Biological Stability for Vacuum UV Advanced Oxidation Treatment of Surface Water

by

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The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, a thesis/dissertation entitled:

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Abstract

Vacuum UV (VUV) involving UV 185 nm has been extensively studied as a viable and robust advanced oxidation process (AOP) for drinking water purification. It is highly efficient for the removal of micro-pollutants including pesticides, herbicides, personal care products and cyanobacterial toxins. However, at the applied ultraviolet (UV) dose for micro-pollutant removal, the natural organic matter (NOM) present in surface water is not completely mineralized. The breakdown of NOM from larger molecular weight fractions leads to an increase in the smaller and more biodegradable molecular weight compounds. This may lead to increases in assimilable organic carbon (AOC) and disinfection by-product (DBP) precursors. An increase in AOC will result in reduced biological stability, triggering bacterial regrowth in the distribution system. Hence, it becomes important to study the impact of VUV AOP on biological stability of the treated water.

In this research, AOC and biodegradable dissolved organic carbon (BDOC) assessments were used to quantify changes in the bio-stability of water. Laboratory scale experiments were carried out in batch and continuous modes using two different setups. The batch setup involved a custom built collimated beam, containing an ozone generating low-pressure amalgam mercury lamp. This was used to study the kinetics of AOC formation during irradiation with 185 and 254 nm UV. Surface water from various sources across BC were used. The second setup consisted of a flow through reactor, equipped with similar VUV lamp, used to investigate the changes in water quality under different operating conditions. Trihalomethane (THM) formation (uniform formation conditions), chlorine demand measurements and size exclusion chromatography analysis further assessed changes in the treated water quality. The results showed increases in the AOC (100 – 200 %
increase) and BDOC (50 – 150 % increase) after VUV treatment (max. 1800 mJ/cm² fluence, 254 nm UV equivalent).

To address the issue of reduced biological stability, biological activated carbon (BAC) treatment was evaluated as a potential treatment, post VUV process. The results for the combined VUV and BAC treatment showed 75% reduction in AOC relative to untreated water, thus significantly improving the water quality.
Lay Summary

Vacuum UV (VUV) is a chemical-free advanced oxidation process (AOP) that utilizes ultraviolet light at wavelengths below 200 nm. Our research group has investigated the capability of VUV to remove a number of micro-pollutants, such as pharmaceuticals, pesticides/herbicides and cyanobacterial toxins, under different water conditions. However, a potential challenge with any AOP including VUV irradiation, is its impact on biological stability of the treated water, creating conditions that promote bacterial regrowth in the distribution system. The partial oxidation of natural organic matter in surface water may lead to an increase in assimilable organic carbon (AOC), a parameter for biostability. This study investigates the impact of VUV on the biological stability of treated water along with changes in other water quality parameters.

The results show an increase in the concentration of AOC after the VUV process. Thus, biological activated carbon treatment was integrated after the VUV process as a secondary treatment to remove AOC and improve water bio-stability.
Preface

My contribution to the work involved literature review, develop research objectives, design of experimental plan and setup, run experiments and perform various analytical test along with data analysis and presentation. The entire work along with this document and manuscript preparation was done under the supervision of Prof. Madjid Mohseni.

This research was carried out in collaboration with Prof. Benoit Barbeau from École Polytechnique de Montréal, the BDOC, chlorine demand and THMs formation potential analytical test being conducted in his laboratory.
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List of Symbols

Φ Quantum yield

[AOC] Assimilable Organic Carbon concentration

OH• Hydroxyl radical

Cl− Chloride

NO3− Nitrate

SO4^{2−} Sulfate

H2O2 Hydrogen peroxide

Fe^{2+} Iron (II) ion (Ferrous)

O3 Ozone
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AOC</td>
<td>Assimilable Organic Carbon</td>
</tr>
<tr>
<td>AOP</td>
<td>Advanced Oxidation Process</td>
</tr>
<tr>
<td>AMW</td>
<td>Apparent Molecular Weight</td>
</tr>
<tr>
<td>AWWA</td>
<td>American Water Works Association</td>
</tr>
<tr>
<td>BAC</td>
<td>Biological Activated Carbon</td>
</tr>
<tr>
<td>BDOC</td>
<td>Biodegradable Dissolved Organic Carbon</td>
</tr>
<tr>
<td>DBP-FP</td>
<td>Disinfection By-Product- Formation Potential</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>FC</td>
<td>Flow Cytometry</td>
</tr>
<tr>
<td>FEEM</td>
<td>Fluorescence Excitation Emission Method</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular Activated Carbon</td>
</tr>
<tr>
<td>HPSEC</td>
<td>High Performance Size Exclusion Chromatography</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural Organic Matter</td>
</tr>
<tr>
<td>SHA</td>
<td>Slightly Hydrophobic Acids</td>
</tr>
<tr>
<td>SUVA</td>
<td>Specific UV Absorbance</td>
</tr>
<tr>
<td>THM</td>
<td>Trihalomethane</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>UVA</td>
<td>UV Absorbance at 254 nm</td>
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<td>VHA</td>
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<td>Vacuum UV</td>
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Last but not the least, to my family back home, thanks for always being there.
Chapter 1: Background

1.1 Drinking Water Treatment Processes

Drinking water purification and treatment can be broadly classified into conventional and non-conventional processes. The conventional processes involve basic treatment techniques, such as coagulation, flocculation, sedimentation and filtration, while some of the non-conventional processes include ion exchange, membrane filtration and advanced oxidation.

The growing public awareness for the need of clean drinking water, stringency in water quality regulations and the emergence of micro-pollutants have paved the way for the application of more advanced treatment processes. Among the advanced treatment technologies, advanced oxidation processes (AOPs) offer a promising and robust alternative with the potential conversion of organic contaminants into harmless products. AOPs in drinking water are carried out by the generation of hydroxyl radicals that act as an oxidant during the chemical reaction. The generation of this hydroxyl radical can be facilitated by different methods including ozonation, ozone + hydrogen peroxide (O₃/H₂O₂), ozone + UV (O₃/UV), UV + hydrogen peroxide (H₂O₂/UV) and vacuum UV (VUV).

1.2 Vacuum UV

VUV corresponds to a specific range of photons with wavelengths between 200 and 10 nm in the ultraviolet region of the electromagnetic spectrum. Hence, its photons are energetic enough to photolyze the water molecules, generating strongly oxidizing hydroxyl radicals. As such, VUV finds application in drinking water treatment, as it facilitates the oxidation of contaminants present in water through reaction with hydroxyl radicals. VUV offers a chemical free approach to AOP
and is highly capable of removing micropollutants (e.g., pharmaceuticals, agricultural, cyanotoxins) from water [1–3], which is particularly suitable for small and remote systems.

1.3 Biological Stability

After treatment, drinking water is either stored and then distributed or directly distributed to the consumers along various pipes known as the distribution system. The distribution network can sometimes be extensive and the average time spent by the purified water along these pipes can be significantly long. Hence, it becomes important to ensure the maintenance of the water quality while it is being distributed to the consumers throughout the entirety of the distribution system. The microbial content in the water is an important parameter for water quality and for a biologically stable water it should be constant along the distribution system.

During AOP treatment for micropollutant degradation under commercially feasible conditions, the natural organic matter (NOM) present in surface water is not completely mineralized [4,5]. The partial oxidation of NOM into smaller and more biodegradable species could impact the bio-stability of treated water [6]. Thus, it becomes important to monitor the bio-stability of water, after any AOP including VUV, along various stages of the distribution system to eliminate bacterial regrowth and biofilm formations.

Biological stability is assessed by measuring the assimilable organic carbon and biodegradable organic carbon. The threshold limits suggested for bio-stability are 20 µg/L of AOC and 200 µg/L of BDOC [7]. Another study has recommended a 10 µg/L value for AOC as the limit for biological stability [8].
1.4 Thesis Layout

- Chapter 2: This chapter provides a literature review on the latest issues and studies concerned with AOPs, with a special focus on UV-based AOPs followed by problems pertaining to NOM-containing surface water. The importance of biological stability in drinking water and other water quality parameters are also highlighted.

- Chapter 3: This chapter presents the research objectives along with the industrial significance of this study.

- Chapter 4: This chapter describes the experimental methodology with a brief description of the various experimental setups and surface waters used in the research. The various analytical methods used are also described, along with their respective procedures.

- Chapter 5: In this chapter, the research outcomes of the various analytical test involving both laboratory and pilot studies for assessing the changes in water quality for VUV AOP are discussed in detail.

- Chapter 6: This chapter describes the BAC treatment as a potential secondary. The chapter includes design and fabrication of the BAC columns and the comparative study and results for the application of VUV and BAC process in series.

- Chapter 7: This chapter summarizes the results and main conclusions of the research and provides recommendation for future works.
Chapter 2: Literature Review

2.1 Advanced Oxidation Processes

AOPs as a water treatment method are facilitated by the generation of hydroxyl radicals (OH’), which react non-selectively with the pollutants present in water [9]. Hydroxyl radicals are a very reactive, non-selective chemical oxidant species with an oxidation potential of 2.8 eV, just below fluorine. Hence, it makes AOP a viable process for the treatment of many organic contaminants in water, including agricultural pesticides (e.g., herbicides), pharmaceuticals, personal care products and cyanotoxins traces [10].

The AOP for drinking water treatment can be carried out using different methods like ozonation [11], catalytic ozonation [12], photocatalysis [13], Fenton’s reaction (H$_2$O$_2$ + Fe$^{2+}$), combination of ozone-UV- H$_2$O$_2$ [14–16], as well as by the application of vacuum UV [17].

In the past few years, AOPs have been extensively used and commercialized in North America and Europe; there have been more than 500 installations in these regions. However, there still is tremendous potential of its application especially in the developing nations, with growing interest in countries like India and China.

2.2 UV Based AOPs

UV based AOPs are becoming popular with more than 50 new full-scale installation in the last ten years globally [10]. Trojan Technologies is one of the leading manufacturers and providers of UV based technologies for drinking water treatment, including AOP and disinfection processes. Many facilities use UV/H$_2$O$_2$ AOP with successful degradation of various contaminants. One example of a full-scale installation includes the PWN’s water treatment facility in the Netherlands. Here, a
UV dose of 540 mJ/cm² and H₂O₂ concentration of 6mg/L are used to generate the advanced oxidation conditions for the removal of organic micropollutants [15].

VUV is another UV based AOP that utilizes the shorter wavelength UV photons (wavelength below 200 nm) to generate hydroxyl radical. The reaction is carried out with the lower wavelength photons, photolyzing the water molecules. The main reactions that take place (using 185 nm) are shown below [18,19], with the quantum yield being dependent on the wavelength of photons:

\[
\text{H}_2\text{O} + \text{hv} \rightarrow \text{OH}^\bullet + \text{H}^\bullet \quad \Phi_{1849 \text{ Å}} = 0.33 \tag{2.1}
\]

\[
\text{H}_2\text{O} + \text{hv} \rightarrow \text{OH}^\bullet + \text{H}^\bullet + \text{e}^- \quad \Phi_{1849 \text{ Å}} = 0.045 \tag{2.2}
\]

VUV offers the simplest AOP approach, with only the use of an ozone generating low-pressure mercury lamp. Being a chemical free process, it is particularly suitable for small and remote systems. Extensive lab-scale studies have been carried out demonstrating the efficacy of VUV for the degradation of a range of model pollutants [1–3]. A kinetic study for dichlorophenoxyacetic acid (2,4-D) (i.e., a herbicide) showed a removal rate of 90% from an initial concentration of approximately 1.5mg/L [1] at UV 254nm equivalent dosage of 938 mJ/cm². The 2,4-D degradation rate was affected (up to 72% reduction) in the presence of alkalinity and NOM in water, due to their scavenging effects on hydroxyl radical and VUV photons absorption. Removal efficiency of 96% was also observed for Atrazine from initial concentration of 180µg/L approximately at a UV dosage of 790mJ/cm² [2].

Microcystin-LR (MC-LR), a cyanobacterial toxin has been demonstrated to degrade by direct photolysis with the use of 254 nm wavelength [3]. However, the application of 185 nm in addition to 254 nm leads to generation of hydroxyl radicals that greatly enhance the process of MC-LR degradation through advanced oxidation, thereby decreasing the MC-LR concentration to below the regulatory requirements (i.e., guidelines from Health Canada). It has been reported that a UV
dosage of 200 mJ/cm\(^2\) was capable of removing MC-LR from an approximate initial concentration of 15\(\mu\)g/L to less than 0.5 \(\mu\)g/L in natural water having DOC in range of up to 6 ppm [3]. VUV AOP was also efficient in degrading MC-LR in natural waters impacted with severe algae bloom (i.e., cyanobacterial cell density: 230,000 \(\pm\) 6,000 cells/mL) using a UV dose of 140 mJ/cm\(^2\) [3].

