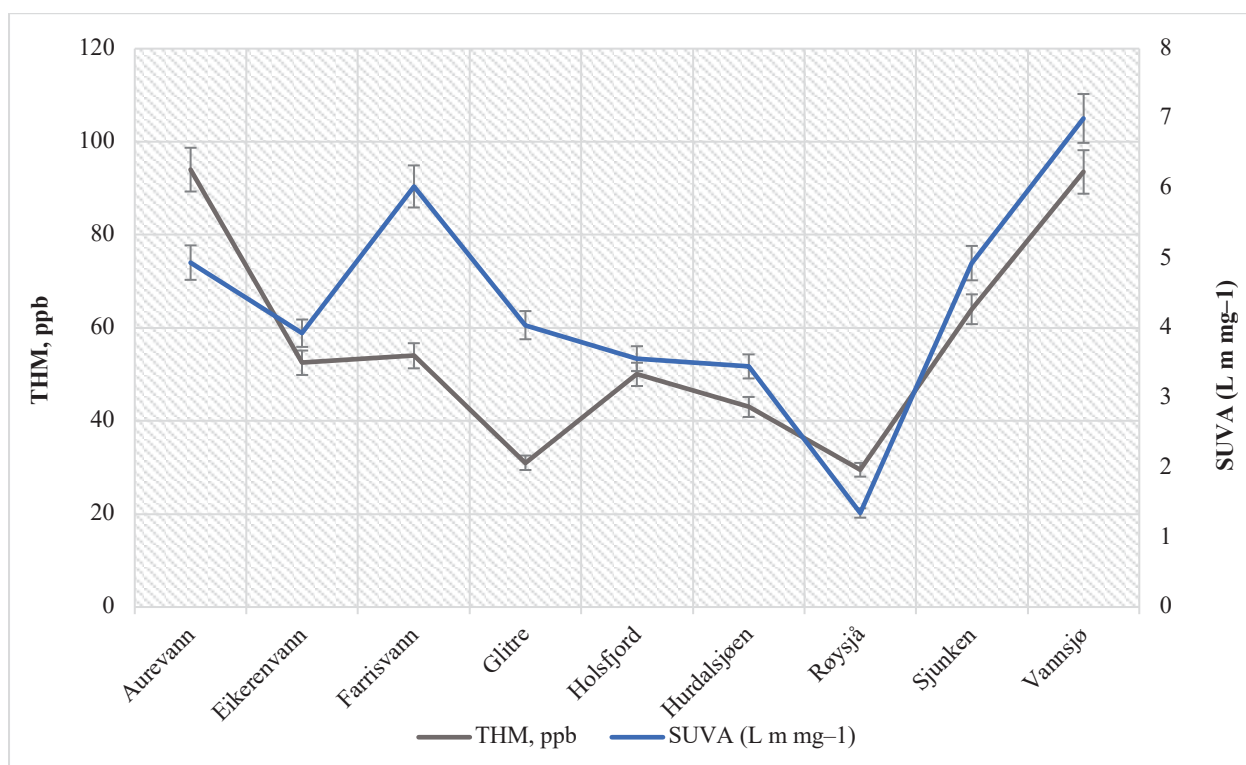


Figure 23 – SUVA VS THMFP results

From the figure above, we can observe fluctuated dependents among investigated water samples. The SUVA values were ranging from 1.35 to 7.00 (L m mg⁻¹). Aurevann, Farrisvann, Sjunken and Vannsjø have the higher SUVA values, which means higher present of aromatic compounds in water. Higher concentration of aromatic compounds leads to greater THMFP, what can be observed on Figure 23. SUVA is an important indicator of organic change under different treatment process.

Another, surrogate parameter, which helps to determine NOM content in a water is UV₂₅₄ (Spectral Absorption Coefficient). In the frame of our research, the absorbance of full spectrum (190 – 840 nm) was measured for each sample. Afterwards, two specific absorbance values at wavelength 254 nm and 272 nm were excluded for the SUVA calculation and water characterization.

The UV₂₅₄ is a common water quality parameter which based on light utilizing at the 254 nm with the organic matter detection in water. The UV₂₅₄ is the most applicable measurement, because most organic compounds absorb light at this wavelength.

The UV₂₇₂ was chosen based on research by Korshin (Korshin, Chow, et al., 2008), which proved that THMS and UV₂₇₂ have strong correlation. The absorbance results for raw water samples are presented in Table 10.

Table 10 – Absorbance results for raw water samples

WATER SOURCE	ABSORBANCE DATA FOR RAW WATER			
	A ₂₅₄	A ₂₇₂	A max	λ. nm
Aurevann	0.301	0.254	0.372	227.0
Eikerenvann	0.102	0.085	0.388	195.5
Farris	0.235	0.201	0.519	194.5
Glitre	0.105	0.088	0.125	231.0
Holsfjord	0.121	0.102	0.201	197.0
Hurdalsjøen	0.131	0.107	0.223	200.5
Røysjø	0.031	0.027	0.182	190.5
Sjunken	0.271	0.227	0.341	226.5
Vannsjø	0.328	0.277	1.109	208.5

Based on results, presented in Table 10, there is no big difference between UV₂₅₄ and UV₂₇₂. Thus, we have decided to use UV₂₅₄ for all further explanation and measurements; based on literature review (Hua, Reckhow, et al., 2015), (Wang, Ruan, et al., 2014) UV₂₅₄ has higher tendency to aromatic organic compounds determination, which has double-ring structure and caused the most complicated form of organic in water (Szerzyna, Mołczan, et al., 2017).

Figure 24 represents data correlation between UV₂₅₄ and THMFP.

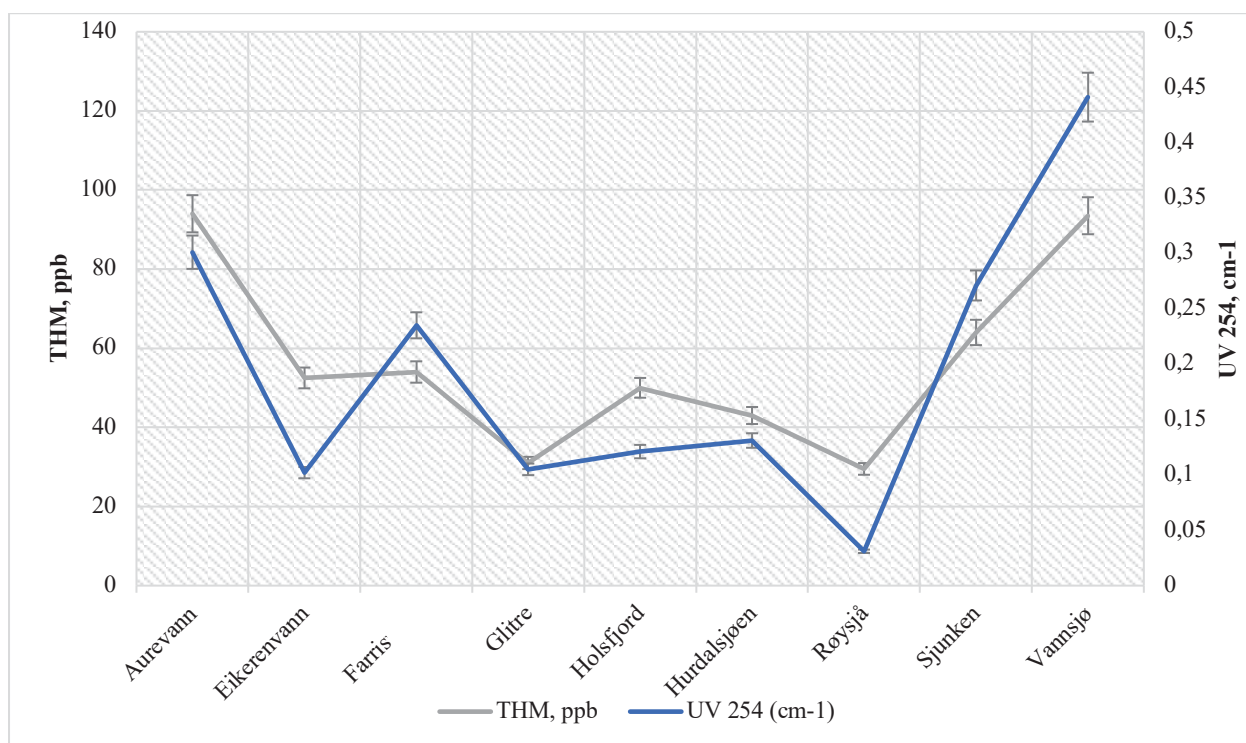


Figure 24 –UV₂₅₄ VS THMFP results

The UV 254 for water samples was ranging between 0.031 (cm⁻¹) and 0.328 (cm⁻¹). There is gradually difference between two curves. Can be concluded, that THMFP directly depends on UV₂₅₄ values. The absorbance for full spectrum can be found in Appendix.

4.3.6 TU

Turbidity was measured to obtain the physical characteristic of water. In this research, raw water turbidity results ranged from 0.35 to 5.37 NTU. The maximum average value (5.37 NTU) was reported in Vannsjø source, while the minimum average value (0.35 NTU) was in Røysjø. Such turbidity data are good, and almost go into the frames of drinking water quality standard (<5 NTU). However, the correlation between THMFP and turbidity was lower than 64 %. That is can happened, because turbidity mainly caused by non-dissolved material. In turn, THMFP greatly depends on dissolved organic matters in the water. On the Figure 25 the Turbidity results are presented.

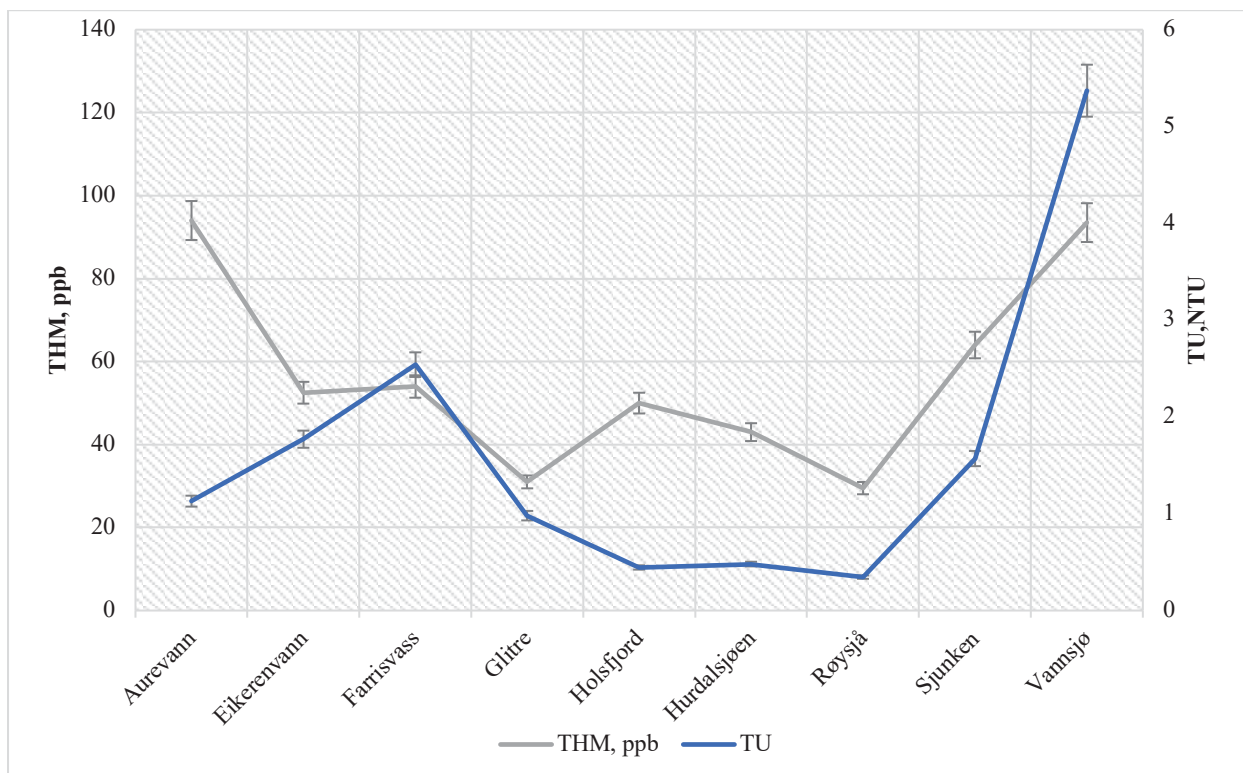


Figure 25 – Turbidity VS THMFP results

From the Figure above, we can see that Glitre, Holsfjord, Hurdalsjøen and Røysja have approximately same turbidity range. Interestingly, that Aurevann water which tend to create high THMs concentration has relatively low turbidity. However, it has higher SUVA and TOC values, which indicate the high level of dissolved organic compounds. In this case, turbidity does not play the main role in THMFP. Our data suggest that TU could be used in order to create the THMs prediction model, therefore the main focus should be on color, UV_{254} , TOC and TOD which represent organic presence.