2.3 Limitations of the VUV AOP

185 nm radiation is strongly absorbed by water and most of the photons (90\%) are absorbed in a path length of 0.65 cm at a temperature of 25\(^\circ\)C [2,20]. The absorption coefficient at 185 nm of pure water is 0.79 \(\pm\) 0.11 cm\(^{-1}\) at 3.6 \(^\circ\)C and increases to 1.53 \(\pm\) 0.09 cm\(^{-1}\) at 25\(^\circ\)C [20]. As a result, VUV reactors are limited to the treatment of smaller volumes of water, consequently making the hydrodynamics of the system very important, such that there is effective mixing to maximize pollutant-hydroxyl radical interactions. For instance, Bagheri and Mohseni [21] showed that mixing and introduction of circular zone/vortexes (using baffles) significantly increase the degradation of target pollutants with lowered energy cost.

At the applied UV dosage for micropollutant degradation in VUV AOP (as discussed in Section 2.2), the NOM present in surface water is not completely mineralized. NOM can be degraded and almost completely mineralized with application of higher UV dose. In a study by Imoberdorf and Mohseni [22], it was observed that the total organic carbon (TOC) of water decreased from 4.95 ppm to 0.3 ppm with an UV irradiation time of 180 minutes. The corresponding radiation flux for 254 nm photons from the VUV-Hg lamp was 37.59 mW/cm\(^2\), while the flux for 185 nm photons was 3.21 mW/cm\(^2\). Thus, the energy requirement for NOM degradation is considerably high and might not be commercially feasible. This in turn might impact the treated water quality as the partially oxidized NOM might be more biodegradable and lead to reduced biological stability.
2.4 Natural Organic Matter

NOM is a complex mixture of organic molecules present in water and is composed of groups such as: humic substances, carboxylic acids, bio-polymers, amino acids and hydrophilic acids. The majority of these dissolved organic molecules are introduced into the source water by the microbial degradation of the remains of organisms (i.e., plants and animals, including their waste) and leaching process in the soil, thereby entering into the streams and watershed system [23,24]. NOM characterization and quantification is very important as it heavily influences the treatment processes and their efficiency. An overview of different characterization techniques for NOM has been described by Matilainen et al. [25].

Although NOM does not pose any direct health concerns, its presence in raw water is undesirable. Presence of NOM in water can lead to disinfection by-product formation, as it has been observed to be a precursor to trihalomethane formation, as well as responsible for increasing chlorine demand [5,26]. It results in increased fouling of membranes, attenuates UV, increases ozone demand and scavenges oxidants such as OH radicals during AOPs [1,14]. Finally, the presence of NOM creates conditions that promote bacterial regrowth in the distribution system [6], affecting the biological stability of water.

2.5 Biological Stability

“Biological stability” in drinking water refers to potable water where the regrowth of microbes is inhibited and has constant characteristics of the microbial community (i.e., abundance, viability and composition of the community) from the treatment plant to the consumers’ tap. The World Health Organization (WHO) guidelines for drinking water state that “the water entering the distribution system [must] be microbiologically safe and ideally bio-stable” [27]. Water that is not
biologically stable can lead to uncontrolled growth of bacteria along the distribution system. This can lead to taste and odor issues, affecting the aesthetic quality and causing dis-coloration of water, as well as biofouling and corrosion of pipes. Moreover, it can cause serious health concerns, inviting opportunistic pathogens for their invasion [28].

2.5.1 Biological Stability Challenges with AOPs

The hydroxyl radicals generated in AOP, being nonselective, react with the NOM in addition to the target contaminants. Thus, NOM breaks down and undergoes structural changes and the incomplete mineralization results in the formation of smaller molecular weight fractions from partial oxidation of the larger molecular weight fractions [4]. This increases the biodegradability of organic species as the smaller molecular weight fractions are more easily assimilated by the microbial community [29], thereby impacting the biological stability.

The effect on biological instability after ozonation was demonstrated by van der Kooij et al. [30] and the results showed a linear AOC increase with ozone dosage (ozone value < 1 mg O$_3$/ mg of C). Moreover, the relationship between AOC increase and UV absorbance decrease was also found to be linear. The important conclusion derived from this study was that the aromatics in humic and fulvic acid break down due to ozonation and form carboxylic acid of lower molecular weight that could be utilized by the bacteria. A detailed kinetic study for the evaluation of lower molecular weight NOM species with ozone exposure was investigated by Hammes et al. [31]. It was established that a majority of byproducts formed by oxidation of organic compounds on exposure to ozone comprised 60-80% AOC. It was even demonstrated that laboratory scale model experiments were sufficient to describe the lower molecular weight compounds formation during
ozonation for a full-scale treatment plant treating surface water. These models and mechanistic information could be used for the scale-up from laboratory to full scale operations.

For UV/H\textsubscript{2}O\textsubscript{2} AOP, some preliminary studies on biostability by Toor and Mohseni [32] reported increases in the biodegradable organic species in treated water. After application of UV/H\textsubscript{2}O\textsubscript{2} (500mJ/cm\textsuperscript{2} UV\textsubscript{254} fluence and 20 mg/L of H\textsubscript{2}O\textsubscript{2}), the AOC concentration of the treated water increased from an initial value of 62 µg/L to 100µg/L, while BDOC showed approximately 40% increase [32]. Further, detailed biological stability assessment for UV/H\textsubscript{2}O\textsubscript{2} process was carried out by Bazri et al. [6] along with molecular weight distribution. The biological stability deteriorated 3 – 4 times over the treatment process (~10 mg/L initial H\textsubscript{2}O\textsubscript{2} conc., 2000 mJ/cm\textsuperscript{2} UV dose max.). The source water characteristics (initial TOC and NOM) influenced the biostability profile of the UV/H\textsubscript{2}O\textsubscript{2} treated water.

2.5.2 Assimilable Organic Carbon

AOC is the fraction of the DOC that can be assimilated by the microbial community for their rapid growth and is a parameter for biological stability [8,33,34]. There are various methods developed for AOC measurements including heterotrophic plate count (HPC), adenosine tri-phosphate (ATP) and flow cytometry (FC). These have been described and compared in the literature [35].

The conventional method of AOC quantification uses heterotrophic plate count regrowth of bacteria, developed by van der Kooij [8]. This method however is quite tedious, highly variable in cell culturability and requires a long incubation time of 10 – 14 days, which has made it less practiced for routine experiments. It was modified by LeChevallier et al. [34], whereby the incubation temperature and inoculum density was increased in order to reduce the incubation time. This modified method involves ATP luciferin -luciferase method to enumerate organisms.
However this method, like the plate count bioassays, still requires initial inoculum seeding with pure strains (i.e., Pseudomonas fluorescens P-17 and Spirillum NOX). This results in restrained information on the biostability, as all the AOC might not be accounted for by just using the two standard pure strains. All these factors have been leading to neglection in AOC determination by water practices. A simpler and easy method, recently developed by Hammes and Egli [36], using flow cytometry with fluorescence staining of nucleic acids in cells is a more straightforward approach, which quickly enumerate test organisms. The FC technique also allows for detection of inactive and uncultivable micro-organisms, a limitation associated with the ATP and plate count method. As a result, the traditionally used pure strains are replaced with natural microbial consortium (of the raw water being analyzed), allowing for a broader range of microorganism substrate to be covered, a more realistic interpretation of AOC concentration [36,37].

The flow cytometry method is becoming popular for AOC determination as it is rapid, efficient and easily reproducible, with an incubation time of three days; obtaining results relatively quickly as compared to the other methods [6,35]. FC method has been successfully adopted for the determination of AOC after an ozonation process [31] and UV/H₂O₂ treated water using indigenous consortium [6]. The residual H₂O₂ from treated water samples were quenched using immobilized catalase on polymeric substrate which otherwise might negatively impact the AOC bioassay and water quality.

2.5.3 Biodegradable Dissolved Organic Carbon

BDOC is the biodegradable fraction of DOC that can be assimilated and mineralized by the bacteria present in water over a period of several days. It is generally comprised of 10 to 20% of the DOC concentration in water [38]. It is another parameter for biological stability with bacterial
regrowth in the distribution system [38,39]. The incubation time for BDOC is 30 days, which means it takes longer to obtain the results as compared to AOC measurement for biological stability. On one hand, there have been some studies showing positive correlation between BDOC and AOC. Bazri et al. [6] concluded that the correlation could be represented in the form BDOC = a × AOC (where ‘a’ is constant). This was demonstrated for UV/H₂O₂ process carried out in the laboratory as well as in pilot-scale multistage treatment, consisting of alum coagulation and settling, ozonation AOP and biologically active ultrafiltration membrane process (powdered activated carbon UF bioreactor) [6]. On the other hand, some studies have reported that no clear correlation exists between the two parameters. For example, Escobar and Randall [38] found no correlation during AOC and BDOC assessments for a full scale membrane filtration process. In another study by Escobar et al. [41], in agreement to their previous work, no significant correlation was observed while monitoring bacterial growth in two different distribution systems; one treating water with ozone and the other treating water using nanofiltration. Nevertheless, with the little knowledge available in literature, it has been recommended to measure both AOC and BDOC to better understand the changes in bio-stability [6].

2.6 Disinfection By-Product Formation Potential (DBP-FP)

DBPs are formed due to the reaction of NOM with chlorine during the disinfection process for drinking water treatment. The most common DBPs include trihalomethanes (THMs), halo acetic acids (HAAs), haloketones and haloacetonitriles [26,42]. Monitoring DBPs in drinking water is important as these compounds pose significant health hazards, due to their suspected carcinogenic and teratogenic potentials [43]. There are strict guidelines or standards set up by various health and environment agencies across different countries to regulate the concentrations of several
DBPs. For instance, Health Canada’s drinking water quality guideline sets a maximum THM level of 100 μg/L in drinking water [44] while the US EPA has set 80 μg/L as the maximum level acceptable in drinking water [45].

In AOPs, application of lower oxidant dosage at commercially feasible conditions (i.e., sufficient for target pollutant but not for NOM mineralization) do not lead to a reduction in the DBP-FP. Substantial DBP reduction can be achieved from AOPs with application of rigorous oxidant conditions under which NOM would be completely mineralized. There have been various reports in the literature for UV/H₂O₂ based AOPs suggesting that decreases in THM formation potential was only observed after 1500 mJ/cm² of UV fluence and H₂O₂ concentration of 23 mg/L [5,32]. Another study by Kleiser and Frimmel [46] for ozonation process reported that the reduction in THM-FP was observed after application of 1.5mg ozone mass/mg DOC.

In addition, the partial oxidation of NOM into more biodegradable and smaller weight fractions might lead to slight increases in DBP-FP. Kleiser and Frimmel [46] observed an increase in THM concentration (max. 20%) with the application of short irradiation time for UV/H₂O₂ process. The THM was found to decrease to 75% of the initial value after an irradiation time of 1050 minutes (emitted radiation power: 3.3 W, determined by ferrioxalate actinometry) and 5.6mg/L of hydrogen peroxide consumption.

2.7 Biofiltration Process

AOPs are often followed by a downstream biological treatment. This allows for the treatment of the biodegradable fraction formed during chemical oxidation which would otherwise not degrade by the action of bacteria. Biological treatment offers a solution to the remaining residual contaminants and organic oxidation by-products. It is relatively low cost and easy to implement
with robust operational efficiency, downstream of an expensive chemical oxidant treatment. 

*Nogueira et al.* [47] used UV/H$_2$O$_2$ oxidation process followed by biofiltration as a tertiary treatment for wastewater from an oil refinery meant for the reuse of water. Biofiltration alone was able to reduce total organic carbon (TOC) and UV$_{254}$ absorbance by only 46 % and 23 % respectively. Whereas, combined UV/H$_2$O$_2$ and biofiltration provided TOC and UV$_{254}$ absorbance reduction of 88 % and 79 %, respectively.

Another example is from the work of *Lee et al.* [48], who used ozonation combined with biofiltration, enabling the reduction of BDOC. For ozonation process, UV$_{254}$ absorbance reduction was found to correlate well with the reductions in non-biodegradable DOC. However, BDOC profile showed an increase, accounting for the byproducts generated during the chemical oxidation process. But, the application of downstream biofiltration significantly reduced the biodegradable products (nearly 50% of BDOC removed) formed during the ozonation process.

### 2.7.1 Biological Activated Carbon Treatment

Biological activated carbon (BAC) is the most common biological system used in drinking water treatment [48]. BAC treatment consist of granulated activated carbon (GAC) serving as the growth media for biomass accumulation, rather than adsorption [49]. GAC can support a 4-8 times denser biomass population (per gram media) compared to sand or anthracite. Some of the properties that make GAC such an efficient growth media are its high porosity, surface area, roughness and adsorption capabilities [50]. Empty bed contact time (EBCT) and temperature are important parameters for BAC treatment [51], whereby the efficiency is linearly related to the contact time. *Chien et al.* [52] showed 86% removal in AOC (using BAC columns, 15 cm diameter & 200 cm height of the column) with a contact time of 6.6 minutes. Typically 15 – 20 minutes of contact
time is maintained to remove THMs and improve the biological stability [52,53]. Another important factor is the growth of biomass and the assimilation time of microbial community on the surface of activated carbon, which can take some days to develop. Toor and Mohseni [32] reported an assimilation time of 7 days, feeding the lab scale bio-reactor continuously with raw water. Additionally, it becomes important to quantify the biological growth colonizing the BAC columns, which could be crucial for modelling and improving their performance. The analysis of biomass can be done by several methods which have been described by Stoquart et al. [54]. Some other factor that can influence the performance of BAC treatment are type of GAC, backwashing regime and hydraulic conditions [55,56]. The impacts of all these factors on the biomass growth and BAC performance have not been extensively studied and still unknown [49].

BAC is extensively used to resolve the biological stability in drinking water, removing the AOC and BDOC by microbial activity. The bacterial community thrive and flourish on the extra biodegradable organics fed through the influent stream and in the process enhancing the final water quality. The DBP precursors can be lowered significantly; Toor and Mohseni [32] reported 43% decrease in DBPs with respect to raw water after combined UV/H₂O₂ AOP-BAC process. A pilot-scale BAC system used for ozonated water demonstrated a decrease in DOC and AOC which was proportional to the contact time [57]. Lohwacharin et al. [58] investigated the AOC removal efficiency for BAC filters of various service time (i.e., BAC filters with 13-week, 44-week & 6-year service time). Total AOC removal of 28%, 58% and 66% were reported with 13-week, 44-week and 6-year service time BAC filters, respectively.
Chapter 3: Research Objective

3.1 Knowledge Gap

Vacuum UV as an AOP has been proven to be a robust and efficient technology for the treatment of several micropollutants. Being a chemical free process, it offers tremendous potential for its application in small and remote communities, which often have limited resources and not able to maintain a continuous supply of required chemicals (oxidants, coagulants, etc.). Besides the oxidation of target contaminants, VUV (lamps having outputs of 254 nm along with 185 nm) will provide disinfection as it simultaneously provides inactivation of pathogens in water.

At an applied UV dosage to achieve advanced oxidation, the NOM present in water is not completely mineralized. Rather, the partial oxidation of NOM might result in the increase of AOC and BDOC which can impact biological stability of the treated water in the distribution system. Also, the formation of smaller molecular weight fractions of NOM can significantly affect the DBP formation potential of the treated water. Hence, it becomes important to quantitatively study the impact of VUV process on biological stability and DBP formation potential.

3.2 Research Objectives

1) To investigate the biological stability of VUV AOP treated surface water by quantitative measurement of AOC and BDOC. Performing batch and continuous laboratory scale experiments with natural waters from various community sources having different organic carbon concentrations. Further, to validate the laboratory scale data with experiments using a pilot scale setup in a remote community site employing a mobile water treatment unit equipped with a VUV photoreactor.
2) To evaluate BAC treatment downstream of the VUV treatment to investigate improvement in biological stability and DBP precursors. Performing laboratory scale experiments with natural waters, using bench scales VUV flow through reactor and BAC columns in series. Further, to validate the quantitative assessment of changes in water quality parameters (i.e., AOC, BDOC and THM formation) with qualitative assessment of the impacts on apparent molecular weight distribution of NOM for the combined process.

3.3 Research Significance

The results from this research will be useful for water engineers and operators to maintain the water quality of VUV treated water along the distribution system. The kinetic study of AOC increase with respect to UV dosage is not only of scientific significance, but also has practical applications in determining the right treatment process downstream of VUV treatment. Higher AOC or BDOC levels are not a grave concern for the point-of-entry treatment systems, however they could be a serious issue for central treatment processes, where the average age of water from the treatment facility to consumers’ tap stretches from several hours up to over a day [59]. The assessment of changes in chlorine demand and DBP precursors will help to determine the right chlorine dosage when used as a secondary disinfection. Moreover, BAC treatment combined with VUV treatment will help in mitigating any challenges and concerns towards biological stability, offering a simpler technology that is chemical free.
Chapter 4: Experimental Methodology

4.1 Preparation of Laboratory Tools and Glassware

Maintaining carbon free labware is very important, as the slightest contamination of the glassware can notably vary the output data. Some of the measures undertaken to ensure cleanliness of the glassware and laboratory tools are provided below:

AOC free glassware was prepared following guidelines specified in Standard Methods 9217 [60]. All glassware (Pyrex® beaker and 40mL borosilicate vials) were washed with soap and warm water followed by rinsing with DI water. The glassware was kept in 0.1N hydrochloride acid bath for 12 hours. The acid removed any traces of inorganic carbon. Finally, the glassware was rinsed with DI water three times followed by heating in a furnace at 550°C for 5 hours.

Teflon-lined septa plastic caps were used for the 40mL borosilicate vials, these were first washed with soap and warm water, then rinsed with DI water three times. To remove any traces of organic carbon, they were soaked in 10% (w/v) sodium persulphate solution at 80°C for least 1 hour. The 60 mL plastic syringes were rinsed three times with DI water while the syringe filters were rinsed by flushing 60 mL of DI water. All pipette tips for sampling were only used once.

4.2 Chemicals

The chemicals used during the course of study are listed in Table 4.1. All chemicals were used as received from the suppliers, without any modification.
Table 4.1: List of Chemicals.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Grade</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYBER GREEN I</td>
<td>10000X</td>
<td>Life Technology</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>Acid Reagent 37%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sodium persulfate</td>
<td>≥ 98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4.8(99.998%)</td>
<td>Praxair</td>
</tr>
<tr>
<td>Potassium Iodide</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Potassium Iodate</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Sodium Borate Decahydrate</td>
<td>Reagent</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Potassium Nitrate</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Dipotassium phosphate</td>
<td>99.99%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sodium Acetate</td>
<td>99.99%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide</td>
<td>HPLC grade</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>≥99%</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Sodium Azide</td>
<td>≥99.5%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Zwittergent 3-12</td>
<td>≥99% by TLC</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>EGTA</td>
<td>≥97%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Tris Buffer</td>
<td>Microbiology</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Peptone</td>
<td>Microbiology</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>R2A Agar</td>
<td>Microbiology</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>
4.3 Source Water and Raw Water Characterization

Experiments were carried out on surface waters from various community sources located across the province of British Columbia (BC), Canada, with different TOC concentrations. Raw water was collected from Van Anda Improvement District, Cedar Creek Community and Middle River Reserve (of the Tl’azt’en Nation). Van Anda Improvement District’s surface water supply, known as Priest Lake, is located on Texada Island, one of the Northern Gulf Islands in the Strait of Georgia off the coast of BC. Cedar Creek is the source of a small seasonal community located on the Vancouver Island, BC. Middle River is a small First Nation community (one of the three reserves of the Tl’azt’en Nation) and is located about 100 km north west of Fort St. James, BC.

For the BAC experiments, water from Jericho Pond was used. Jericho Pond is located west of the seaside neighborhood of Kitsilano in the city of Vancouver, BC. It is 5 km from the UBC Point Grey Campus. The NOM concentrations and characteristics were subject to changes in all these surface water with time and season. The average characteristics of each raw water source at the time of sampling and testing are summarized in Table 4.2.
Table 4.2: Raw water characteristics. The surface waters were collected at different time; Van Anda was collected during month of January & August 2016, Middle River & Cedar Creek in month of June 2016 while Jericho Pond in January 2017.

<table>
<thead>
<tr>
<th>Water body</th>
<th>Middle River</th>
<th>Van Anda</th>
<th>Cedar Creek</th>
<th>Jericho Pond</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>5.3 ± 0.1</td>
<td>5.8 ± 0.1</td>
<td>2.7 ± 0.1</td>
<td>6.8 ± 0.1</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
<td>7.9</td>
<td>6.7</td>
<td>6.8</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>0.67 ± 0.01</td>
<td>4.82 ± 2.58</td>
<td>0.69 ± 0.01</td>
<td>19.70 ± 0.50</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>4.1 ± 0.5</td>
<td>46.5 ± 8.6</td>
<td>0.9 ± 0.1</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>UV₂₅₄ (cm⁻¹)</td>
<td>0.161 ± 0.001</td>
<td>0.174 ± 0.002</td>
<td>0.068 ± 0.001</td>
<td>0.176 ± 0.002</td>
</tr>
</tbody>
</table>

Source water characterisation becomes extremely important when studying the impacts on bio-stability for a drinking water treatment process and future reproducibility of the results. For instance, Bazri et al. [6] observed that the AOC profile of UV/H₂O₂ treated water was influenced by the initial TOC and the source of NOM.

Figure 4.1 illustrates the chromatograms with the apparent molecular weight distribution of NOM present in the surface waters used in the study. The apparent molecular weight was divided into six different regions from T1 to T6 (Table 4.4) [53].

Table 4.3: Relationship between time and apparent molecular weight. Polysulfonate standards were used to correlate the Apparent Molecular Weight.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>7</th>
<th>9</th>
<th>11</th>
<th>13</th>
<th>15</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. Weight (Da)</td>
<td>83000</td>
<td>22300</td>
<td>6000</td>
<td>1600</td>
<td>430</td>
<td>115</td>
</tr>
</tbody>
</table>
The NOM fraction in this molecular weight region (*Table 4.4*) comprises of humic substances (average molecular weight ~1000 Da), building blocks (500-300 Da) and lower molecular weight acids and neutrals (less than 300 Da). Figure 4.2 depicts the distribution of various NOM fractions in each of the surface waters.
Table 4.4: Parameters with their corresponding range of molecular weight.

<table>
<thead>
<tr>
<th></th>
<th>Apparent Molecular Weight (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>1350 - 4000</td>
</tr>
<tr>
<td>T2</td>
<td>1050 - 1350</td>
</tr>
<tr>
<td>T3</td>
<td>750 - 1050</td>
</tr>
<tr>
<td>T4</td>
<td>500 - 750</td>
</tr>
<tr>
<td>T5</td>
<td>300 - 500</td>
</tr>
<tr>
<td>T6</td>
<td>&lt;300</td>
</tr>
</tbody>
</table>

The chromatograms (Figure 4.1) and NOM fraction distribution (Figure 4.2) results suggest that the highest fraction of biodegradable components were present in Jericho Pond raw water (max values of T5 + T6). This was followed by Cedar Creek water, in spite of its lowest DOC concentration among all surface waters, which is confirmed with the higher AOC and BDOC values discussed in the latter chapters.
Figure 4.2: Molecular weight distribution of the NOM fractions present in the raw waters used in the study.

* Refer to Table 4.4 for the molecular weight range represented by parameters T1 – T6.
4.4 Experimental Apparatus and Procedure

4.4.1 VUV Collimated Beam Setup

A VUV collimated beam setup [61] was used to study the formation kinetics of AOC in surface water at different UV dosages. 185 and 254 nm photons were generated using an ozone generating low-pressure mercury amalgam lamp (Light Sources GPHVA357T5VH/4W). To prevent the reaction of 185 nm with oxygen in air (i.e., prevent ozone formation), nitrogen was purged all the time during the course of irradiation. Every time the lamp was switched on, a wait time of 1 hour allowed for the steady output of UV photons. The UV irradiation hit from the bottom onto the petri dish, the bottom surface of which was made of quartz allowing the transmittance of 185 and 254 nm. A magnetic stir bar kept the solution well mixed. The 254 nm UV irradiance on the bottom surface of the petri dish was calculated using the iodide-iodate actinometry procedure (Appendix A). Generally, the 185 nm UV output from the lamp used was approximately 10-20%, while 254 nm was 80-90% [10].

For the AOC formation experiments, 75 mL of water was irradiated at a UV fluence (calculated at 254 nm) ranging from 100 – 1000 mJ/cm² (i.e., 100, 200, 400, 600, 800 & 1000 mJ/cm²). It was found from literature that a maximum UV fluence of 1000 mJ/cm² is sufficient for the degradation of most micropollutants using VUV AOP [2, 3, 22].
4.4.2 VUV Flow Through Reactor

The VUV flow through reactor [2] was used to study the changes in the biological stability and THM formations at different operating conditions (i.e., different flow rates, corresponding to different UV fluence). The setup consists of an ozone generating low pressure mercury lamp (GPHVA357T5L, Light Sources, Inc.) positioned along the axial direction of the flow through reactor. The lamp is protected by a quartz sleeve (natural quartz dome ended sleeve, Light Sources, Inc.). Water flows along the surface of the quartz sleeve, while being radiated by the 185 and 254 nm photons, emitted from the lamp. The outer body of the photoreactor is made of plexiglass. The flow-rate is adjusted using a flow meter. Figure 4.4 shows the schematic of the entire set-up, while Figure 4.5 shows the design and cross-sectional measurements of the flow through reactor.
The flow rates used in the experiments were 2, 1 and 0.5 L/min (2 and 1 L/min: single pass; 0.5L/min: single and double pass) with corresponding residence times of 5, 10, 20 and 40 seconds, respectively. The corresponding UV$_{254}$ dosage ranged between 400 and 1800 mJ/cm$^2$, which was estimated based on the data from the kinetic studies of the collimated beam setup and the AOC formation using the VUV flow through reactor.