4.3.7 pH

It is known fact that pH can effect on DBPs formation. (Hu et al. 2016a, 2016b) highlighted that increase in pH can be a reason of an increase of DBPs in the water.

In our research, all water samples had a pH in a range $6 - 7 \pm 0.1$, which indicate the neutral conditions for all of them. Current pH range does not affect greatly on THMFP compared to other water quality parameters. Such tendency can be explained by different behaviour of THMs and HAAs under pH change. In our research the THMFP was measured as $CHCl_3$ in ppb. Some literature resources (Saidan, Meric, et al., 2016) report that concentration of THMs increased when pH was changed from 5.5 to 8.5. In our research we do not have such gap between pH-values, thus

THMFP less affected. Additionally, Cl-DBPs are more stable against pH change (Abusallout, Rahman, et al., 2017).

4.3.8 Correlation coefficients between THMFP and water quality parameters

Correlation among water quality parameters and THMFP for all water samples are shown in Table 11. There were strong correlations between THMFP and TOD (93%), TOC (92 %), UV₂₅₄ (91%). Strong correlation between THMFP and absorbance or THMFP and TOC was reported in many previous research due to presence of NOM.

Table 11 – Correlation coefficients among water quality parameters and THMFP

Parameters	Correlation coefficients								
	THMFP	SUVA	Color	TU	COND.	pH	TOD	TOC	UV ₂₅₄
THMFP	1								
SUVA	0.74	1							
Color	0.85	0.92	1						
TU	0.64	0.83	0.79	1					
COND.	0.59	0.74	0.81	0.85	1				
pH	0.07	0.12	-0.07	0.20	-0.20	1			
TOD	0.93	0.85	0.91	0.76	0.80	-0.08	1		
TOC	0.92	0.74	0.88	0.57	0.69	-0.23	0.95	1	
UV₂₅₄	0.91	0.90	0.96	0.81	0.83	-0.08	0.98	0.94	1

In this study, there were no significant correlation between THMFP vs pH (7%) and THMFP vs Conductivity (59 %). This was due to small ranging in pH and conductivity among samples.

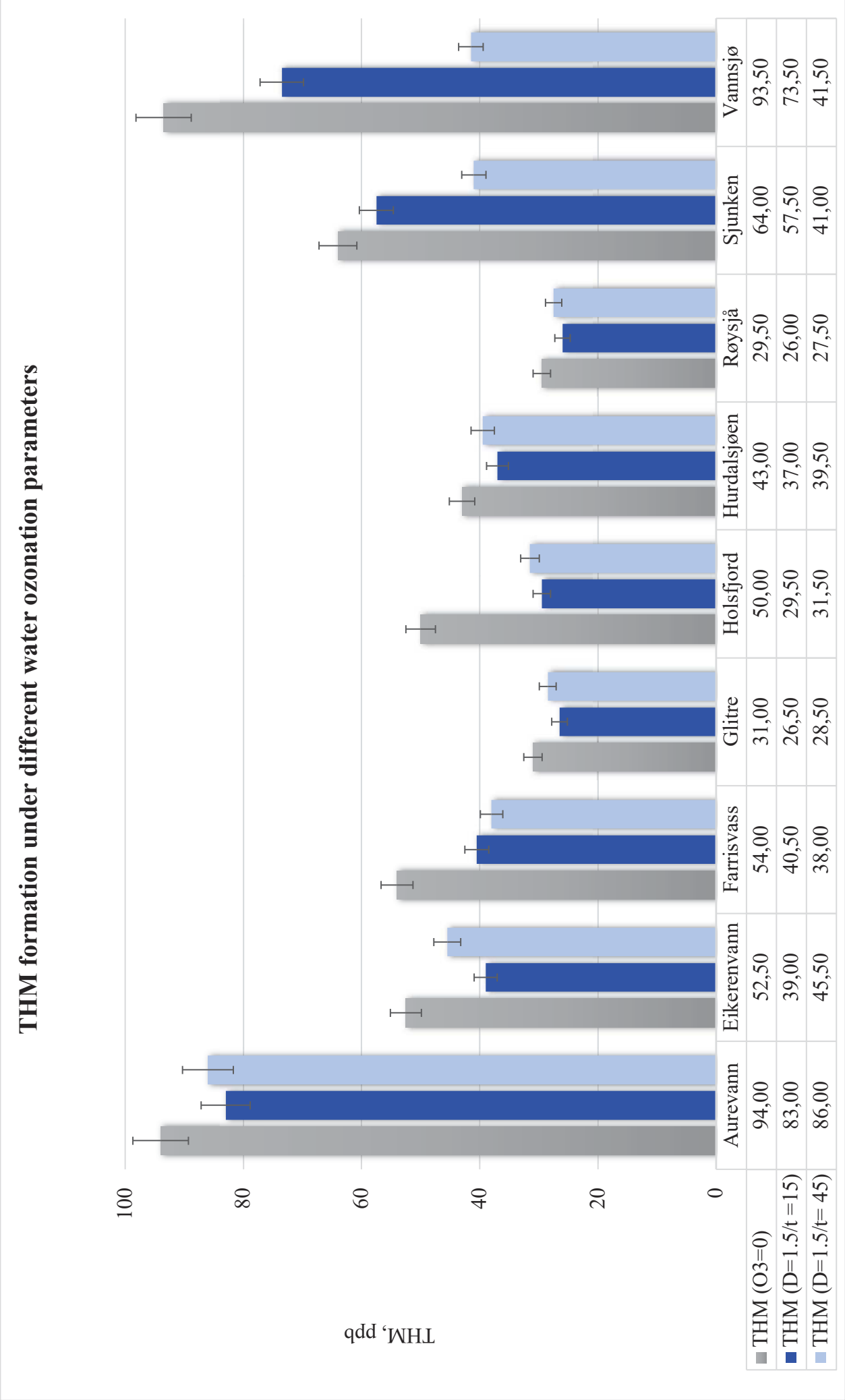
4.4 Ozonation experiments

Ozonation experiments were performed using two ozone dosages 1.5 & 3.0 mg-O₃/l and two contact times 10 & 45 min respectively. After the ozonation water samples were treated with chlorine 2 mg/l. The conducting ozonation experiments helps to evaluate the effect of ozone on THMs formation. The detailed description of Materials and Methods can be found in Chapter 3. The disinfection processes were occurred under same temperature 14±2 °C.

4.4.1 Influence of ozone dose and contact time on THMs formation.

For each water sample, ozone dose and contact time were performed two experiments to have average values and include standard deviation. On the Figure 26 the achieved data from the ozonation experiments can be observed.

Figure 26 - THMFP vs low ozone dose and different contact time



Changes in water quality after the ozonation were investigated through THMs determination. The grey columns (first) show THMFP for raw water without ozonation applying, under the same chlorine dosage 2 mg-Cl/l. Blue column characterizes THMFP after applied ozone dose 1.5 mg/l and contact time before the chlorination – 15 minutes. As can be seen, the use of ozone with dose 1.5 mg/l during short contact time tends to reduce THMFP for all waters. This reduction ranging from 10 to 40 %, depending on the water quality parameters (the highest THMs reduction belongs to Holsfjord; the lowest to Sjunken). This result concurs well with results described by (Wang, Ruan, et al., 2014) where the significant decrease in chloroform formation was achieved by applied ozonation.

As we can see, the increasing the ozone contact time from 15 min to 45 min under constant ozone dose 1.5 mg/l has different effect on investigated water samples. Under described conditions, the THMs formation increased for Aurevann, Eikervann, Glitre, Holsfjord, Hurdalsjøen and Røysjø, in the range 3 - 16% in comparison to contact time 15 min. This fact can be explained by assuming that NOM present in current waters may contain some functional groups which are reactive to ozone and chlorine within short time. With increasing of ozone contact time, the formation of hydroxyl radicals can be occurred, which may increase chlorine reactivity together with THMs formation ($\text{H}_2\text{O} + \text{O}_3 \rightarrow \text{O}_2 + 2 \text{HO}\bullet$; $\text{DOC} + \text{HO}\bullet \rightarrow \text{DOC radical}$).

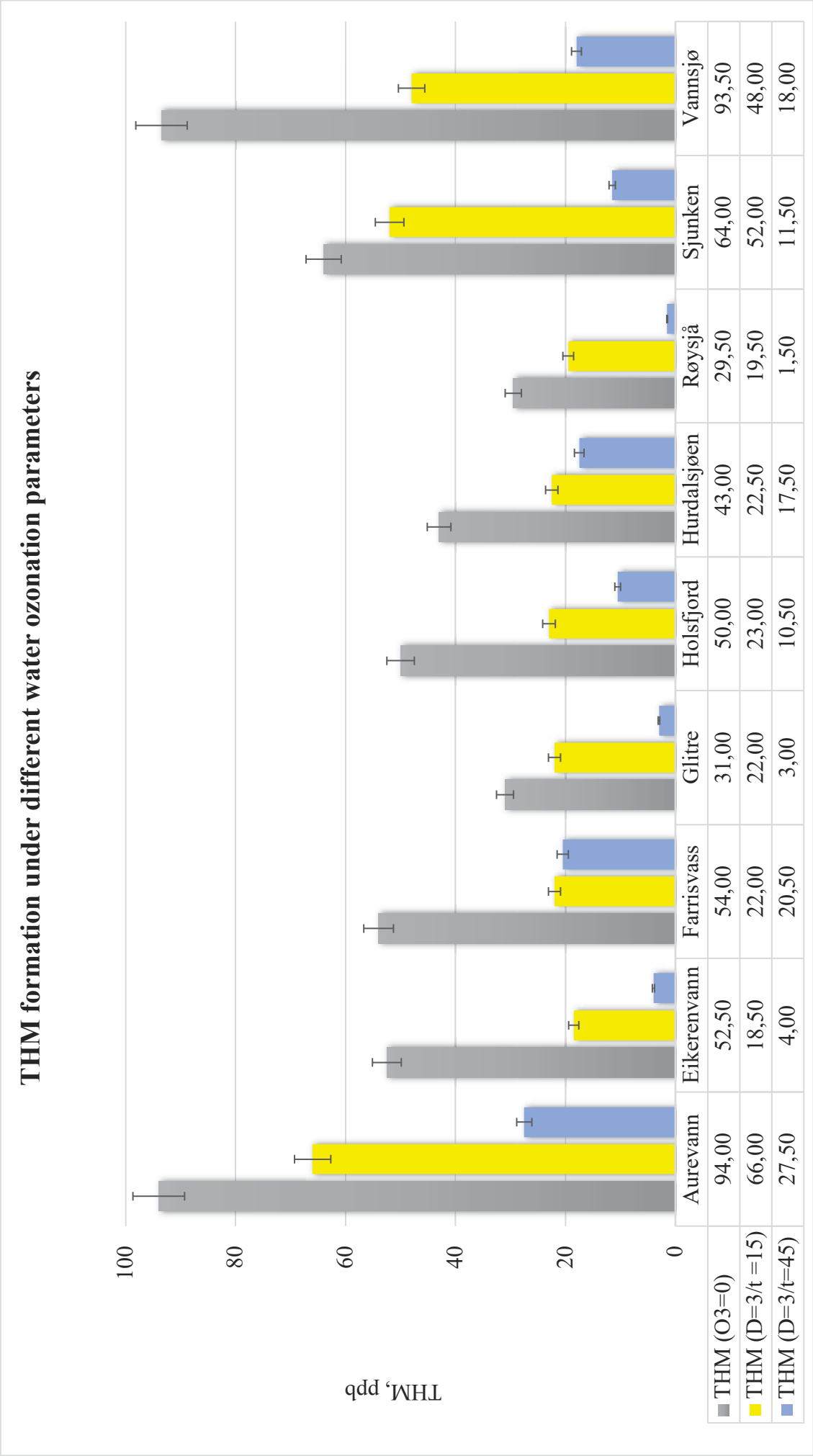
However, at the same time, THMs formation decreased for Farrisvass, Sjunken and Vannsjø. It can be explained by raw water quality parameters, especially organic compounds. These waters may have functional groups of NOM, which easily oxidized by ozonation within longer time.

Thus, the addition of ozone decreased formation of THMs as chloroform in ppb. The increasing of ozone contact time may tend to THMs formation increase for some waters, which are insignificant, compared to THMs formation without ozonation. The achieved variation of THMs for source water samples under different conditions is helpful in a creation of reliable THMs predictive model.

Additionally, the doubled ozone dose - 3 mg/l was applied under same conditions for all water samples to see the change in THMs formation.