Figure 4.4: VUV flow through reactor experimental setup [2, 20]
4.4.3 Pilot-Scale VUV Photoreactor

Pilot scale studies at an increased flow rate were carried out using the RES’EAU-WaterNET mobile water treatment unit. The mobile unit was equipped with two ultraviolet (UV) reactors (Expurgo™ Model SP01D20L1GTB-C15, Spectral Innovation Ltd; custom designed). The reactor unit irradiated 254 and 185 nm wavelengths using amalgam UV lamps. The UV irradiation annulus was 7 mm thick and the lamp was a Heraeus 160 W amalgam “VUV” lamp, having 185 nm photons output of 9% of the total output power, while the rest was 254 nm.

For the pilot study, experiments were carried out in the remote community of Van Anda Improvement District, BC, with a population of roughly 550 people. Raw water was obtained from Priest lake, which serves as the community’s primary water source. The power input requirement was 300 watts, 2.5 Amps nominal at 120 VAC.
The flow rates used were 5, 10 & 20 L/min and the two VUV reactors were operated in series. For 5 L/min flow rate operations, samples were collected after the treatment with both the first and second VUV reactors, while for flow rates 10 & 20 L/min, samples were collected after the treatment with first VUV reactor only. The corresponding residence times were 4, 7, 14 and 29
seconds operating at the aforementioned flow rates. The UV dosage at different residence times was estimated using the lab-scale data for AOC formation kinetics and correlating it with the AOC formation during VUV irradiation at the residence time mentioned above.

Table 4.5: Input energy and UV dosage at corresponding residence time.

<table>
<thead>
<tr>
<th>Residence Time (Seconds)</th>
<th>4</th>
<th>7</th>
<th>14</th>
<th>29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Energy (kw/m³)</td>
<td>0.13</td>
<td>0.27</td>
<td>0.53</td>
<td>1.07</td>
</tr>
<tr>
<td>UV dosage (mJ/cm²)</td>
<td>352</td>
<td>739</td>
<td>805</td>
<td>1199</td>
</tr>
</tbody>
</table>

4.5 Assimilable Organic Carbon Analysis

AOC concentration was determined using the flow cytometry cell count method as proposed by Hammes and Egli [36]. This analytical method involves a series of steps, for example - natural consortium cultivation, sample preparation, incubation and cell count. These have been described in sequence in the following sub-sections.

4.5.1 Natural Microbial Consortium Cultivation

The first step is to cultivate the microbial consortium that will be used to inoculate the samples. In this research, a natural microbial consortium was used for each of the respective raw waters. This is different from the standard method, which involves using pure strains comprised of Pseudomonas Fluorescens P17 and Spirillum NOX. Using natural consortium allows for a broader range of organic carbon utilization by the microorganisms and from a theoretical point of view, it can be argued that the natural microbial community grows best in their respective water [37].
To prepare the natural microbial consortium [36], 30 mL of the natural water was rinsed using 0.22 µm filter directly into 40 mL AOC-free borosilicate vials. This step removes all bacteria and particulates from the surface water. Next, it is inoculated with 10 µL/mL (unfiltered/filtered of same surface water), capped and vortexed. This is followed by incubation at 30°C until a steady growth phase is reached.

4.5.2 Bacterial Removal

In order to remove the bacteria from the surface water, 0.22 µm filter (SLGP033RS, Millex®, sterile) was used to filter the water. As this is not a sterilization step, some bacterial cells pass through the filters, but this number is significantly low and will not alter the final results [36, 55].

4.5.3 Incubation Time

The incubation time is the time required for the cell growth to reach a steady stationary state. The cell concentration was monitored (for natural water and natural water spiked with 100g/L of acetate) every 24 hours for a period of 120 hours (i.e., 24, 48, 72, 96 & 120) and it was observed that the microbes reached a stationary growth phase by 72 hours.
Incubation time determination for Middle River surface water. Cell concentration was monitored for both raw water and 100 µg/L of sodium acetate spiked water. Cell growth was found to reach steady state after 72 hours of incubation.

* Error bars represent standard deviation from triplicate experiments.

### 4.5.4 Mineral Buffer

Mineral buffer solution was added to the samples to ensure that the AOC was the limiting reagent of cell growth. This ensures that all of the essential nutrients are present in excess for microbial growth. The mineral buffer solution [37] consisted of 171 mg/L K$_2$HPO$_4$, 767 mg/L NH$_4$Cl and 1.44g/L KNO$_3$ prepared in DI water and AOC free glassware.

### 4.5.5 Sample Preparation

To determine the AOC concentration, 15 mL of the water sample was filtered with 0.22µm filter in 40 mL borosilicate vials. Then, 2.5 µL/mL of mineral buffer solution/sample prepared as described in Section 4.5.4. was added, making sure carbon is the limiting agent for cell growth.
Then, the natural consortium prepared as described in Section 4.5.1. was added, such that the cell concentration be about $10^4$ cells/mL in the sample [35, 55]. Next, the vials were securely capped, vortexed and left to incubate at 30°C for 72 hours.

### 4.5.6 Cell Staining

Cell count is measured using the flow cytometry technique, which requires the DNA cell staining of the bacteria with a dye. The incubated samples were vortexed exhaustively and 1mL of the sample was pipetted into polystyrene flow cytometry test tubes. This was stained with 10 µL Syber Green nucleic acid that had been diluted 1:100 in dimethyl sulfoxide [35] and stored at -20°C before use. The stained samples were kept in the dark for 20 minutes at 20°C before further analysis.

### 4.5.7 Cell Count using Flow Cytometry

Cell count was carried out using a Macs Quant bench top analyzer in the Flow Core Unit at the Biomedical Research Center at the University of British Columbia. The advantage of using flow cytometry over other AOC analysis (i.e., Heterotrophic plate count, ATP method) is that it is quick, rapid and provides high degree of reproducibility [35]. For cell count, stained samples as described in Section 4.5.6., were placed in the 24-tube rack. Filtered samples were used to remove background noise as 0.22µm filter removes all microbial cells. The events corresponding to filtered sample were less than 10. These were mainly due to the particulate matter present in surface water rather than the stained cells. Gates were marked to distinguish between positive cells and background noise. The count obtained from flow cytometry instrument was in units of per mL.
4.5.8 Yield Coefficient

The cell count data was converted to the AOC concentration using the yield coefficient factor. Hence, each water had a separate calibration plot prepared with different concentration of sodium acetate – C (i.e., 0, 50, 100 & 150 µg/L). All carbon from acetate is considered assimilable by the bacteria, and hence, were counted as AOC. The plot of the cell count at different acetate-C was linear and the yield coefficient was determined by the slope of the linear fit trendline.
Figure 4. Yield coefficient plot for three different raw waters (Van Anda, Middle River & Cedar Creek).

*Error bars represent standard deviation from triplicate experiments.
4.6 Analytical Techniques and Procedure

4.6.1 TOC Measurements

The TOC present in surface water was determined using a Shimadzu TOC-VCPH and a GE Autosampler and Sievers M5310 C. The reaction taking place in the Shimadzu analyzer is through catalytic oxidation at an elevated temperature. The organic carbon is measured using the non-purgeable organic carbon (NPOC) method. The Sievers TOC analyzer uses the acid oxidizer method involving a two stage process. It measures the total carbon (TC) and inorganic carbon (IC) from an acid aliquot and the TOC is determined by subtracting the IC from the TC. The software for both the instruments reported average of three significant figures.

4.6.2 BDOC Measurements

Biodegradable dissolved organic carbon measurements were carried out in collaboration with École Polytechnique de Montréal, at Dr. Barbeau’s research laboratory. Prepared samples were shipped to Montréal at 4°C. The method used is described elsewhere [40]. Although the procedures are relatively simple, an incubation time of 30 days makes it difficult to perform in routine experiments.

A brief summary of the procedure is as follows: (1) water samples were filtered into 125 mL glass bottles, (2) the natural microbial inoculum was introduced to the samples (2%v/v), followed by (NH₄)₂SO₄ and KH₂PO₄ addition such that the final sample contained about 10 µg/L of P and 200mg/L of N, and (3) TOC was analyzed in the resultant sample (TOC_initial) and the remaining samples were incubated in the dark at 20°C for 30 days. After completion of incubation, the TOC
of the samples was determined again (TOC_{final}). BDOC is reported as the difference in the value of the two TOC determined in the span of 30 days (BDOC = TOC_{initial} - TOC_{final}).

4.6.3 Chlorine Demand

Chlorine reacts with organic and inorganic species in water, undergoing a substitution and oxidation reaction. In drinking water, chlorine demand is the amount of chlorine that undergoes a reaction with NOM (and other compounds) after maintaining a residual amount in the final water. This analysis was also carried out at École Polytechnique de Montréal; a 24-hour chlorine demand study was performed yielding a chlorine residue of about 1±0.5 mg/L of Cl₂/L. The samples were kept in the dark for the 24-hour duration of the test at 22°C and pH 8 (phosphate buffer).

4.6.4 Disinfection By-Product Formation Potential

As a continuation step to the chlorine demand analysis, a disinfection by-product formation study was conducted using Uniform Formation Condition (UFC) procedure. The details of the method are described elsewhere [59]. Samples were tested for the total THM comprised of chloroform, bromodichloromethane, dibromochloromethane and bromoform. Most of the THMs were accounted for as chloroform (~99%) and the rest by bromodichloromethane (< 1%).

<table>
<thead>
<tr>
<th>THM</th>
<th>LDM (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>2.0</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>1.4</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>1.6</td>
</tr>
<tr>
<td>Bromoform</td>
<td>2.3</td>
</tr>
</tbody>
</table>
4.6.5 UVA254

UV absorbance at 254 nm was measured using an Agilent Technologies Cary 100 UV-Vis Spectrophotometer. It was operated in double beam mode using a 10 mm path length quartz cuvette. Between each sample, the cuvettes were rinsed once with DI water and three times with the same sample to be tested. All samples were in triplicates from independent experiments.

4.6.6 High Performance Size Exclusion Chromatography Analysis

High performance size exclusion chromatography (HPSEC)[4] was used to determine the molecular weight distribution in raw and treated waters. A Waters HPSEC (HPLC Waters 2695 Separation Module with Waters Protein-PakTM125 Å column and Waters 2998 Photodiode Array Detector) equipment served as the detecting module at 260 nm. The eluent was a phosphate buffer (0.02M, pH 6.8, Laboratory grade, Fisher Scientific) having an ionic strength of 0.1N NaCl. The flow rate was 0.7 mL/min for the mobile phase. Polysulfonate standards (15 kDa PSS15K, 7 kDa PSS7K, 4 kDa PSS4K, 3 kDa PSS3K, American Polymer Standards Corporation) were used to correlate the apparent molecular weight.

4.6.7 Fluorescence Excited Emission Method (FEEM)

FEEM is being used extensively for characterization of NOM components that includes fulvic acid, humic acid and protein compounds. FEEM is comprised of fluorescence excitation and emission matrices, whereby each of the components of NOM have a unique fluorescence signature which is exploited to identify them. Theoretically, when the chromophore is excited through radiation of photons and then relaxed to the ground state, fluorescence occurs. The intensity is dependent on various factors including quantum yield, absorptivity, cell path length and
concentration (of chromophore). In this research, FEEM analysis was performed at the Department of Earth, Ocean and Atmospheric Sciences (Dr. Mark Johnson’s research laboratory). The details of the method are described elsewhere [62]. Typically, the scanning involves an excitation wavelength from 240 – 500 nm, consequently acquiring the corresponding emission spectrum from 250 – 600 nm. The fluorescence intensity was extracted using MATLAB code (Appendix C) along the unique excited-emission wavelengths typical to NOM components.
Chapter 5: Impact of Vacuum UV on Bio-stability & DBP Precursors

This chapter discusses the results of research investigating the impact of VUV AOP on the quality of treated surface waters. The results from various experiments using the lab scale collimated beam (Section 5.1) and bench scale flow-through reactor (Section 5.2) are presented. The results obtained while using the collimated beam setup include the kinetics of AOC increase upon irradiation with 185 nm UV. Additionally, a qualitative assessments of changes in NOM structure, which includes size exclusion chromatography and fluorescence excitation emission analysis, is discussed and correlated. The presented results of flow through experiments include AOC and BDOC, as well as changes in 24-hour chlorine demand and DBP formations analysis using uniform formation conditions. Finally, lab scale results are validated at pilot scale and discussed in Section 5.3.

5.1 Batch VUV Experiments with Collimated Beam Setup

Three different natural surface waters (i.e., Van Anda, Middle River & Cedar Creek) were used for the VUV experiments with the collimated beam setup. Van Anda and Middle River surface waters had similar DOC concentration (~5ppm) while Cedar Creek had a lower DOC concentration (~ 2.5 ppm) [see Table 4.2]. AOC, UV$_{254}$ absorbance and DOC were monitored for all the experiments.

5.1.1 AOC Formation Kinetics

Figure 5.1 shows changes in the AOC concentration of the three surface waters irradiated with VUV using the collimated beam set-up. The initial AOC concentrations in the Middle river, Van Anda and Cedar Creek water were 17.46, 16.54 and 23.66 µg/L, respectively. A consistent increase in the AOC concentration was observed with the increase of UV fluence (measured at
254 nm) for all three surface waters. Greater increases in AOC profile were observed for Van Anda and Middle River waters, having a higher DOC concentration as compared to that of Cedar Creek. The results are in good agreement with those of Bazri et al. [6], who reported a similar profile for the kinetics of AOC increase for UV/H₂O₂ process with both synthetic and natural waters.

Figure 5.1: AOC profile versus UV fluence using Middle River, Van Anda and Cedar Creek surface water. VUV is 10-15% of total UV radiance.

*Error bars represent standard deviation from triplicate experiments. Refer Appendix C for data, standard deviation, coefficient of variation and 95% confidence interval (Table C.1).

To better understand the AOC increase with UV fluence, the AOC concentration after treatment with different UV fluences were normalized by the initial AOC concentration of their respective raw water. Figure 5.2 demonstrates the normalized AOC increase with UV fluence. The AOC increased 1.5 to 2.5 times in the surface water during UV irradiation (1000 mJ/cm² max.). Similar
results were obtained for an ozonation process by *van der Kooij et al.* [30], who reported a linearly increasing AOC concentration with applied ozone dosage at low concentrations (i.e., 1.5 mg O₃/mg C).

![Graph showing the increase in AOC with UV irradiance.](image-url)

**Figure 5.2:** The increase in AOC with UV irradiance. AOC concentration at different UV dose is normalized with the initial value of respective raw water. 1, 2 & 3 represents the linear fit equations for Van Anda, Middle River and Cedar Creek respectively.

*Error bars represent standard deviation from triplicate experiments. Refer Appendix C for data, standard deviation, coefficient of variation and 95% confidence interval (Table C.2).*

The trend of the plot towards linearity suggests that the rate of reaction for AOC change follows zero-order kinetics with respect to the applied UV fluence or UV irradiation time. The deviation of the observed R² values from ‘1’, for the linear fits could be explained due to the complexity and number of steps involved in AOC measurement method, that could lead to higher error and
deviation. The UV fluence is the fluence intensity multiplied by the irradiation time. The fluence intensity was determined experimentally using iodide-iodate actinometry and was constant during the course of the experiments.

\[ \frac{d[AOC]}{dt} \propto [UV \text{ fluence}]^0 \]  

(5.1)

This suggests that a constant amount of AOC is generated with the application of 185 nm UV per unit of fluence or time, for fluences of less than 1000 mJ/cm\(^2\). Moreover, the slope of the linear profile is found to be dependent on the NOM concentration of the raw water. Higher DOC concentrations were showed to have a steeper profile and vice-versa.

\[ \text{slope} \propto \text{DOC}_{\text{initial}} \]  

(slope: slope of the linear fit of the data plot)  

(5.2)

Similar increases in AOC was observed for all the three surface waters in the range of lower UV dose (< 400 mJ/cm\(^2\)), with a gradual decrease in the steepness of the AOC profile for Cedar Creek. This could be attributed to the difference in the amount of humic substances in the surface waters. Previous studies on AOP (for ozonation process), have reported incomplete mineralization of humic substances in surface water to be responsible for the AOC increase [30]. Cedar Creek has the lowest amount of humic substances (from HPSEC, Figure 4.1 & 4.2) when compared to the other surface waters. Thus, the initial low concentration of humic species get reduced with the application of a 400 mJ/cm\(^2\) UV dose, after which further increases in UV fluence does not lead to similar increase in AOC. While Van Anda and Middle River surface waters have higher amount
of humic substances, they also show a greater relative AOC increase when compared to Cedar Creek, in the range of 400-1000 mJ/cm\(^2\) UV dose applications.

### 5.1.2 Effect of VUV Irradiation on UVA and SUVA

Employing UV\(_{254}\) absorbance and SUVA helps to identify the aromatic carbon fractions in the NOM. *Figure 5.3* shows the UV\(_{254}\) for water irradiated at different UV fluences. The UV\(_{254}\) absorbance decreased with VUV irradiation, suggesting ring cleavage, decreasing the aromatic fractions of NOM. However, the changes in UV\(_{254}\) absorbance (~ 10% for both Middle river and Van Anda; ~ 5% for Cedar Creek) were not significant at the applied UV dosage and are consistent with literature data [22]. The greater percentage decrease in UV\(_{254}\) for the Van Anda and Middle River samples suggest a greater conversion of aromatic compounds into AOC. Therefore, it could be concluded that the majority of the AOC is produced with the more aromatic organic species during the VUV process. A similar hypothesis was also suggested for the ozonation process, with AOC and UV\(_{254}\) following an inverse correlation [30]. *van der Kooij et al.* [30] explained this correlation with an argument that the aromatic rings in humic and fulvic acids, responsible for UV absorption, partially oxidizes into carboxylic acids of lower molecular weights.

The SUVA profile at different UV dosages is illustrated in *Figure 5.4*. The changes in SUVA are mainly due to the decrease in the UV absorbance (as shown earlier), as no significant change in the TOC was observed at the applied UV dosage. At a UV\(_{254}\) dosage of 1000 mJ/cm\(^2\), DOC decreased by less than 10% from its initial concentration for all the three surface waters studied.
Figure 5. 3: UV254 absorbance versus UV fluence using Middle River, Van Anda and Cedar Creek Surface water. VUV is 10-15% of total UV radiance.

Figure 5. 4: SUVA versus UV irradiance using Middle River, Van Anda and Cedar Creek Surface water. VUV is 10-15% of total UV radiance.

*Error bars in both figures represent standard deviation from triplicate experiments.*
5.1.3 Impact of VUV Treatment on AOC/TOC Ratio

The ratio of AOC to TOC can be used to represent the relative amount of readily available biodegradable carbon in NOM which could be assimilated by the bacteria. The AOC/TOC ratio increased during VUV treatment (Figure 5.5), which was primarily due to the increase in AOC. In all scenarios, the AOC/TOC ratio was seen to almost double during VUV irradiation. This shows that the VUV process inflicts changes to the TOC in a way that it has more impacts on the AOC. It was observed that the Cedar Creek AOC/TOC was higher, mainly due to the lower TOC concentration, as compared to that of the Middle river and Van Anda. Similar findings was reported by Bazri et al. [6] for a UV/H₂O₂ process, whereby a higher increase in AOC/TOC in surface water characterized by smaller molecular weight NOM species and lower DOC, but with similar initial SUVA values. Hence, it was hypothesized that the OH radicals generated during the process are mostly scavenged by larger molecules leading to the formation of smaller species. Thus, depending on the size of the primary molecules, the AOC profile will be influenced. Moreover, the highest percentage reduction in SUVA (parameter for relative aromaticity) was observed for Cedar Creek water, indicating its inverse correlation with the AOC/TOC data.
Figure 5.5: AOC/TOC ratio at different UV dosage. Middle River, Van Anda and Cedar Creek Surface water used. VUV is 10-15% of total UV radiance.

*Error bars represent standard deviation from triplicate experiments.

5.1.4 Impact on Apparent Molecular Weight Distribution of NOM Fractions

The HPSEC analysis was conducted for the Van Anda surface water after 600 and 1000 mJ/cm² of UV irradiation. The chromatographs in Figure 5.6 show that a wide range of molecular weight fractions of NOM, spanning between 500 – 4000 Da, are responsible for the AOC and BDOC increase. The apparent molecular weight fractions of NOM <300 Da correspond to the biodegradable species, i.e., AOC and BDOC. The greatest decrease was observed to occur with the humic fractions, suggesting that the larger molecular weight species comprising humic substances were the main scavengers of OH radicals. However, little change was observed in the smaller molecular weight region (<500 Da), although the AOC profile showed significant increase (Figures 5.1 and 5.2). It is important to note that HPSEC analysis is entirely dependent on the UV
absorbance of the organic molecules at 260 nm, so biodegradable organic species (i.e., non-aromatic & non-conjugated double bond compounds) may not have been detected. Further, the changes in biodegradable organic species concentration are in very low range (i.e., ranging between 20 - 40 µg/L) to be able to observe significant differences. Similar studies conducted by Bazri et al. [6] and Hem and Efraimsen [29] have reported that the organic species from all size categories contribute to AOC, although smaller molecules have a dominant role.

Figure 5. 6: Size Exclusion Chromatography of NOM fractions after 600 mJ/cm² (UV 600) and 1000 mJ/cm² (UV 1000) irradiation using Van Anda surface water.
5.1.5 FEEM Analysis

FEEM has been used for NOM characterization in marine, coastal and freshwater environments [63] and is gaining momentum in the field of drinking water [64–67]. Traditional analysis of FEEM data involves peak picking, in which the maximum intensity peak of the fluorescence is identified with its position on the excitation-emission band and correlated to a specific compound (Table 5.1). Some of the limitations of this method include its failure to account for the heterogeneity of the NOM and its neglect of some potentially relevant chromophores. A multivariate technique involving principal components analysis (PCA)[67] and parallel factor analysis (PARAFAC) [68] can be used to further extract useful information. The different NOM fractions analyzed with FEEM and their corresponding excitation-emission ranges are listed in Table 5.1.

Table 5.1: The NOM fraction with unique signature regions.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein like</td>
<td>275</td>
<td>&lt; 300</td>
<td>Amino acids, free or bound in proteins[69]</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>310</td>
<td>Tyrosine-like[63]</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>340</td>
<td>Tryptophan-like[63]</td>
</tr>
<tr>
<td>Humic like</td>
<td>260</td>
<td>380-460</td>
<td>Terrestrial humic-like- Humic Acid[63]</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>420-480</td>
<td>Terrestrial humic-like- Fulvic Acid[63]</td>
</tr>
<tr>
<td></td>
<td>300-370</td>
<td>400-500</td>
<td>Humic-like[70]</td>
</tr>
</tbody>
</table>

For simplicity and presentation purposes, the different excitation and emission regions described in Table 5.1 are represented by parameters assigned as P1 to P3 and T1 to T3 in Table 5.2.
Table 5.2: Different parameters and their excitation and emission range with unique signature region from Table 5.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Excitation wavelength (nm)</th>
<th>Emission wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>275</td>
<td>&lt; 300</td>
</tr>
<tr>
<td>P2</td>
<td>275</td>
<td>310</td>
</tr>
<tr>
<td>P3</td>
<td>275</td>
<td>340</td>
</tr>
<tr>
<td>T1</td>
<td>260</td>
<td>380 - 460</td>
</tr>
<tr>
<td>T2</td>
<td>350</td>
<td>420 - 480</td>
</tr>
<tr>
<td>T3</td>
<td>300 - 370</td>
<td>400 - 500</td>
</tr>
</tbody>
</table>

Van Anda, Middle River and Cedar Creek surface waters undergoing UV irradiation at 600 & 1000 mJ/cm² were analyzed for FEEM. The fluorescence intensity for the treated samples in different excitation-emission range (i.e., P1, P2, P3, T1, T2 & T3) were normalized with their respective intensity of raw water NOM components.
Figure 5.7: Location of various peaks based on literature data with boundaries defining excitation and emission wavelengths [71].

Figures 5.8 (a), (b) and (c) illustrate changes in the fluorescence intensity with VUV irradiance in different regions of excitation/emission wavelength for the Van Anda, Cedar Creek, and Middle River surface waters, respectively. The data represents both raw water samples and samples irradiated with VUV at 600 and 1000 mJ/cm². The data labeled on top of the columns show the percentage change in the fluorescence intensity compared to those of the corresponding raw water value for the same component. A consistent decrease was observed in net intensity for parameters P1, P2, P3, and T1, while an increase was observed for T2 & T3.

The increase in T2 and T3 can be related to the components of NOM corresponding to lower molecular size species. Further comparison of the results with the literature data presented in Table 5.1 and Figure 5.7 suggests that after VUV irradiation at the applied UV dosage (≤ 1000 mJ/cm²), there was degradation in the protein-like component of NOM fraction pertaining to amino acids,
Tyrosine-like and Tryptophan-like components. The degradation of tryptophan-like component (P3) was significantly high compared to other protein components. The humic acid component (T1) showed a decrease in all surface water, while an increase of 10-15% was observed (except Middle River, which showed an increase of approx. 2%) in the NOM fractions related to the hydrophobic acids (T2). Contrarily, Sarathy and Mohseni [5] demonstrated apparent reduction in the fractions of very hydrophobic acids (VHA) during a UV/H₂O₂ process with an initial H₂O₂ concentration of 5 and 15 mg/L and fluence of 0-2000 mJ/cm². A possible reason in the increase in T2 fractions could be its association with the slightly hydrophobic acid (SHA) fractions, that increases even though there might be reductions in VHA components (and overall decrease in the net hydrophobicity) that are not accounted in the analysis.

(a)
Figure 5.8: Changes in total fluorescence intensity in different excitation-emission region after 600 & 1000 
ml/cm² of VUV irradiance using (a) Van Anda, (b) Cedar Creek and (c) Middle River surface waters.