On the Figure 27, we can see the difference in THMs formation with ozone dose 3 mg/l and contact time 15 & 45 minutes respectively, compared to THMs formation without ozonation.

Figure 27 - THMFP vs high ozone dose and different contact time



As can be seen from Figure 27, the injection of ozone dose 3 mg/l leads to THMs formation decrease by 18 – 65 %. A possible explanation for this might be related to TOC values of raw waters and high ozone dose. All raw waters have TOC in a range 2.3 – 6.3 mg/l, which is typical for good quality source waters. Injected ozone dose 3 mg/l can easily oxidizes and breaks all present organic compounds in the water. Generally, after ozonation under high ozone dose, no more organics which are able to react with followed chlorine and form THMs. Increasing of the contact time under high ozone dose has the opposite effect in some cases in comparison to low ozone dose -1.5 mg/l. We can see from the figure above, that the THMs reduction goes drastically down with longer contact time; and it has reached 95 % in the case of Røysjå water.

These findings suggest that in general the addition of ozone decreased formation of THMs with subsequent chlorination. Increasing of ozone dosage tended to decrease THMs formation further. The extended ozonation contact time has different effect on waters under applying low ozone dose, and greatly decrease THMs formation under high ozone dose. According to (Wang, Ruan, et al., 2014) the chloroform decreasing can be achieved by ozonation, at the same time the increase of ozone dose helps to reduce chloroform further, which fits well with our findings.

4.4.2 pH change

The raw water pH value greatly influences on decay of ozone in water. It decreases in acidic environment and increases in alkaline environment. The ozone decomposition occurs in the first 15 – 25 min at pH range from 7 to 10.

It is interesting to note that for all nine waters of this study the decreasing of pH was observed after the ozonation step for all water samples. It seems possible that these results are due to the accumulation of hydrogen ions in the reaction mixture in accordance with the equations (Chapter 1.6). After the applied chlorination, the pH was decreased also due to forming hypochlorous acid (HOCl).

4.4.3 UV₂₅₄ change

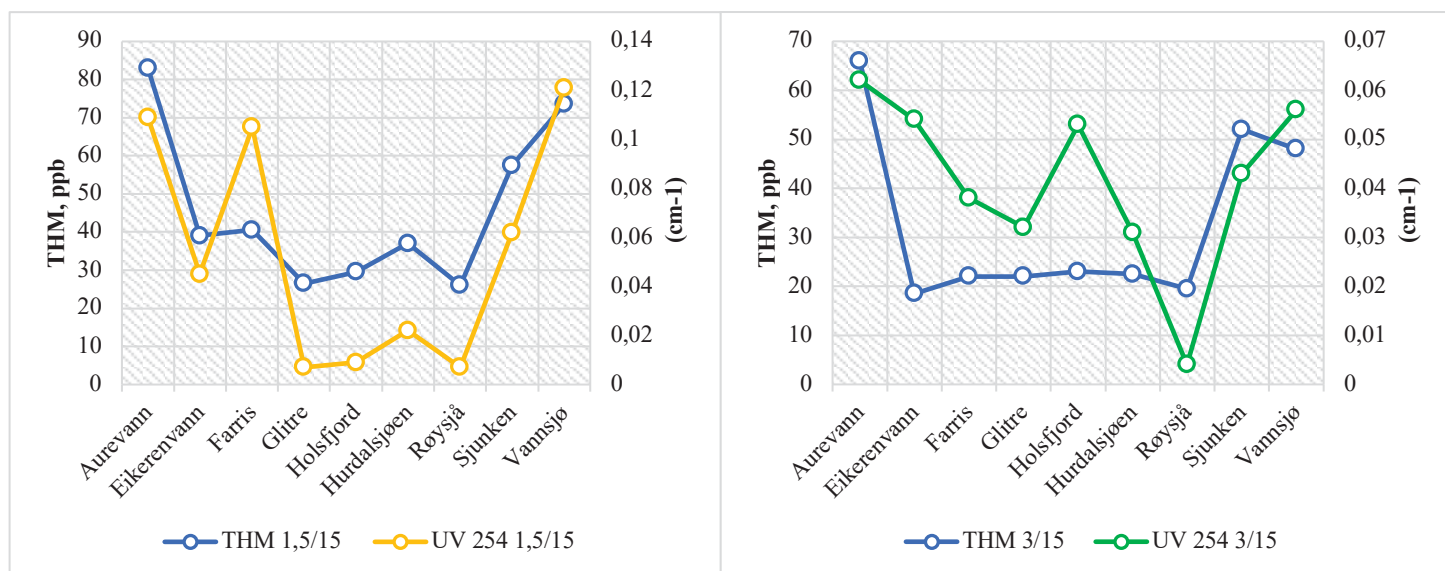
In this research, the UV₂₅₄ was mainly decreased after application different ozone doses with followed chlorination. This fact can indicate about the organic concentration decreasing due to breaking bonds and its oxidation by disinfectants. Table 12 represents UV₂₅₄ data under the dosage 1.5 mg/l and contact time 15 min.

Table 12 – UV 254 under different ozone dose

WATER SOURCE	UV 254 raw	UV 254 O ₃ &Cl ₂ D(1.5)/t(15)	UV 254 O ₃ &Cl ₂ D(3.0)/t(15)
Aurevann	0.301	0.109	0.062
Eikerenvann	0.102	0.045	0.054
Farris	0.235	0.105	0.038
Glitre	0.105	0.007	0.032
Holsfjord	0.121	0.090	0.053
Hurdalsjøen	0.131	0.022	0.031
Røysjå	0.031	0.007	0.004
Sjunken	0.271	0.062	0.043
Vannsjø	0.341	0.121	0.056

* - This table includes average data from duplicate results

As we can see from results presented in Table 12, the ozone dose increasing leads to UV 254 decrease, compare to UV254 in raw water samples. However, the Glitre and Eikerenvann do not support the current tendency. There are several possible explanations for this result. One of the reason could be the formation of other DBPs or presence of ozone radicals in water (Hansen, Spiliotopoulou, et al., 2016). The better understanding of the UV 254 changes in the both ozonated (different dose and contact time) and chlorinated waters, we can get from Figure 28.



a)

b)

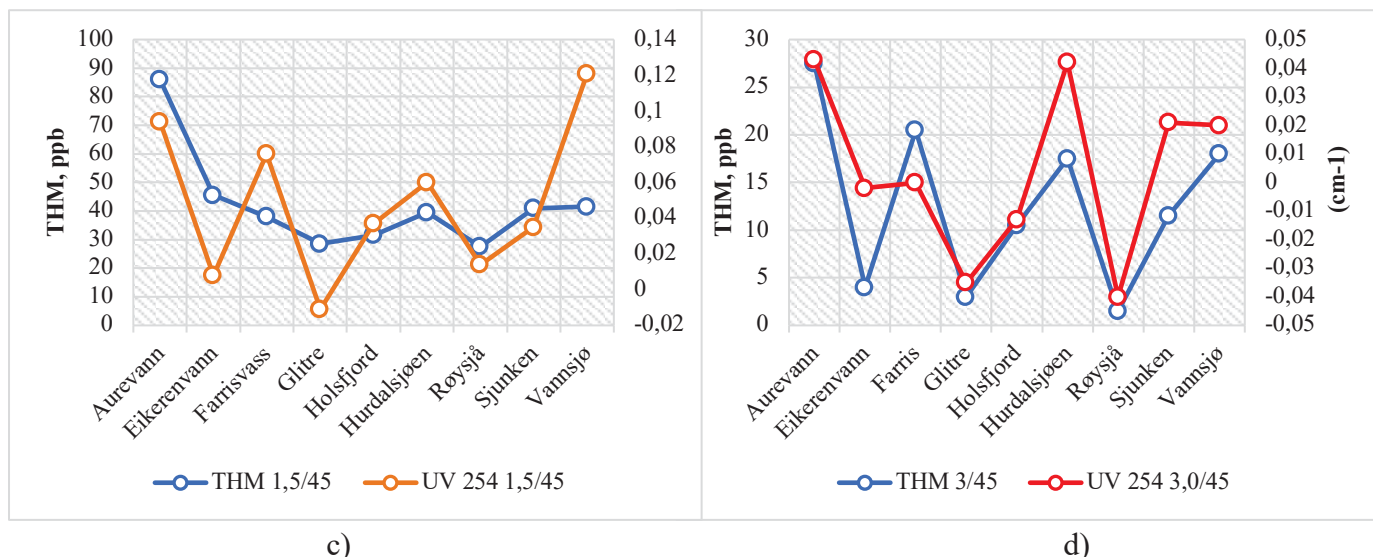


Figure 28 – The THM VS UV254 correlation: a) Ozone dose 1.5 mg/l & contact time 15 min; b) Ozone dose 3 mg/l & contact time 15 min; c) Ozone dose 1.5 mg/l & contact time 45 min; d) Ozone dose 3 mg/l & contact time 45 min.

From the figure 28 (a-d), we can see correlation between UV 254 and THMFp under different ozone doses and contact time. The Farris water tends to form high UV 254 in case of applying low ozone dose with same contact time. Such tendency can be explained presence of some inorganic compounds or groups, which don not effect on THMs formation, however possibly can form other DBPs.

The UV 254 for all experiments together with full absorbance graphs are presented in Appendix.

4.5 Prediction models

Many DWTPs have some problems related to DBPs formation and controlling. Nowadays, there are various water quality analysis, which help to estimate further DBPs formation. However, big number of water utilities do not have possibility to measure advanced parameters like TOD, TOC and asses SUVA values. Moreover, the disinfection type and parameters can be different. That is why, in our research, we have created three prediction models which are directly related to research aims:

1. Predictive model includes parameters, which can be easily measured at any DWTPs: UV 254, pH, conductivity, colour and turbidity;
2. Predictive model includes simple parameters (UV254, pH, conductivity, colour and turbidity) together with advanced parameters (TOC and TOD);
3. Predictive model includes all parameters together with different ozonation conditions (UV254, pH, conductivity, colour and turbidity, TOC, TOD, O₃ dose, O₃ contact time).

To assess THMs formation under different water quality indicators and ozonation parameters, the Unscrambler software was used. Each water quality parameter and experiment were performed twice to calculate average values. During predictive model creation in Unscrambler, we have used one value for model validation and second value for model calibration.

4.5.1 PCA of water quality

In this research, in advance to predictive models, The Principle Component Analysis was done for understanding dependences and relations between water quality indicators and water sources.

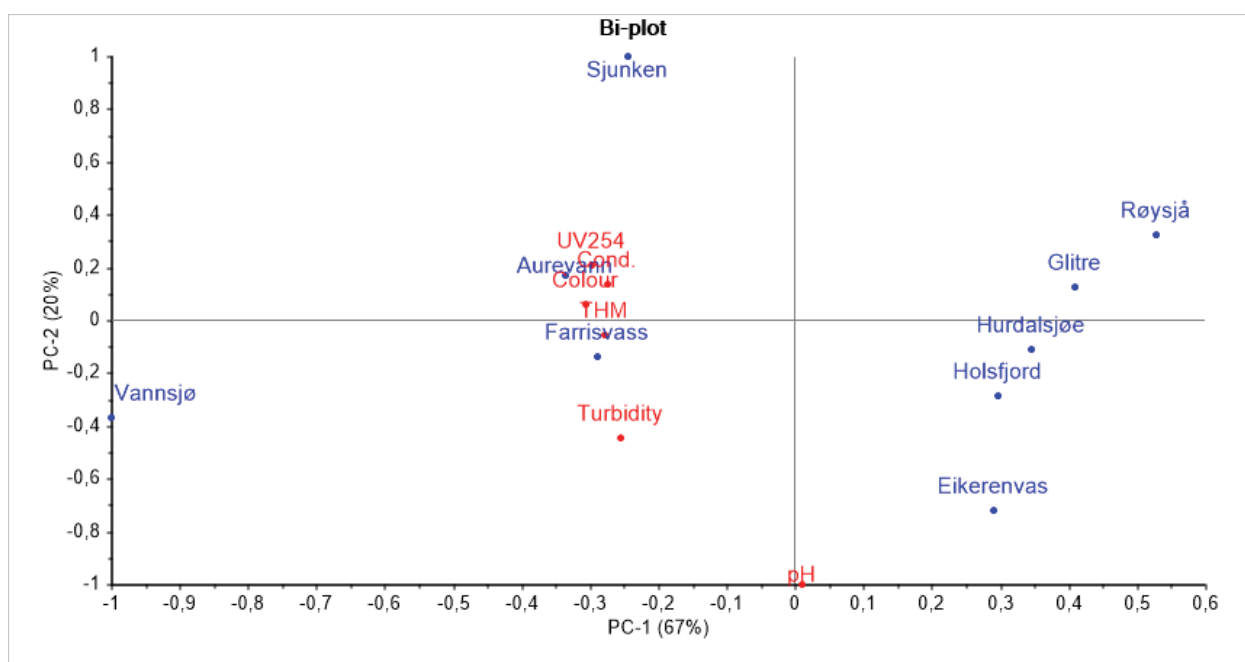


Figure 29 - Bi-plot of first two principal components

From the Bi-plot graph, we can see that there are two main clusters. The first cluster includes Glitre, Røysjø, Hurdalsjøen, Holsfjord and Eikernvas waters, the second cluster includes Aurevann, Farissvann. The cluster formation may indicate about similar water quality. The Sjunken and Vansjø have different quality, which is differ from others.

4.5.2 Predict model for simple water quality parameters

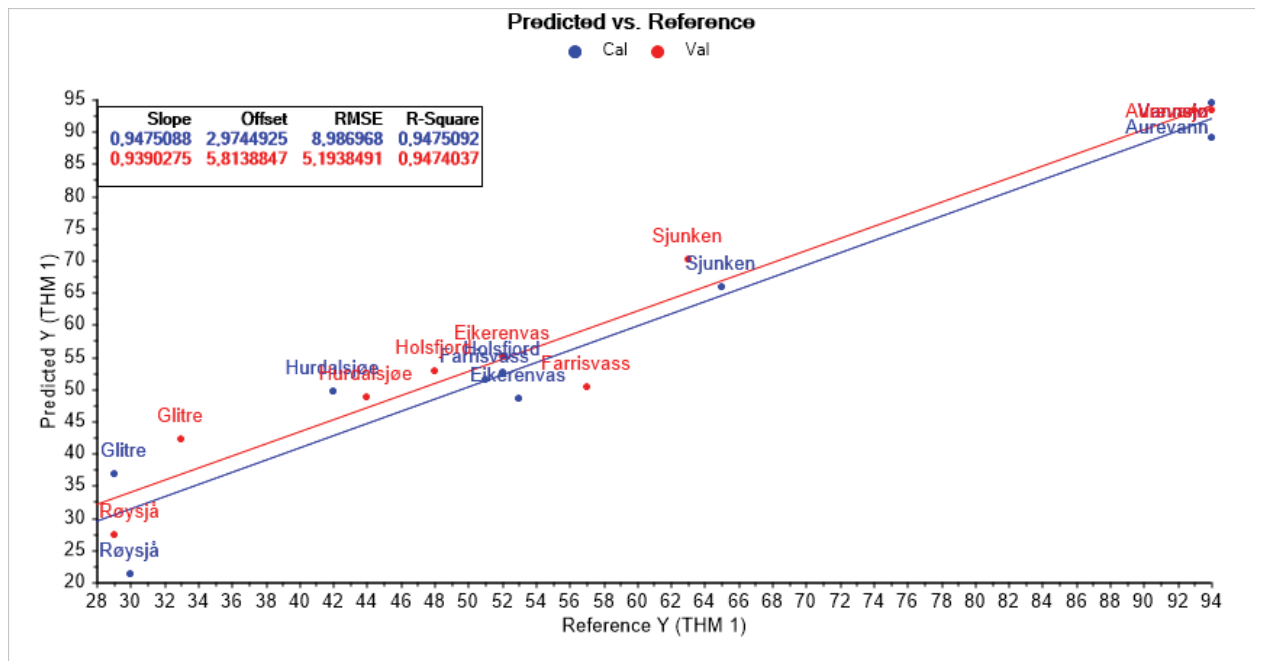


Figure 30 - Multiple Linear Regression (MLR) for simple water quality parameters

Figure 30 shows observed THMs formation based on water quality variable and predicted THMs formation with 95 % confidence intervals. Some THMs observations are outside of the confidence intervals, which is to be expected. It can be seen that the data points are spread out around the lines which is an indication of model's ability to predict THMs formation with reasonable precision based on simple water quality parameters.

From these data, the following multiple linear regression equations were formulated for THMs prediction. This equation includes easily-measured indicators in the raw water:

$$\text{THMFP} = -142.66 + 21.90[\text{pH}] + 4.97[\text{Turbidity}] - 2.02[\text{Colour}] - 0.05[\text{Conductivity}] + 626.24[\text{UV254}]$$

The MLR gotten in Unscrambler was compared with ANOVA and shows identical results.

4.5.3 Predict model for simple and advanced water quality parameters

Figure 31 shows observed THMs formation based on simple and advanced water quality variable and predicted with 97 % confidence intervals.

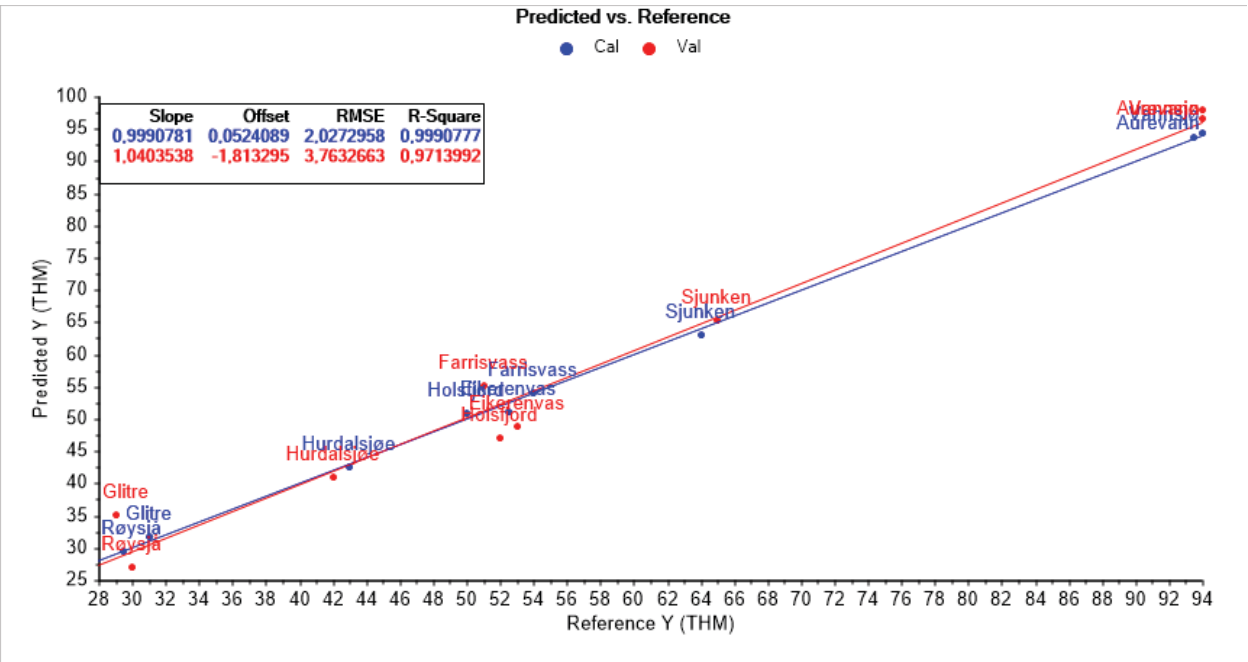


Figure 31 - Multiple Linear Regression (MLR) for simple and advanced water quality parameters

The residuals were plotted as a function of the predicted THMs values as illustrated in Figure 32. There is no obvious pattern in the residual plots for current model, which means all information in the data was utilize by model. Moreover, it can be seen from the graph that the residuals points are distributed above and below zero line, which indicates that the achieved variance is constant and does not depend on the THMs predicted value.

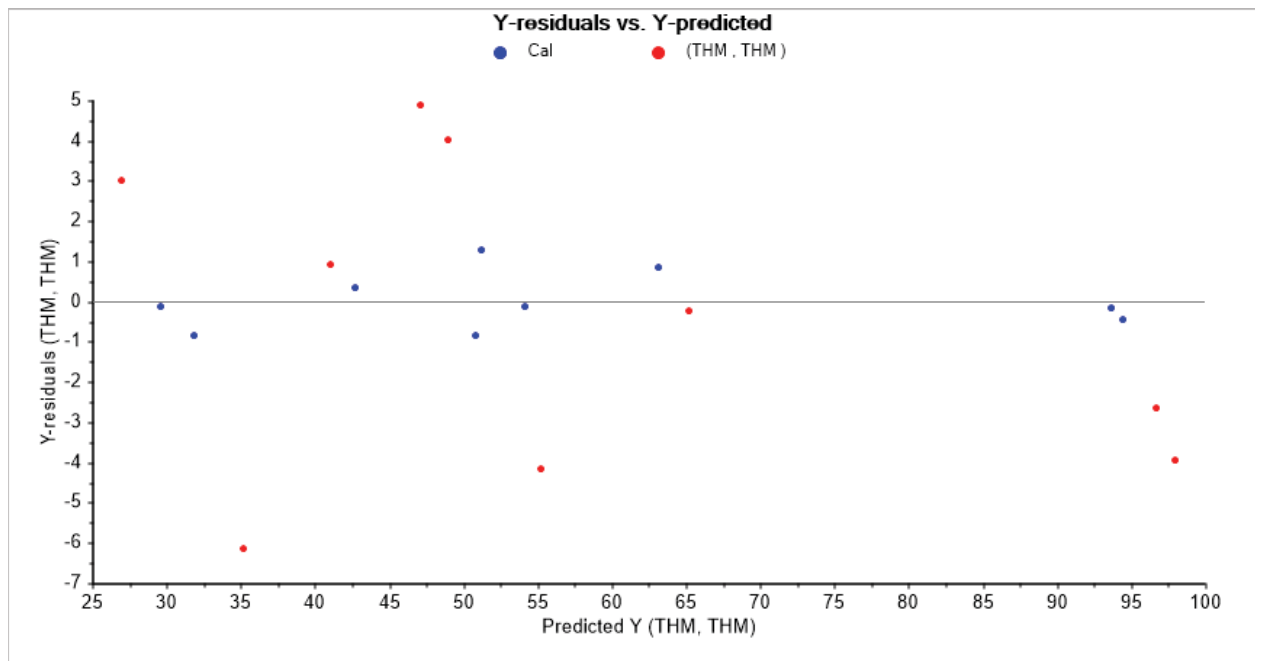


Figure 32 - Residuals versus predicted values for simple and advanced water quality parameters

From these data, the following multiple linear regression equations were formulated for THMs prediction. This equation includes easily-measured together with advanced indicators in the raw water:

$$\text{THMFP} = 38.94 + 7.28[\text{pH}] - 0.97[\text{TU}] + 1.27[\text{Colour}] - 0.48[\text{COND.}] + 14.19[\text{TOC}] + 10.08[\text{TOD}] - 12.94[\text{SUVA}]$$

Based on achieved results and equations, we can conclude that the TOC, TOD and UV 254 have the highest impact on THMs formation. The TU and pH have the lowest impact in the frame of our research. However, each water source has specific NOM origin and concentration, which can tend to form different DBPs besides the THMs. Thus, when dealing with THMs prediction, the raw water characteristic should be evaluated. The illustrated demonstration of percentage constituent of parameters in THMFP can be found in Appendix.

4.5.4 Predicting model for ozonation

Around 90 experiments with ozone application were conducted for current model creation.

Figure 33 shows observed THMs formation based on simple and advanced water quality variable together with ozonation parameters and predicted with 81 % confidence intervals. This value is lower than two previous models describes, but this fact can be explained by bigger number of variables.