* The data labeled on top of the columns show the percentage change in the fluorescence intensity compared to those of the corresponding raw water value for the same component.
5.2 VUV Flow Through Reactor

Experiments using VUV flow through reactor were carried out using Middle River and Cedar Creek surface waters.

5.2.1 Impact on Biological Stability

Figures 5.9 and 5.10 describe the impact of VUV on the biological stability parameters for the treated surface water at different residence times, using the bench scale VUV flow through reactor. A greater relative AOC increase was observed with Middle River surface water as compared to Cedar Creek water. The same trend was observed for the BDOC profile, suggesting the influence of NOM concentration on the reaction rate constant. Middle River water, which contained higher initial TOC, showed more increases in both AOC and BDOC. This is in agreement with the batch study results discussed in Section 5.1. The UV fluence corresponding to the residence times of 5-40 seconds ranged between 400 and 1800 mJ/cm$^2$, which was estimated from the collimated beam studies on AOC formation from the same water sources (Figure. 5.1). The increases in both AOC and BDOC was proportional to the residence time or UV irradiance; that is, the higher the residence time or UV dose, the higher the AOC and BDOC formation. Similar observations were made by Toor and Mohseni [32] for a UV/H$_2$O$_2$ process on biodegradability of water, using a bench scale setup consisting of a flow through annular photoreactor. Their AOP treatment was conducted with 20mg/L of H$_2$O$_2$ and 500 mJ/cm$^2$ fluence, and an increase in AOC concentration from an initial value of 10 µg/L to 70µg/L and a 40% increase in BDOC was observed [32].

Thus, it could be concluded that VUV treatment, like any other AOP, enhances biodegradability of the treated water during commercially feasible range of UV dose applications for trace contaminant removal. This could be potentially mitigated by the application of a pre-treatment or
post-treatment. A considerable increase in the AOC and BDOC profiles of Cedar Creek water (with lower DOC) favors a downstream treatment. This is because lowering the DOC of the influent to VUV treatment might not be effective in improving bio-stability of the effluent. The size exclusion chromatogram data from the kinetic studies in Section 5.1.4 demonstrated that the NOM fraction species with apparent molecular weights 500 – 4000 Da contribute to AOC formation. For a pre-treatment to improve the final biostability, it would be important to remove all the NOM fractions having apparent molecular weight greater than 500 Da. Even the presence of low concentrations of such species can impact the final biostability, by increasing the AOC/BDOC. In drinking water treatment plants utilizing an ozonation process, the biodegradability of water was seen to increase, even with an integrated pre-treatment to AOP [52,58]. Hence, the treatment trains in these plants have been supported with a downstream biological treatment to AOP.
Figure 5. 9: AOC profile at different residence times for flow through reactor using Middle River and Cedar Creek surface water. The UV fluence corresponding to residence time ranged from 400 – 1800 mJ/cm².

*Error bars represent standard deviation from triplicate experiments. Refer Appendix C for data, standard deviation, coefficient of variation and 95% confidence interval (Table C.3).

Figure 5. 10: BDOC changes for VUV reactor operating at different residence times using Middle River and Cedar Creek surface water. The UV fluence corresponding to residence time ranged from 400 – 1800 mJ/cm².
Figure 5.11 demonstrates the correlation between AOC and BDOC data, at their corresponding residence times. A positive correlation is observed with both parameters (increasing together), as biodegradability of VUV treated water increases. The BDOC and AOC comparison data is in agreement with the correlation reported by Bazri et al. [6]. On the contrary, some studies [41] using heterotrophic plate count (HPC) assays to determine AOC concentration, have reported that no correlation exists between AOC and BDOC. In those studies, the AOC bioassays comprised of using pure bacterial strains, laboratory grown mixtures of Pseudomonas fluorescens P17 and Spirillum NOX. An exponential model was used to correlate the HPCs with AOC concentration. One possible explanation for the observed correlation in this study could be the use of natural consortium of the respective surface waters. This was used in the analysis of both AOC and BDOC. Since the natural microbial community thrives best in its natural environment (water source), it could best represent and correlate with the AOC and BDOC fractions.
Figure 5.11: Comparison of BDOC vs. AOC for VUV treated Middle River and Cedar Creek natural waters.

*Error bars for AOC values represent standard deviation from triplicate experiments. For BDOC values, error is reported as the maximum possible error of ± 0.2 mg/L.

The increase in AOC/TOC (Figure 5.12) was mainly due to the increase in the AOC profile with VUV reactor residence times. The change in TOC was not substantial, decreasing from 2.7 to 2.5 mg/L for Cedar Creek at a maximum residence time of 40 seconds, while Middle River decreased from 5.4 to 4.8 mg/L. The AOC/TOC trend from the collimated beam studies (Section 5.1.3) are validated with the flow through reactor results, yielding similar increases in the ratio and much greater for Cedar Creek water than for Middle River water. As discussed in Section 5.1.3 with a similar explanation, Cedar Creek water demonstrates a higher relative affinity towards biodegradability with VUV treatment.
Figure 5.12: Impact on AOC/TOC ratio at different residence times of VUV treatment. Middle River and Cedar Creek Surface water used.

*Error bars represent standard deviation from triplicate experiments.

Figure 5.13 illustrates the decrease in the UV absorbance at 254 nm and SUVA for the surface water treated with VUV at different residence times. Both UVA and SUVA decrease, suggesting a reduction in aromatic compound fractions due to the reaction with hydroxyl radicals. Here again, a higher reduction in SUVA value is observed for Cedar Creek water. Therefore, it could be concluded that SUVA and AOC/TOC from the VUV treatment might have an inverse correlation; one being representative of relative aromaticity while other representing biodegradability of the water. Therefore, the majority of the AOC increase is contributed by the disintegration of aromatic and conjugated double bond compounds of organic carbon present in water. These results are in agreement and reasoning with the kinetic study data presented in Section 5.1.2. Moreover, van der Kooij et al. [30] observed a linear correlation between the production of AOC and the decrease in
UV$_{254}$ absorbance during an ozonation process. The linear correlation was supported by the argument that the aromatic rings in humic and fulvic acids, responsible for UV absorption, partially oxidizes into carboxylic acids of lower molecular weights. These carboxylic acids are easily assimilated by bacteria accounting for the AOC [72].

![Graph showing UV absorbance and SUVA profile at different residence times of VUV treatment.](image)

**Figure 5.13:** UV absorbance (UVA) and SUVA profile at different residence times of VUV treatment. Middle River and Cedar Creek Surface water used.

*Error bars represent standard deviation from triplicate experiments.

### 5.2.2 Impact of VUV on Chlorine Demand and DBP Formations

Previous studies on UV based AOPs with respect to DBPs have demonstrated reductions in DBP-FPs, with strong UV/H$_2$O$_2$ oxidation conditions under which there is substantial reduction in DOC [32, 46]. In low to intermediate fluences and initial hydrogen peroxide concentrations of less than 20 mg/L, few conclusive results regarding DBP-FPs exist, as these studies focused on conditions
for DBPs reduction [14, 32, 46]. Some studies have made detailed accounts on the transformation of NOM during the UV/H₂O₂ AOP in terms of aromaticity and conjugated double bond along with impact on chlorine reactivity, THM-FPs and HAA-FPs [5, 14].

For VUV AOP, using a fluence range within acceptable range for trace contaminant removal, the chlorine demand was observed to increase with VUV irradiation. Higher values for Middle River water compared to Cedar Creek water was due to the higher TOC in Middle River water. The data in Figure 5.14 suggest that there are changes in the NOM fractions and the smaller molecular weight fractions are more susceptible to the chlorination reaction during the disinfection process, maintaining a residual amount of approximately 1 mg/L. The partial oxidation of the NOM fraction is seen to impact the formation of THMs. THM formation also increased with the residence time of VUV irradiation (UV fluence 400 – 1800 mJ/cm²). On the contrary, SUVA and UV₂₅₄ absorbance values, which are a proxy for THM-FPs, decreased (Figure 5.13), thereby showing an inverse correlation. As no substantial change in DOC was observed, the increase in THM formation could only be justified due to the increase in the BDOC profile (Figure 5.10); previous studies have shown BDOC to be associated with DBP precursors [74]. For a UV/H₂O₂ process, an increase in THM-FP (up to 20%) have been reported by Kleiser and Frimmel [46], with a short irradiation time of 250 minutes (emitted power 3.3 W) and initial H₂O₂ concentration of 8 mg/L. Now, VUV AOP could either be coupled with a pre-treatment such as coagulation or membrane filtration, that can reduce TOC leading to decrease in chlorine demand and THMs [5,26]. Alternatively, integrating biological treatment (such as biological activated carbon: BAC) downstream of the VUV process could address: i) DBP precursors, and ii) biodegradable by-products of NOM that reduces biostability [32,52].
Figure 5. 14: Chlorine demand (24 hours incubation) at different residence times of VUV treatment. Experiments carried out with Middle River and Cedar Creek surface waters. The corresponding UV dose ranged from 400 – 1800 mJ/cm².

Figure 5. 15: THM formations (uniform formation conditions: UFC) vs. residence times of VUV treatment. The corresponding UV dose ranged from 400 – 1800 mJ/cm².

*Error bars represent coefficient of variation from duplicate analysis.
5.3 Pilot Scale Testing with VUV Photoreactor

Pilot scale tests were carried out using RES’EAU-WaterNET mobile pilot unit in Van Anda Improvement District with their source water (Priest Lake). The piloting was carried out on August 24th, 2016. The raw water characteristics are provided in Table 5.3.

Table 5.3: Raw water characteristics of Priest Lake (collected 24th Aug. 2016)

<table>
<thead>
<tr>
<th>Water Quality</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>6.3 mg/L</td>
</tr>
<tr>
<td>UV&lt;sub&gt;254&lt;/sub&gt; absorbance</td>
<td>0.135 cm&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>4 mg/L</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;²&lt;sup&gt;-&lt;/sup&gt;</td>
<td>40 mg/L</td>
</tr>
<tr>
<td>Alkalinity (CaCO&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>70 mg/L</td>
</tr>
</tbody>
</table>

Figures 5.16 and 5.17 illustrate the AOC and BDOC profiles respectively. The experiments were performed at increased flow rates, reaching 20 L/min; both AOC and BDOC concentration increased after VUV irradiation. The initial AOC concentration in raw water is high as compared to the lab scale kinetic studies, likely because of the difference in the time and season of the study. This confirms that the AOC changes with time and season and the high AOC in this case can be attributed to the summer month of August where the biological and microbial activity is at its peak. The AOC concentration showed a consistent increase with the maximum value going up to about 3 times the initial concentration. The data from pilot study validates the lab scale results, with similar trend and consistency.
Figure 5.16: AOC profile for pilot scale testing using RES’EAU-WaterNET mobile treatment in a small community, at Van Anda Improvement District. Raw water input was obtained from Priest Lake.

*Error bars represent standard deviation from triplicate experiments. Refer Appendix C for data, standard deviation, coefficient of variation and 95% confidence interval (Table C.4).

Figure 5.17: BDOC profile for pilot scale testing using RES’EAU-WaterNET mobile treatment at Van Anda Improvement District.
5.3.1 Interaction Between Chlorides, Nitrates and NOM with VUV

Previous studies by Imoberdorf and Mohseni [22] and Furatian [75], have demonstrated that the initial water quality, in terms of presence of inorganic compounds (i.e., alkalinity, chlorides, nitrates), impact the radiation propagation at 185 nm and scavenging of hydroxyl radicals. Therefore, the raw water was also spiked with chlorides and nitrates at different concentrations to study their effects and interaction on the reaction with NOM and hydroxyl radicals. It was observed that the AOC concentrations increased in all cases (Figure 5.18, chloride 16ppm & 40 ppm and nitrates 20 ppm & 40 ppm), similar with the VUV application to the raw water in its natural state (Figure 5.16). This suggests that the presence of chlorides and nitrates had no effect on the AOC formation. On the contrary, it was expected that spiked chlorides would interfere with AOC formations and would not be showing similar increases to raw water, as it is known to be a scavenger for hydroxyl radicals. However, spiked nitrates are to remain neutral [75] to AOC formation and this was observed. Also, Van Anda surface water is characterized with higher sulfate ion concentrations as compared to the other surface waters used in the study, but similar AOC increases were observed (in the laboratory study) concluding that these ions (i.e., chlorides and sulfates) have no impact on the changes in biological stability during VUV AOP, despite their interactions with OH radicals. The effect of these background inorganic ions present in natural waters could possibly be noticeable and dominant in surface waters containing higher concentrations of NOM and an application of a lower UV dose.
Figure 5. 18: AOC concentration increases compared at different level of chlorides and nitrates. Raw water was spiked with chloride (16 & 40 ppm) and nitrate (20 & 40 ppm) for the comparison.

*Error bars represent standard deviation from triplicate experiments.
Chapter 6: Biological Activated Carbon as a Secondary Treatment

6.1 Introduction

Biological activated carbon treatment was added post VUV AOP as an abatement step to improve the water quality and issues of biological stability. This is a simple process, without the use of any chemical reagents. It involves a naturally grown microbial community that can feed on the partially oxidized fractions of NOM and smaller molecular weight compounds generated during VUV treatment. For this purpose, lab scale columns containing granulated activated carbon were designed and fabricated. Experiments were carried out with VUV and BAC treatments, separately and in combination, to compare and understand the changes in water quality.

6.1.1 Design and Fabrication of BAC Columns

Figure 6. 1: Process flow diagram of VUV Treatment and BAC process in combination.

Four identical BAC columns were fabricated to run in parallel, having an empty bed contact time (EBCT) of approximately 20 minutes. Each column was packed with granular activated carbon (Picabiol®) and the biomass was established by circulating natural waters through the columns for
at least 30 days. Sufficient biomass growth was confirmed using the procedure described by Camper et al. [76], to desorb the bacteria from GAC and then following 9215 D Standard Method [77] for the biomass measurement using the heterotrophic plate count technique (detailed procedures described in Appendix B).

Water was fed into the columns using a peristaltic pump at a flow rate of about 13 mL/min. The dimensions of each BAC column are summarized in Table 6.1.

Table 6.1: BAC column design specifications.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Acrylic plastic</td>
</tr>
<tr>
<td>Inner diameter</td>
<td>3.4 cm</td>
</tr>
<tr>
<td>Length</td>
<td>30 cm</td>
</tr>
<tr>
<td>Volume</td>
<td>270.9 mL</td>
</tr>
<tr>
<td>EBCT</td>
<td>20 minutes</td>
</tr>
</tbody>
</table>

Table 6.2: Picabiol® GAC specifications. This GAC was also used in previous study by Black [53].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Density (dry, g/mL)</td>
<td>0.18 - 0.26</td>
</tr>
<tr>
<td>Moisture (as packed, %)</td>
<td>5 max.</td>
</tr>
<tr>
<td>Ash (wt. %)</td>
<td>5% max.</td>
</tr>
<tr>
<td>Iodine No. (mg I₂/g GAC)</td>
<td>900 min</td>
</tr>
<tr>
<td>Uniformity Coefficient</td>
<td>&lt; 1.5</td>
</tr>
<tr>
<td>Effective Size</td>
<td>0.85 - 1.1 mm</td>
</tr>
</tbody>
</table>
6.2 Impact on Bio-stability

Experiments for combined VUV and BAC treatment were carried out using surface water from Van Anda and Jericho pond. Van Anda surface water had a lower AOC concentration, while Jericho pond offered a lower bio-stability with a high concentration of AOC. This enabled a better comparison and performance evaluation for the BAC columns in terms of bio-stability control. Thus, the maximum potential of BAC treatment was explored with the Jericho pond water to reduce AOC level.

Figure 6.2 demonstrates the effect on the BDOC profile after using the BAC process, post-VUV. Van Anda surface water treated at different VUV residence times was passed through the BAC column. One of the BAC columns was used as a control, whereby raw water (without VUV treatment) was continuously passed (Figure 6.2, the first column). The BDOC value increased to a maximum value of 0.59 mg/L (from initial value: 0.16 mg/L), approximately after VUV treatment (20 seconds of UV irradiation). However, after BAC treatment, the BDOC decreased by nearly 50% from the increased concentration of 0.59 mg/L. Numerous studies have reported similar results on BDOC reductions [32, 47, 48, 78] using a BAC process. For instance, in O3 - BAC combined treatment, Liao et al. [78] reported increases in BDOC from an initial value of 1.39 mg/L to 2.84 mg/L, after combining pre-ozonation, coagulation-sedimentation and post-ozonation processes. However, following the BAC process, the BDOC concentration decreased to 0.56 mg/L from 2.84 mg/L, achieving a removal of 80.3%. For studies involving a combined UV/H2O2 and BAC process, Toor and Mohseni [32] observed an increase of 50% in BDOC and from 62 to 100 µg/L in AOC after UV/H2O2 AOP; these were reduced significantly after BAC treatment. In-fact, AOC subsequently returned to its original level.
Figure 6.2: BDOC changes after VUV process (at different residence time) and BAC (EBCT 20 mins). Van Anda surface water was used. The white bar graph is BDOC data after VUV only while black bar graph denotes the BDOC profile after combined VUV and BAC.

Changes in AOC for the combined VUV-BAC treatment were demonstrated using Jericho Pond water (DOC: 6.8 mg/L, AOC: 301 µg/L). Figure 6.3 illustrates the AOC profile after different treatment processes. The AOC profile increased after the application of VUV at a fluence of 1200 mJ/cm². This decreased significantly after the BAC treatment. The AOC decreased to 1/3 of its initial concentration when raw water was passed only through the BAC column, demonstrating the robustness of BAC treatment for reducing the biodegradability of water. It should be noted that under the current practice, in a full scale drinking water treatment plant, generally an AOP is followed by a downstream treatment, to address the increased biodegradability of the AOP treated water [30, 31]. For instance, in the water treatment plants (e.g., Rotterdam water supply, Joop Rook) in the Netherlands, an ozonation process (ozone dose ranging from 1 – 3 mg/L, against taste and odor components, and color removal) is followed by least one filtration process involving biological activity (e.g., GAC filtration, dual-media filtration, rapid or slow sand filtration) [30].
In Switzerland, the drinking water treatment of Lengg in Zurich, after an ozonation upstream (ozone dose 1.1 mg/L) uses a rapid sand filtration process which has biological growth, yielding significant reduction in AOC [31].

![Figure 6.3: AOC profile after different treatment processes using Jericho pond raw water. VUV irradiance time was 20 seconds with UV dose of approximately 1200 mJ/cm² of 254 nm equivalent.](image)

*Error bars represent standard deviation from triplicate experiments. Refer Appendix C for data, standard deviation, coefficient of variation and 95% confidence interval (Table C.5).

Moreover, the DOC of raw water was observed to decrease by 11% (Figure 6.4, 4th column) when subjected to the BAC column, accounting for the biodegradable fraction of DOC. This confirms that the fraction of DOC removed during BAC treatment is the BDOC component of NOM. The DOC concentration was observed to be affected the most in the combined VUV+BAC process, confirming an increase in biodegradable fractions during VUV, which were consumed by the microbial community in the BAC column.
A qualitative assessment of the changes in NOM molecular weight distribution was performed using size exclusion chromatography for different treatment processes (Figure 6.5). The NOM fraction corresponding to humic substances decreased after VUV irradiation, but an increase was observed in the region of building blocks and lower molecular weight substances. The building blocks and lower molecular weight species of NOM play a major role in the bacterial growth potential and are known to be DBP precursors[4]. For the UV/H$_2$O$_2$ process, Sarathy and Mohseni [4] reported similar increases in the NOM components with apparent molecular weight fractions <650 Da, with applied initial H$_2$O$_2$ concentration of 15 mg/L and up to a maximum fluence of 1350mJ/cm$^2$. The combined VUV+ BAC profile addresses this issue, showing reductions in all weight fractions, including the lower molecular weight species of NOM.
Figure 6.5: Size exclusion chromatography for Jericho pond water undergone different treatment process.

An area count below the different molecular weight fractions was performed for the size exclusion chromatograph data in Figure 6.5. This enabled clarity and the understanding of minute changes in different molecular weight fraction during various treatment processes, thereby obtaining a relative quantitative analysis represented by % changes. Figure 6.6 shows an approximate increase of 4% and 21% for the T5 & T6 fractions after VUV, respectively. This change accounts for the AOC/BDOC and the DBP precursors. Furthermore, both fractions are decreased by approximately 48% (T5) and 41% (T6) after the application of BAC. This validates the results of different quantitative measurements carried out for VUV and BAC treatment, including AOC and BDOC assays.

Also, greater reductions in the T1, T2 and T3 fractions, when compared to T4, during the VUV process could be explained by their higher concentrations. Another possible hypothesis may be attributed to the higher reaction rate constants of T1-T3 than T4 with OH radicals. Although OH radicals react non-specifically, their reaction rate constants with chromophoric NOM components
are reported to be dependent on the molecular weight of NOM and its size [4, 79]. The T5 and T6 components (smallest molecular weights) are also susceptible to OH radical attack, but they have lowest rate constant and exist in the lowest concentration. Moreover, their rate of formation surpasses the rate of degradation (with disintegration of T1 – T4 components) which accounts for their increase during VUV AOP.

Figure 6.6: Area count for the chromatograph (Figure. 6.5) in various molecular weight range (T1- T6). The data labelled on top of the columns denote the percentage change with respect to original value of raw water.
6.3 Impact on DBP precursors

Chlorine demand and THM formation analyses for the coupled VUV-BAC process were carried out using Van Anda surface water. Figure 6.7 and 6.8 demonstrate the decrease in chlorine demand and THM formation (uniform formation condition) after the application of BAC as a secondary treatment. For the VUV process, chlorine demand and THM formation follow similar trend as those for Middle River surface water with a similar DOC concentration, as discussed in Section 5.2.2. The extent of THM decrease after BAC treatment is largest when the residence time in the VUV treatment was 20 seconds and the same trend could be observed in the chlorine demand data (Figure 6.7). A possible explanation for this phenomena could be the more biodegradable fractions formed at 20 seconds of VUV irradiation, which could be easily assimilated by the bacteria through BAC treatment. Toor and Mohseni [32], in their study of DBP reduction using a BAC system for UV/H2O2 AOP, concluded that combining BAC with an AOP, like UV/H2O2, is a viable option. Combined AOP- BAC is a superior alternative to a standalone AOP, as it, i) reduces the chorine demand during secondary disinfection process, thereby reducing DBPs, and ii) addresses the reduced biostability of water after AOP, with its biomass feeding on the additional AOC/BDOC matter. This significantly improves the final water quality to be discharged into the distribution system. Overall, the results show great promised for the application of BAC after VUV treatment, and the fact that optimization of the BAC treatment (i.e., optimum contact time, temperature) could further improve the water quality in terms of biodegradability and DBP precursors.
Figure 6. 7: Chlorine demand after VUV process at different residence times followed by BAC treatment (EBCT 20 mins) using Van Anda surface water. The white bar graph is Cl$_2$ demand after VUV only while black bar graph denotes the Cl$_2$ demand after combined VUV and BAC.

Figure 6. 8: THM-UFC profile after VUV at different residence times and BAC treatment (EBCT 20mins) using Van Anda surface water. The white bar graph is THMs after VUV only while black bar graph denotes the THMs after combined VUV and BAC.

*Error bars represent coefficient of variation from duplicate analysis.
The impacts on aromaticity with the combined VUV-BAC treatment process were also monitored with UV\textsubscript{254} and SUVA analysis. Figure 6.9 illustrates the changes in the UV absorbance and SUVA for the VUV and VUV + BAC treated Van Anda water. The aromatic compounds decreased during the VUV process, which was in proportion to the residence time of UV irradiation, as previously observed in Section 5.2.1. The fraction of aromatic compounds was further decreased after passing through the BAC columns.

Figure 6.9: UV absorbance and SUVA for VUV process (only) and combined VUV + BAC process using Van Anda surface water.

*Error bars represent standard deviation from triplicate experiments.*
Chapter 7: Conclusion and Recommendations

In this research, changes in the water quality (i.e., biodegradability, aromaticity and DBPs) during VUV advanced oxidation of various surface waters was investigated. Experiments were carried out at laboratory and pilot scales, with different setups involving batch and continuous processes. Furthermore, biological activated carbon treatment was evaluated downstream as a potential secondary process to remediate the water quality, aiming to reduce the AOC/BDOC and DBP precursors.

7.1 Overall Conclusion

- The kinetic study data of AOC with UV fluence using surface water from various sources with different TOC concentration illustrated that AOC formation rates followed a zero-order reaction with the applied UV fluence:

\[
\frac{d[AOC]}{dt} \propto [UV \text{ fluence}]^0
\]  

(5.1)

- The slope of the linear fit for AOC profile vs. UV dosage was dependent on the NOM concentration. Hence, a steeper AOC profile was yielded for surface waters containing higher DOC:

\[
slope \propto \text{DOC}_{\text{initial}} \quad (slope: \text{ linear fit of AOC profile with UV dose})
\]  

(5.2)

- AOC was observed to increase 1.7 - 2.5 times during the course of VUV treatment (max UV dosage 1000 mJ/cm², at 254nm equivalent) for all the surface waters studied.

- The data from the bench scale flow through reactor showed an increase in AOC and BDOC, which was proportional to the residence time of VUV irradiation. This confirmed the decrease in biological stability of VUV treated surface water, hence a need for secondary treatment post VUV irradiation.
• The chlorine demand and THM formation (at uniform formation conditions) increased with the VUV irradiance time as a result of the partial oxidation of NOM at an applied UV dosage and an increase in the smaller molecular weight fractions.

• Lab scale studies were validated in pilot testing at increased flow rates with similar trends and increase in the bio-stability parameters. In both studies, an increase of 1.5 – 2 times was observed in AOC concentration.

• AOC increase was similar at increased concentration of chlorides, nitrates and sulfates, suggesting that these ions had no noticeable and apparent impact on the reaction of hydroxyl radical and NOM with respect to impacts on biodegradability.