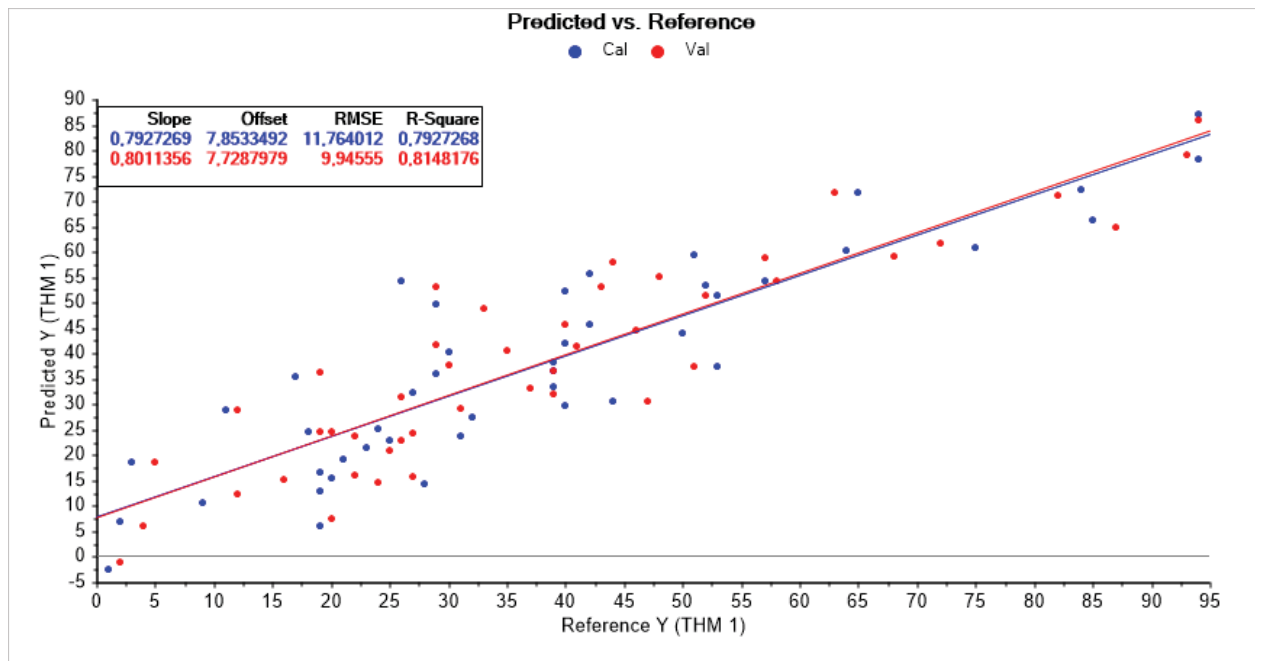


Figure 33 - Multiple Linear Regression (MLR) including ozonation parameters

The figure 34 demonstrates residuals from data with ozonation. It can be seen from the figure that the residuals points are distributed above and below zero line without any tendency, which indicates that the present variance promote the validity of the models in predicting THMs formation concentration level in the source water.

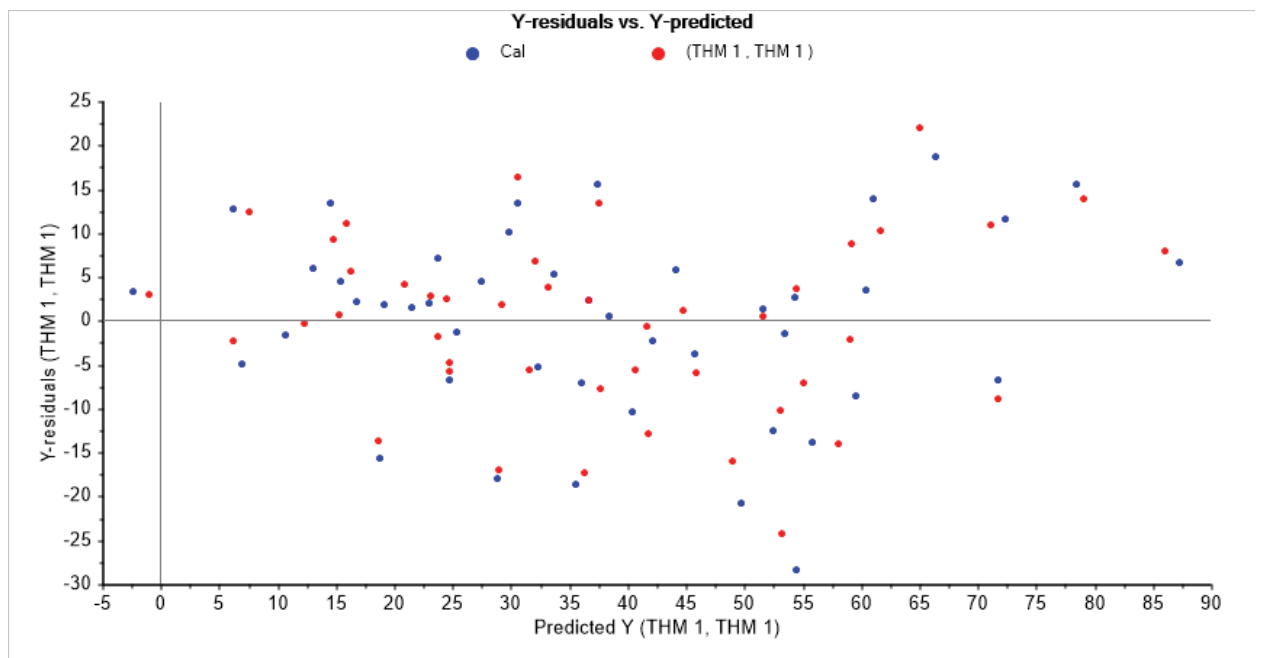


Figure 34 - Residuals versus predicted values for simple and advanced water quality parameters together with ozonation conditions

From these data, the following multiple linear regression equations were formulated for THMs prediction. This equation includes easily-and advanced water quality indicators in the raw water together with ozonation parameters:

$$\text{THMFP} = 65.04 - 7.93[\text{Ozonedose}] - 0.20[\text{Contact.time}] - 2.07[\text{pH}] - 1.08[\text{TU}] + 0.44[\text{Col}] - 0.27[\text{Conductivity}] + 3.32[\text{TOD}] - 2.49[\text{SUVA}]$$

Based on observation through the model creation which involved ozonation parameters, the inversely proportional dependence between THMFP and ozone dose was observed.

CONCLUSION

This research studied the THMFP for nine water sources located in Norway after the combined disinfection ($\text{Cl} + \text{O}_3$). This study has investigated the association between water quality parameters and THMFP. Additionally, the test with imitation of possible worst scenarios (THMFP test) was made. Overall, the conducted experiments with ozone application showed the reduction of THMs in the water. Therefore, the treatment consequence taken from the Coquitlam DWTP has proved the efficiency of DW treatment and reduction of THMs. Coquitlam DWTP has the average THMs concentration in treated water 33 ppb; For Norwegian waters in our research, this value equally to 37 ppb. Thus, we can conclude, that Norwegian and Canadian lakes have consimilar water qualities; and the combined ozonation ($\text{O}_3 + \text{Cl}$) can be a potentially good solutions for Norwegian DWTPs in order to control and reduce DBPs.

Based on the experimental results of this study the followed conclusion can be made:

1. The performed THMFP test with incubation time 7 days, temperature 12 °C and two chlorine doses 2 & 6 mg- Cl_2 /l showed that water samples tend to form THMs concentrations at zero time, which are lower of the existing guidelines (THMs =100 ppb/l). However, within the time the THMs concentrations increases in 3 - 5 times for some waters. Such a significant increase can be explained by the presence of some THMs precursors, which can quickly react with chlorine with continues formation of THMs species.
2. Turbidity, color, pH, conductivity, TOC, TOD, and UV 254 were measured for each water samples. The investigated water sources had different parameters, and THMs was also different. Based on it, the correlation between water quality parameters and THMFP for all water samples were investigated. Achieved results summarized, that there are strong correlations between THMFP and TOD (93%), TOC (92 %), and UV254 (91%) respectively.
3. The applied ozone dose and further its increasing leads to UV 254 decrease, compare to UV254 in raw water samples.
4. The addition of ozone decreased the formation of THMs with subsequent chlorination. Increasing ozone dosage tended to decrease THMs formation further. This reduction ranging from 10 to 40 % under low ozone dose and up to 95 % under high ozone dose, depending on the water quality parameters
5. The extended ozonation contact time from 15 minutes to 45 minutes has a different effect on waters under applying low ozone dose, and significantly decrease THMs formation under high ozone dose.
6. The best water quality demonstrates Røysjø water source; the most polluted is Vannsjø water based on measured water quality indicators.

7. In our research, based on results from conducted experiments, we have created three prediction models which are directly related to research aims: 1) Predictive model for easily measured analysis; 2) Predictive model for the combination of simple parameters and advanced parameters; 3) Predictive for all investigated water quality parameters together with different ozonation conditions (dose and contact time).

RECOMMENDATION FOR FURTHER RESEARCH

Based on the results of this study and literature review, the followings are recommended for further study:

1. Further research can be conducted to evaluate the effect of the temperature and seasonal variation on the stability of DBPs for the same list of water sources.
2. Additional effort should be placed on performing more extensive NOM analysis with their detailed fraction identification.
3. The concentration of Br and I can also be measured for the analyzing of their contribution to the DBPs formation.
4. Chromatographic separation (GS) or detection by mass spectrometry (MS) methods can be applied for the additional HAAs concentration measuring and the comparison with THM Plus method under same water quality conditions.
5. The pH range should be more extensive for a better pH/THMs correlation.
6. The experiment with additional sonication, as disinfection step, might be an interesting direction in this research.
7. The performing experiments with pre and post-ozonation or repeated ozonation are one of the most promising strategies for THMs reduction.
8. Some articles show that the water boiling process can reduce THMs by 90 -97%. The interesting idea is to use the current value of THMs for raw water and measure THMs before and after boiling under the same disinfection conditions.

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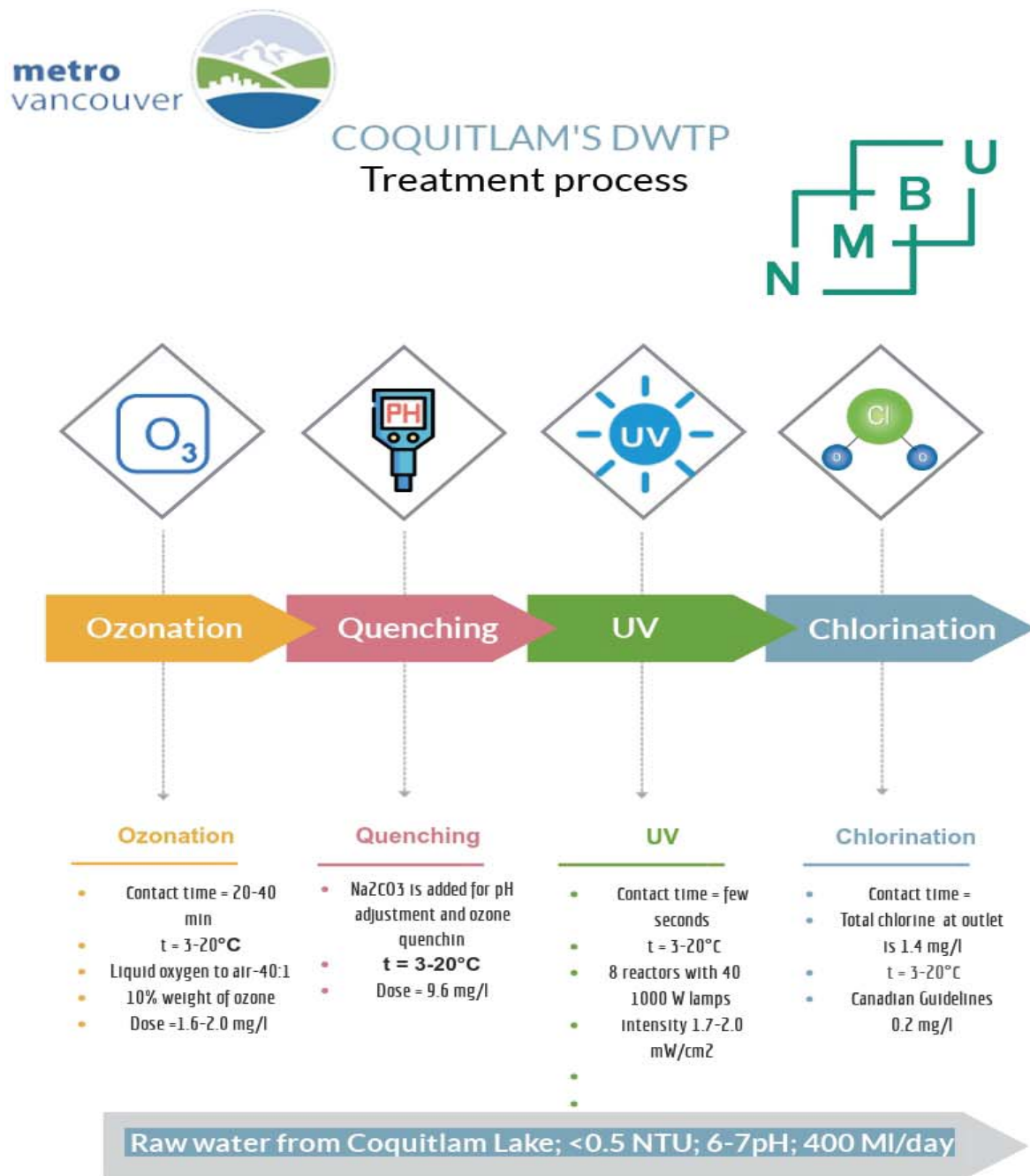
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APPENDIX

A. Treatment process at Coquitlam DWTP (Study case)

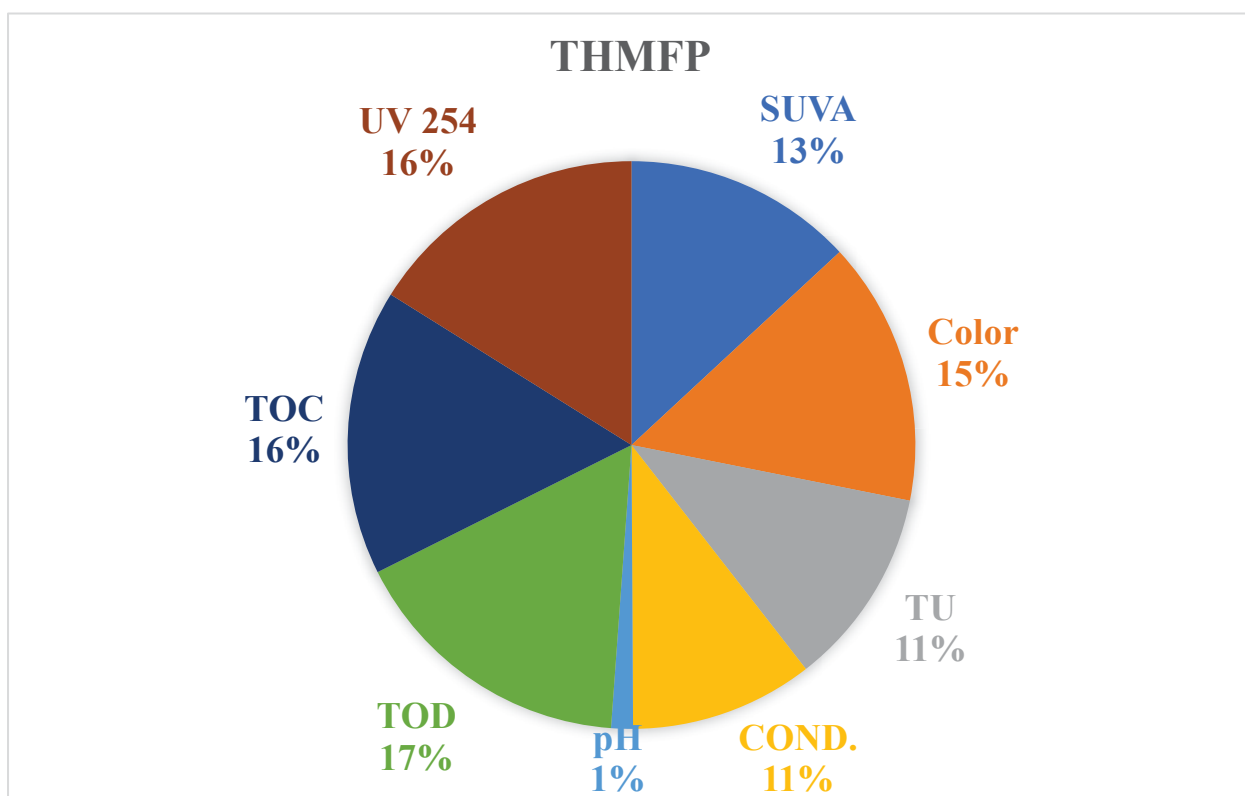


CREATED BY
Evelina Koltsova / NMBU

B. Experiments matrix

	Water/ Parameter	Aureva nn	Vanns jø	Røysj å	Farrisvan n	Eikeren vann	Glitre	Hurdalsj øen	Holsfjø rd	Sjunk en
1	Contact time/ O ₃ dose	10 min /1.5 mg-O ₃ /l	10 min /1.5 mg-O ₃ /l	10 min /1.5 mg-O ₃ /l	10 min /1.5 mg- O ₃ /l	10 min /1.5 mg- O ₃ /l	10 min /1.5 mg-O ₃ /l	10 min /1.5 mg- O ₃ /l	10 min /1.5 mg-O ₃ /l	10 min /1.5 mg-O ₃ /l
2		10 min /3.0 mg-O ₃ /l	10 min /3.0 mg-O ₃ /l	10 min /3.0 mg-O ₃ /l	10 min /3.0 mg- O ₃ /l	10 min /3.0 mg- O ₃ /l	10 min /3.0 mg-O ₃ /l	10 min /3.0 mg- O ₃ /l	10 min /3.0 mg-O ₃ /l	10 min /3.0 mg-O ₃ /l
3		45 min /1.5 mg-O ₃ /l	45 min /1.5 mg-O ₃ /l	45 min /1.5 mg-O ₃ /l	45 min /1.5 mg- O ₃ /l	45 min /1.5 mg- O ₃ /l	45 min /1.5 mg-O ₃ /l	45 min /1.5 mg- O ₃ /l	45 min /1.5 mg-O ₃ /l	45 min /1.5 mg-O ₃ /l
4		45 min /3.0 mg-O ₃ /l	45 min /3.0 mg-O ₃ /l	45 min /3.0 mg-O ₃ /l	45 min /3.0 mg- O ₃ /l	45 min /3.0 mg- O ₃ /l	45 min /3.0 mg-O ₃ /l	45 min /3.0 mg- O ₃ /l	45 min /3.0 mg-O ₃ /l	45 min /3.0 mg-O ₃ /l

C. The percentage constituent of parameters in THMFP

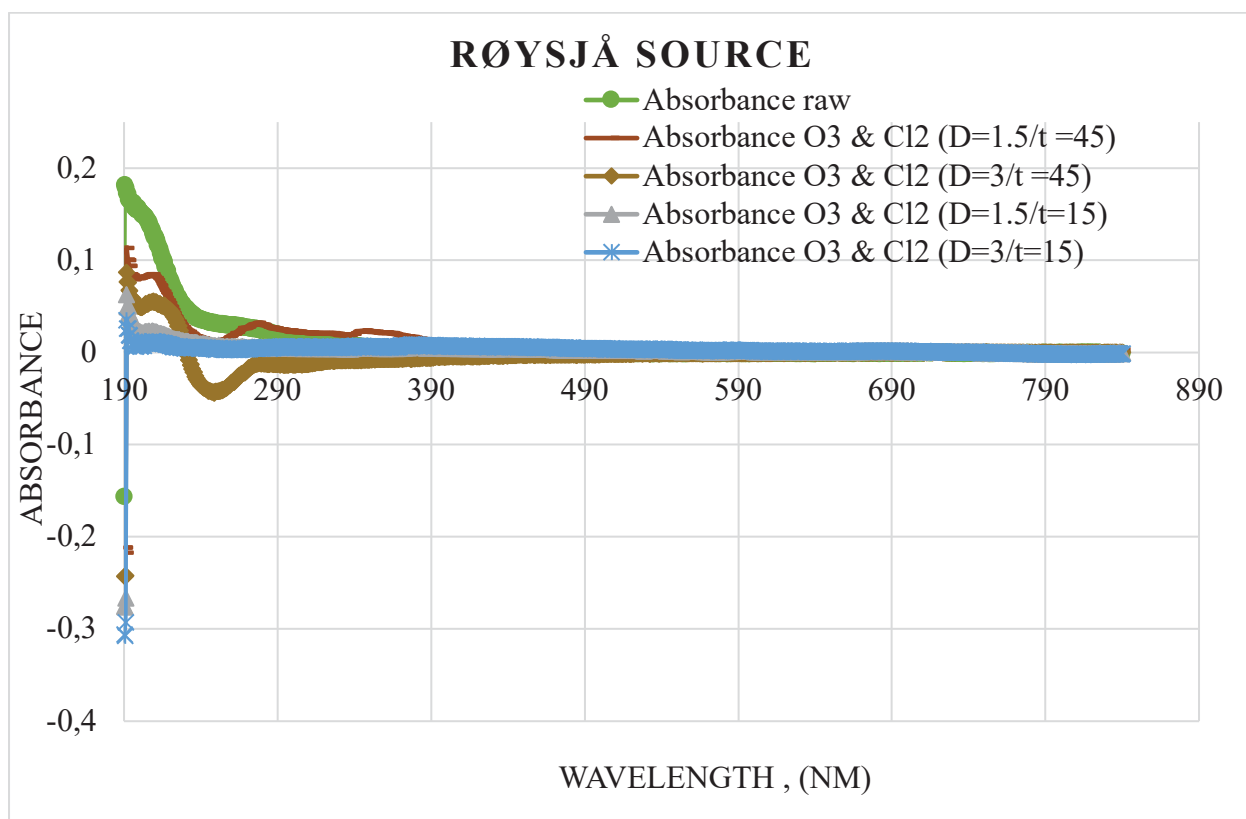
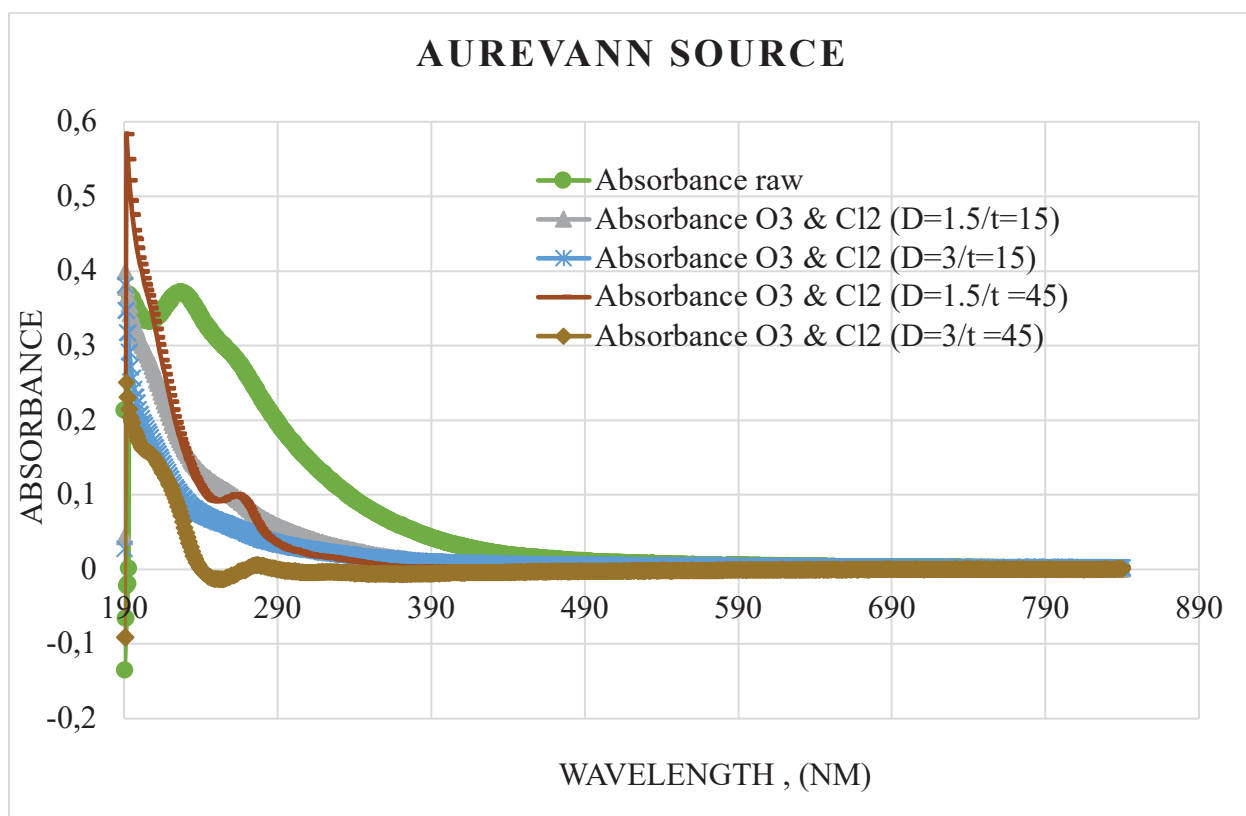


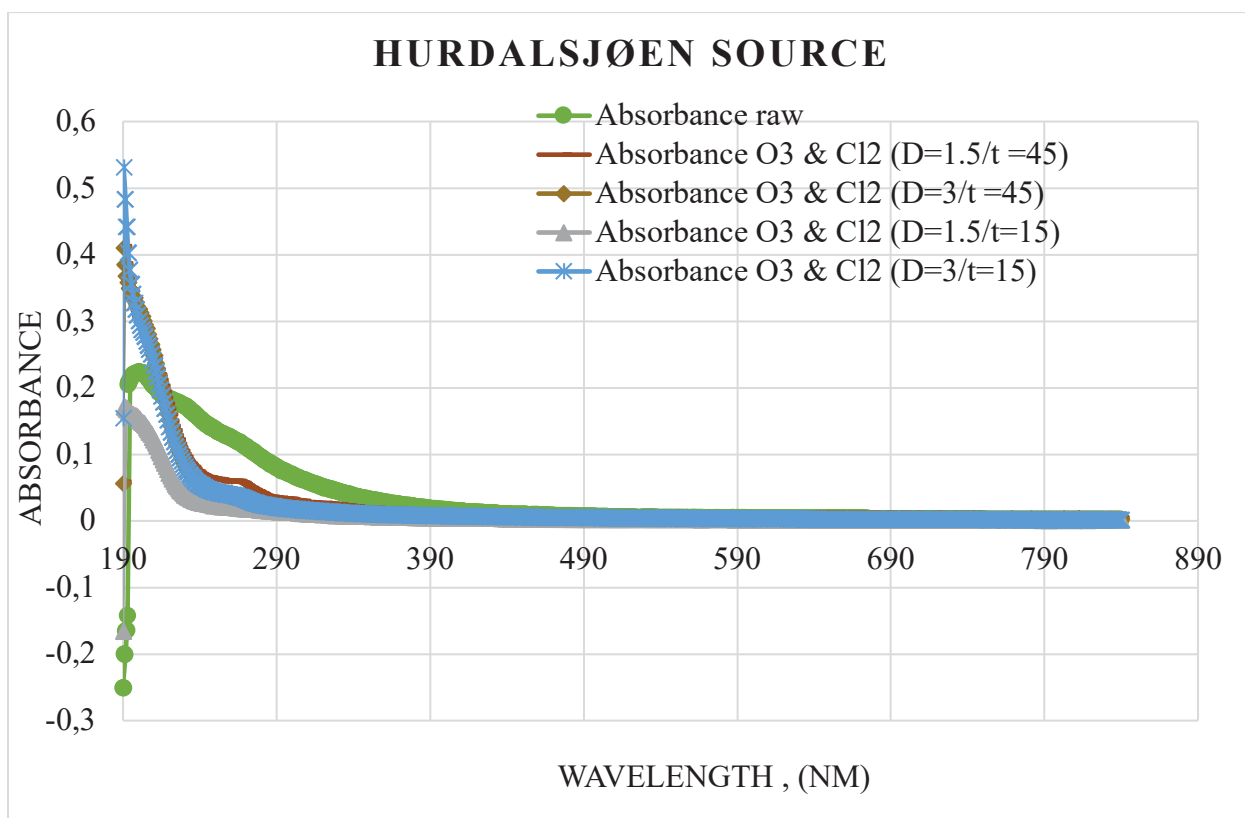
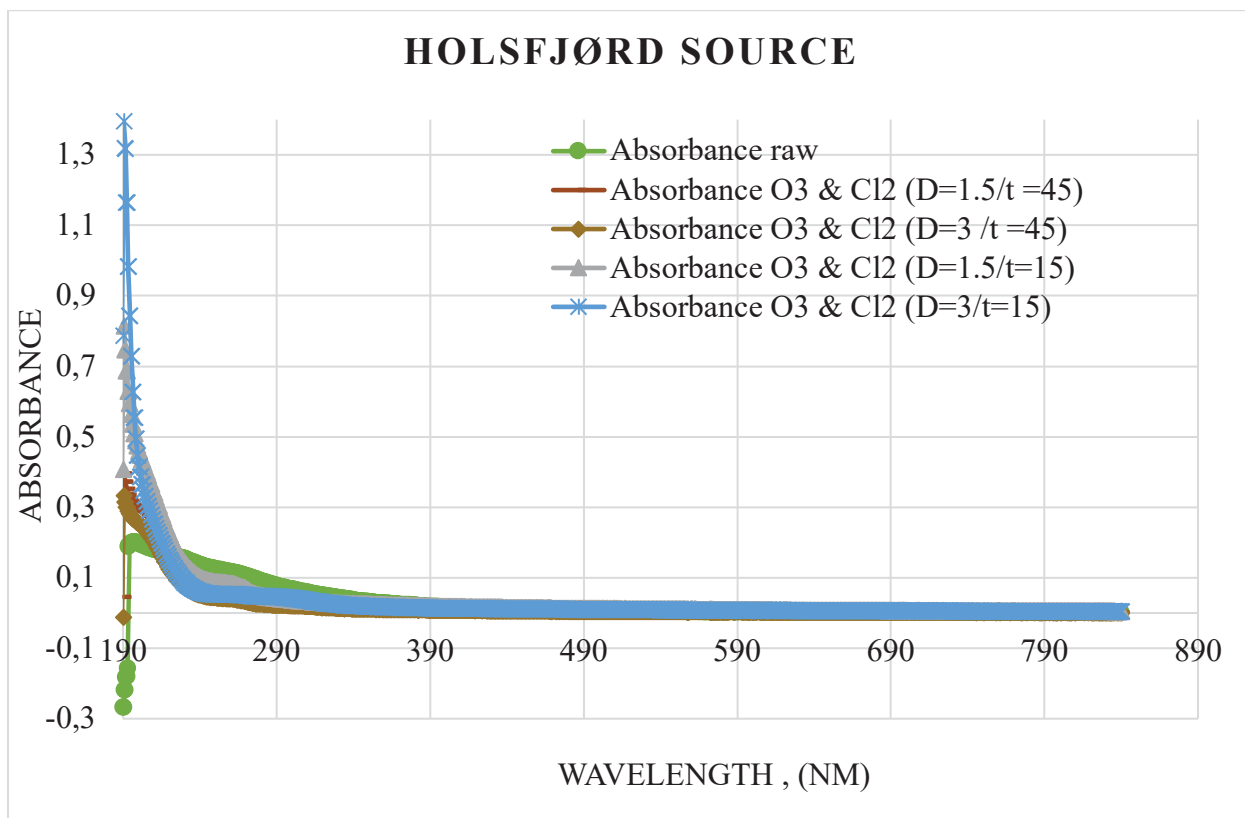
D. Absorbance for UV 254 and UV 272

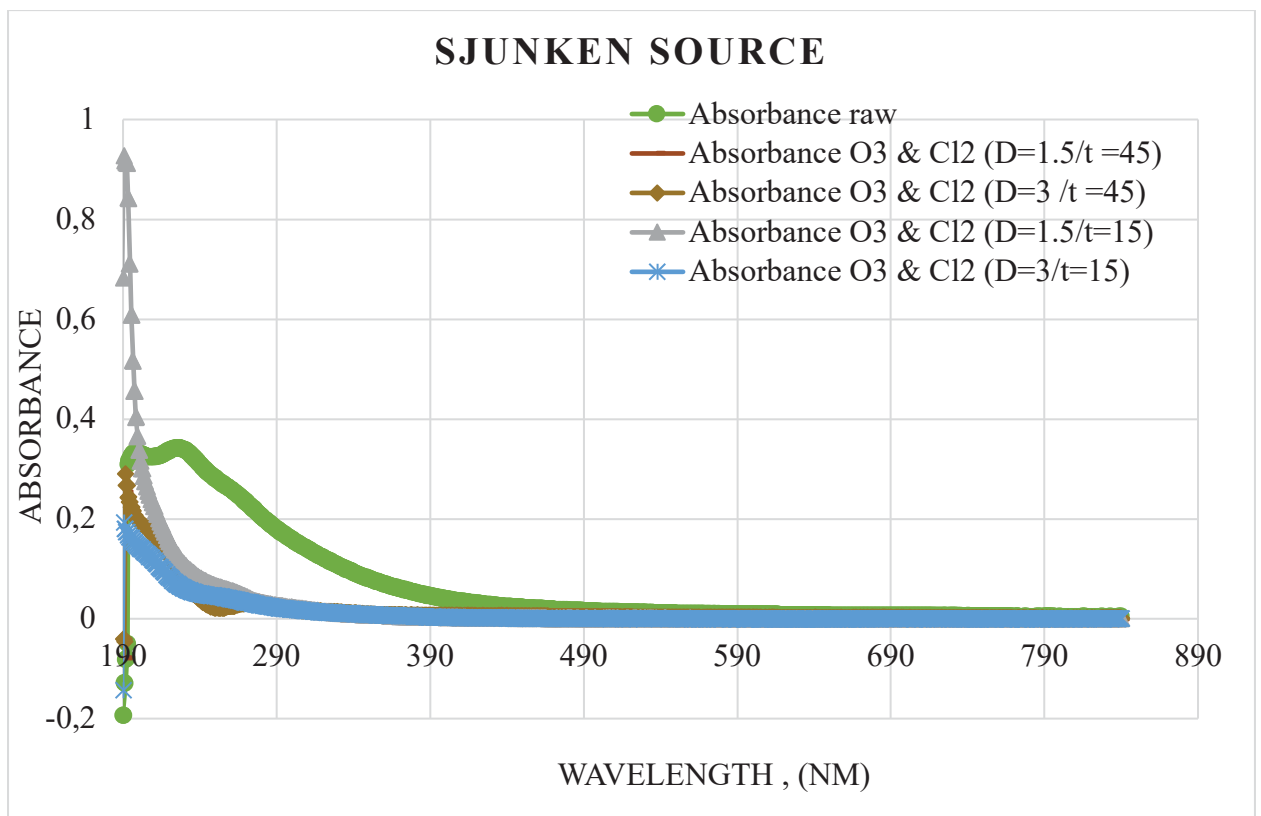
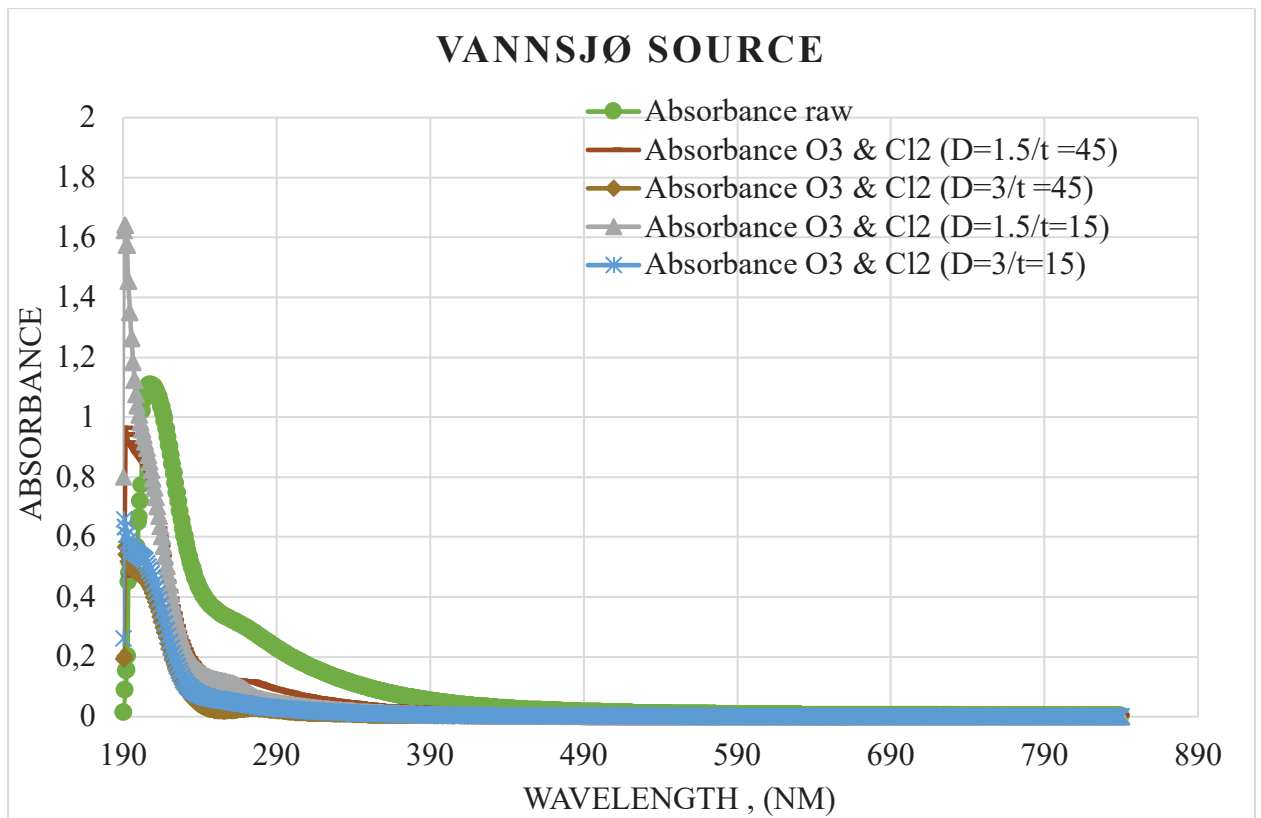
WATER SOURCE	Wavelength nm	Absorbance raw	Absorbance O_3 (C=1.5/ τ =15)	Absorbance O_3 & Cl_2 (C=1.5/ τ =15)	Absorbance O_3 (C=3/ τ =15)	Absorbance O_3 & Cl_2 (C=3/ τ =15)
Aurevann	254	0.301	0.136	0.109	0.062	0.062
	272	0.254	0.112	0.081	0.050	0.046
Eikerenvann	254	0.102	0.057	0.045	0.054	0.054
	272	0.085	0.046	0.033	0.047	0.045
Farris	254	0.235	0.109	0.125	0.061	0.038
	272	0.201	0.072	0.068	0.052	0.036
Glitre	254	0.105	0.029	0.007	0.034	0.032
	272	0.088	0.022	0.002	0.028	0.024
Holsfjord	254	0.121	0.118	0.090	0.042	0.053
	272	0.102	0.092	0.062	0.038	0.049
Hurdalsjøen	254	0.131	0.042	0.022	0.048	0.031
	272	0.107	0.033	0.018	0.036	0.027
Røysjå	254	0.031	0.020	0.007	0.019	0.004
	272	0.027	0.016	0.005	0.019	0.004
Sjunken	254	0.271	0.088	0.062	0.042	0.043
	272	0.227	0.071	0.040	0.029	0.032
Vannsjø	254	0.341	0.119	0.121	0.291	0.056
	272	0.291	0.097	0.078	0.210	0.040

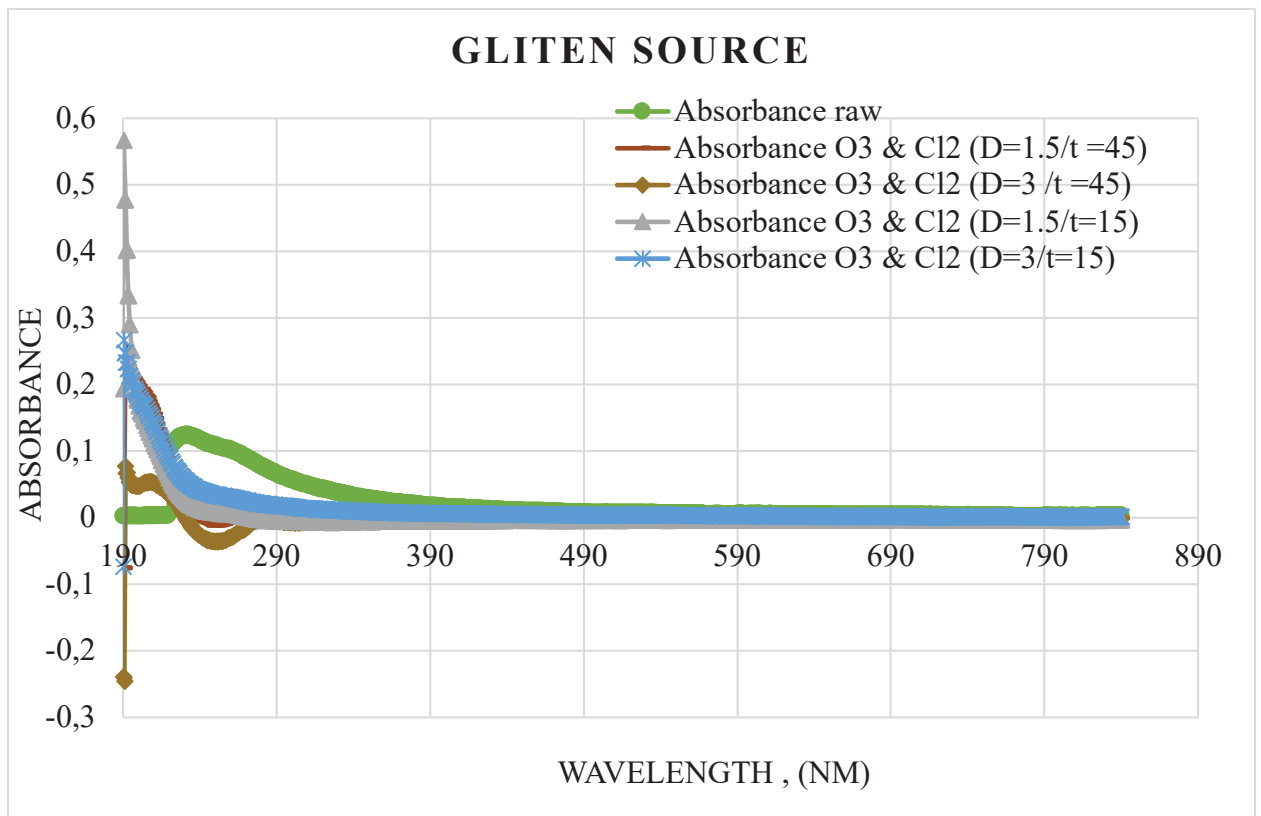
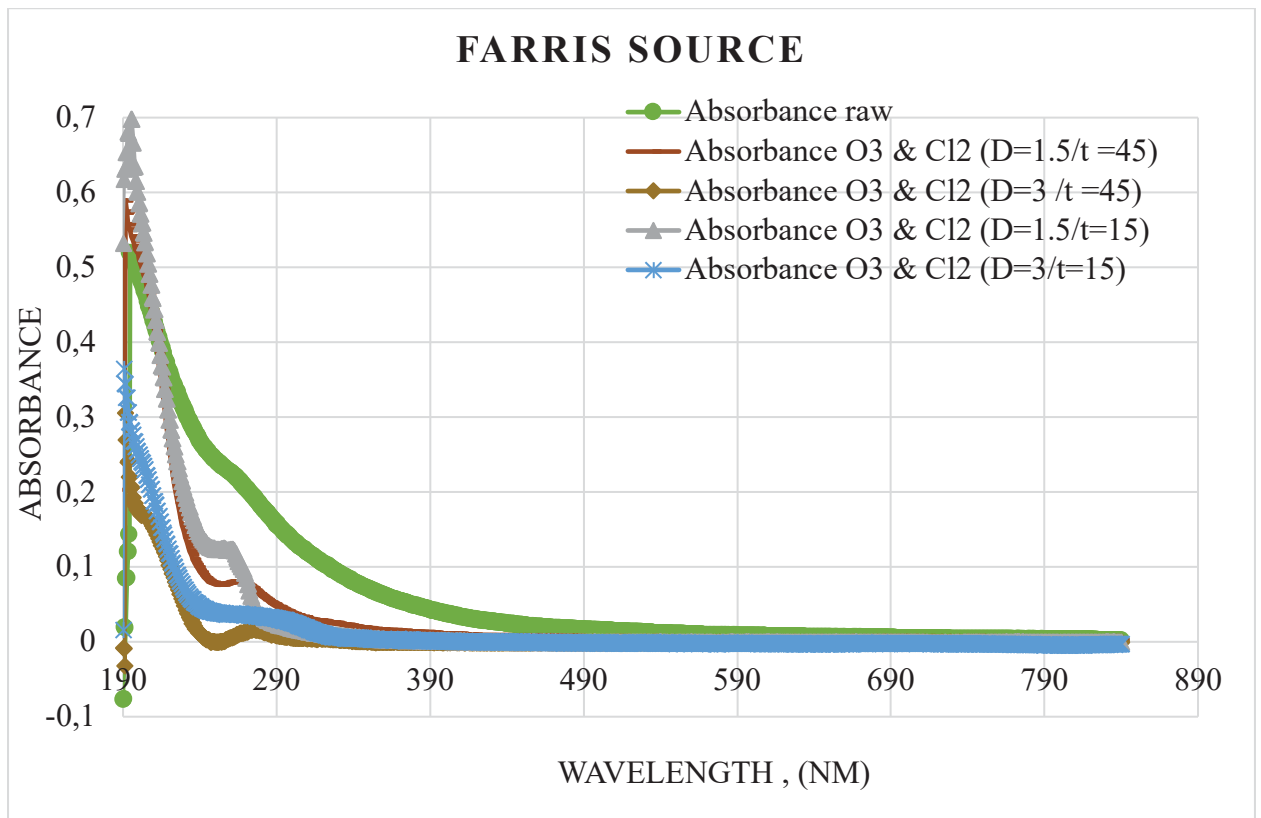
WATER SOURCE	Wavelength nm	Absorbance raw	Absorbance O_3 (C=1.5/ τ =45)	Absorbance O_3 & Cl_2 (C=1.5/ τ =45)	Absorbance O_3 (C=3/ τ =45)	Absorbance O_3 & Cl_2 (C=3/ τ =45)
Aurevann	254	0.301	0.056	0.094	-0.007	0.413
	272	0.254	0.063	0.075	0.012	0.003
Eikerenvann	254	0.102	-0.023	0.008	-0.023	-0.002
	272	0.085	-0.0006	0.024	0.002	0.016
Farris	254	0.235	0.072	0.076	-0.012	-0.0001
	272	0.201	0.077	0.074	0.010	0.016
Glitre	254	0.105	-0.017	-0.011	-0.039	-0.035
	272	0.088	0.005	0.006	-0.012	-0.010
Holsfjord	254	0.121	0.034	0.037	0.044	-0.013
	272	0.102	0.027	0.027	0.033	0.030
Hurdalsjøen	254	0.131	0.052	0.060	0.026	0.042
	272	0.107	0.043	0.049	0.020	0.030
Røysjå	254	0.031	-0.014	0.014	-0.030	-0.040
	272	0.027	0.009	0.030	-0.013	-0.016
Sjunken	254	0.271	0.040	0.035	0.006	0.021
	272	0.227	0.051	0.043	0.022	0.033
Vannsjø	254	0.341	0.087	0.121	0.029	0.020
	272	0.291	0.091	0.117	0.045	0.029

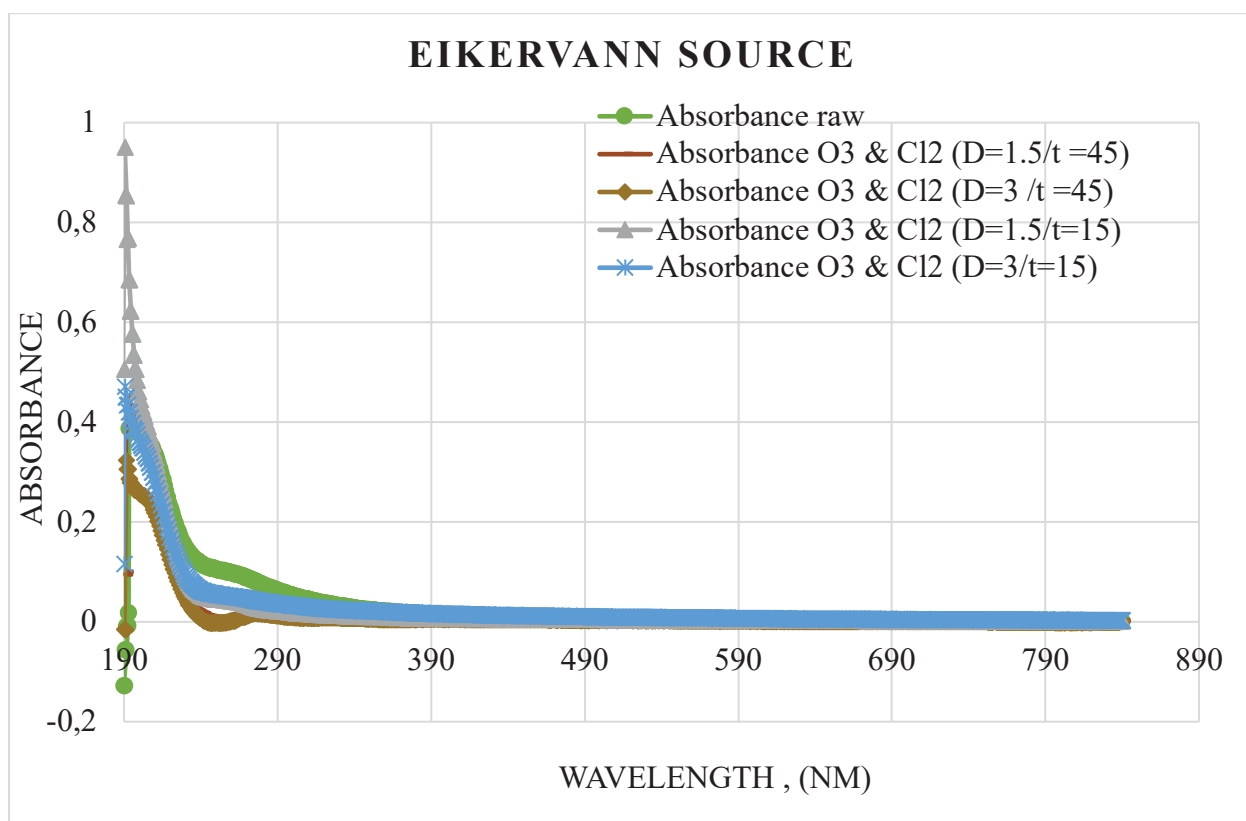
E. Absorbance of full spectrum (190 – 840 nm)













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