• A positive correlation between the AOC and BDOC profile was established with both parameters increasing together.

• AOC and BDOC increases, even for a low DOC source water (2-3 ppm), confirms post treatment over pre-treatment to resolve the impact on biostability for VUV treated surface water.

• The BAC application was demonstrated to be a successful treatment downstream of the VUV process. The AOC and BDOC concentrations decreased significantly, along with decreases in the chlorine demand and DBP precursors.

• Qualitative assessment of the NOM fractions demonstrated a range of molecular weight fractions responsible for AOC/BDOC increase after VUV AOP, which was successfully mitigated by application of biological process involving BAC.
7.2 Recommendations and Future Work

- VUV treatment leads to an increase in the AOC of the treated water which can affect the bacterial re-growth potential downstream, but further assessment of its application in the drinking water system can help to better understand its impact on bio-stability. For small system applications, where the treatment system is decentralized or point of entry (POE), VUV may not significantly impact the bacterial re-growth potential. The increase of AOC will be prominent when the age of the water along the distribution system and storage stretches for several days. As bacterial re-growth could also be a function of the size of the system, the volume of the storage involved, distance the water must travel, average daily temperature, etc. Thus, it will be important to consider all these factors to determine the real impact of VUV process application for a community.

- Biological activated carbon treatment demonstrated that the issue of bio-stability along with chlorine demand and THMs formation potential could be easily resolved when implemented as a secondary treatment. In practice, mostly any AOP (involving ozone or UV/H$_2$O$_2$) is followed by a biological process. Hence, BAC treatment could be optimized to further improve the biodegradability of the final effluent. It would be interesting to investigate the effect of the water temperature on the BAC process, as there can be a considerable difference in the water temperature during summer and winter. Furthermore, a study of the bacterial and microbial community present in the BAC could be important for the design of a more biologically efficient column.
Bibliography


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2011.


[33] D. van der Kooij, A. Visser, and W. A. M. Hijnen, “Determining the concentration of easily assimilable organic carbon in drinking water Determining the concentration of easily


Appendices

A: Actinometry

Iodide-Iodate Actinometry was used to measure the 254-nm incident irradiance for the collimated beam setup. These instruction and method are compiled by Laith Furatian from our research group, modified from procedures written by Drs. J. Boltan and M. Stefan, as a part of protocol drafted for AWWA Research Foundation Project No. 2593, headed by Prof. James P. Malley, Jr., University of Hampshire.

A.1 Procedure

- Stock solution was prepared: 0.60 M KI, 0.10 M KIO₃ and 0.01 M Na₂B₄O₇·10H₂O in DI water.

- Using the spectrophotometer, the 1cm absorbance was measured for the stock solution using a 10 mm pathlength quartz cuvette at 300 nm and 352 nm. The absorbance value for 300 nm should be 0.58 and at 352 nm should be 0.02. This serves as quality check, if the difference in measured value was >10%, fresh stock solution should be prepared. The initial absorbance at 352 nm served as the blank \( A_{352}^{\text{blank}} \) against which the irradiated solution was compared.

- The internal diameter \( d \) of the beaker used for irradiance was measured using a Vernier calipers and noted.

- 75mL (sample volume) of the stock solution prepared was irradiated for 30 seconds (exposure time) on the collimated beam setup (with both 185 nm and 254 nm) and the absorbance at 352 nm was measured, calling this - \( A_{352}^{\text{sample}} \).
A.2 Calculations

- The Area was calculated using the internal diameter of the beaker.
- The general formula for the irradiance is $E' \text{ (m W/cm}^2\text{)}$:

$$E' = 23.373 \frac{[A_{352\text{(sample)}} - A_{352\text{(blank)}}]}{\text{Area(cm}^2\text{)} \times \text{Exposure time (s)}} \times \text{Sample Volume (mL)} \quad (A.1)$$

A.3 Results

Table A.1: Actinometry results.

<table>
<thead>
<tr>
<th>Irradiation time (s)</th>
<th>30</th>
<th>30</th>
<th>30</th>
<th>45.44 (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel diameter (mm)</td>
<td>45.26</td>
<td>45.26</td>
<td>45.78</td>
<td>45.64</td>
</tr>
<tr>
<td>Vessel area (cm$^2$)</td>
<td>16.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Volume (mL)</td>
<td>75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank Absorbance at 352 nm</td>
<td>0.022</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>Absorbance at 352 nm</th>
<th>Average</th>
<th>STD DEV</th>
<th>Irradiance</th>
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<tbody>
<tr>
<td>1</td>
<td>0.272</td>
<td>0.278</td>
<td>0.282</td>
<td>0.277</td>
</tr>
<tr>
<td>2</td>
<td>0.275</td>
<td>0.277</td>
<td>0.285</td>
<td>0.279</td>
</tr>
<tr>
<td>3</td>
<td>0.287</td>
<td>0.288</td>
<td>0.281</td>
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</table>

<table>
<thead>
<tr>
<th>Irradiance Average $0.932$ m W/cm$^2$</th>
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</thead>
<tbody>
<tr>
<td>STD DEV $0.014$</td>
</tr>
</tbody>
</table>
B: Biomass analysis

Biomass analysis was performed to quantify the biological growth on the GAC surface in the biofiltration columns. HPC method was used for the biomass quantification as per 9215 D Standard Method, APHA 1992.

B.1 Desorption of Biomass from GAC

Stock solution was prepared using the following chemicals listed in Table B.1.

Table B. 1: List of chemicals with the concentration for solution to desorb biomass from activated carbon.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zwittergent 3-12</td>
<td>10^{-6}M</td>
</tr>
<tr>
<td>EGTA*</td>
<td>10^{-3}M</td>
</tr>
<tr>
<td>Tris Buffer</td>
<td>0.01M, pH 7.0</td>
</tr>
<tr>
<td>Peptone</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

*Ethylene-bis (oxyethylenenitrilo) tetraacetic acid

0.1 g ww (wet-weight) activated carbon sample from each column was homogenized for 3 min at 16,000 rpm at 4°C, in 100 ml stock solution.

B.2 Membrane Filtration Technique 9215 D Standard Method

Medium: R2A agar

- Preparation of plates: 5mL portion of sterile medium was dispensed onto 50 × 9 mm petri dishes. It was kept to solidify at room temperature. (Then could be stored inverted in a plastic box in a refrigerator for up-to 2 weeks)
- Sample size: Volume to be filtered 20-200 CFU per filter.
• Procedure: Appropriate volume was filtered through sterile 47mm, 0.45micron pore-diameter, grid membrane. Then filter membrane was placed on the plate. The funnel was rinsed with 20-30 mL portions of sterile dilution water thrice, in between each of the samples.

• Incubation: R2A agar medium needs 7 days incubation at 28°C.

B3. Results
Biomass was quantified in CFU per gram of GAC ww. *Table B.2* lists the results for each column.

*Table B. 2: Biomass quantification values determined for BAC columns using HPC method.*

<table>
<thead>
<tr>
<th>Column</th>
<th>Biomass in CFU/g of GAC ww</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column 1</td>
<td>$12.2 \times 10^7$</td>
</tr>
<tr>
<td>Column 2</td>
<td>$6.6 \times 10^7$</td>
</tr>
<tr>
<td>Column 3</td>
<td>$15.5 \times 10^7$</td>
</tr>
<tr>
<td>Column 4</td>
<td>$31.1 \times 10^7$</td>
</tr>
</tbody>
</table>
C: Statistical Analysis

The experiments for AOC formation using the collimated beam apparatus and the flow through reactor were performed in triplicates. To determine the AOC concentration in all cases, each sample was divided into duplicates for culturing bacteria (incubation stage). Then, for the cell count measurements, each incubated sample was further divided into triplicates and analyzed using flow cytometry. Thus, the final AOC concentration was reported as a mean of six values.

Considering the complexity and number of stages involved in AOC analysis, the reproducibility of the data plots was determined in terms of the standard deviation and coefficient of variation. Also, the 95% confidence level, two-tailed interval was calculated for the AOC concentrations. Equation C.1 was used calculated the interval [80].

\[ \mu \pm t \times \frac{\sigma}{\sqrt{n}} \]  

(C.1)

Here, \( \mu \) represents the mean, \( \sigma \) is the standard deviation and \( t \) is the 95% confidence interval value, estimated based on the t-distribution (two-tailed) [80,81].
C1. Batch VUV Experiments

*Table C.1* lists the data from the kinetic study of AOC formation (*Figure 5.1*) using the collimated beam apparatus and *Table C.2* lists the data for the normalized AOC values from *Figure 5.2*, as discussed in *Section 5.1.1*. Experiments with all surface waters were performed in triplicates. Since, any AOC concentration is reported as an average of six values, the total samples (n) from triplicate experiments for each AOC data point was 18. The ‘t’ value obtained from the t-distribution (two tailed) for 95% confidence interval was ‘2.11’.

*Table C.1: AOC concentration values from the kinetic study using the collimated beam apparatus.*

<table>
<thead>
<tr>
<th>Fluence (mJ/cm²)</th>
<th>Middle River (n=6×3)</th>
<th>Van Anda(n=6×3)</th>
<th>Cedar Creek (n=6×3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AOC (µg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>S.D.</td>
<td>C.V.</td>
</tr>
<tr>
<td>Raw</td>
<td>17.46</td>
<td>1.93</td>
<td>11</td>
</tr>
<tr>
<td>100</td>
<td>19.45</td>
<td>2.41</td>
<td>12</td>
</tr>
<tr>
<td>200</td>
<td>21.5</td>
<td>1.96</td>
<td>9</td>
</tr>
<tr>
<td>400</td>
<td>26.35</td>
<td>1.43</td>
<td>5</td>
</tr>
<tr>
<td>600</td>
<td>30.62</td>
<td>3.2</td>
<td>10</td>
</tr>
<tr>
<td>800</td>
<td>33.5</td>
<td>4.47</td>
<td>13</td>
</tr>
<tr>
<td>1000</td>
<td>36.79</td>
<td>6.15</td>
<td>17</td>
</tr>
</tbody>
</table>

*S.D. is the standard deviation, C.V. is the coefficient of variation and 95% interval represents two tailed interval.*

*Data plotted in *Figure 5.1*.  

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Table C. 2: Normalized AOC values from the kinetic study using collimated beam apparatus.

<table>
<thead>
<tr>
<th>Fluence (mJ/cm²)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AOC (µg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Middle River (n=6×3)</td>
<td>Van Anda(n=6×3)</td>
<td>Cedar Creek (n=6×3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>S.D.</td>
<td>C.V.</td>
<td>95% interval</td>
<td>Mean</td>
<td>S.D.</td>
</tr>
<tr>
<td>Raw</td>
<td>1.00</td>
<td>0.16</td>
<td>16</td>
<td>0.08</td>
<td>1.00</td>
<td>0.16</td>
</tr>
<tr>
<td>100</td>
<td>1.11</td>
<td>0.18</td>
<td>17</td>
<td>0.09</td>
<td>1.31</td>
<td>0.27</td>
</tr>
<tr>
<td>200</td>
<td>1.23</td>
<td>0.18</td>
<td>14</td>
<td>0.09</td>
<td>1.47</td>
<td>0.32</td>
</tr>
<tr>
<td>400</td>
<td>1.51</td>
<td>0.19</td>
<td>12</td>
<td>0.09</td>
<td>1.67</td>
<td>0.22</td>
</tr>
<tr>
<td>600</td>
<td>1.75</td>
<td>0.27</td>
<td>15</td>
<td>0.13</td>
<td>2.08</td>
<td>0.27</td>
</tr>
<tr>
<td>800</td>
<td>1.92</td>
<td>0.33</td>
<td>17</td>
<td>0.17</td>
<td>2.13</td>
<td>0.29</td>
</tr>
<tr>
<td>1000</td>
<td>2.11</td>
<td>0.42</td>
<td>20</td>
<td>0.21</td>
<td>2.43</td>
<td>0.28</td>
</tr>
<tr>
<td>Slope of linear fit</td>
<td>1.2 ×10⁻³</td>
<td>0.5 ×10⁻³</td>
<td>39 ×10⁻³</td>
<td>0.2 ×10⁻³</td>
<td>1.5 ×10⁻³</td>
<td>0.4 ×10⁻³</td>
</tr>
</tbody>
</table>

*S.D. is the standard deviation, C.V. is the coefficient of variation and 95% interval represents two tailed interval.

Data plotted in Figure 5.2.
C2. VUV Flow Through Reactor

*Table C.3* lists the data for the AOC formations during VUV irradiation (*Figure 5.9*) using the bench-scale flow through reactor, as discussed in *Section 5.2.1*. Experiments with all surface waters were performed in triplicates. Since, any AOC concentration is reported as an average of six values, the total samples (n) from triplicate experiments for each AOC data point was 18. The ‘t’ value obtained from the t-distribution (two tailed) for 95% confidence interval was ‘2.11’.

**Table C. 3: AOC formations during VUV AOP using the flow through reactor at different residence time.**

<table>
<thead>
<tr>
<th>Residence time (sec)</th>
<th>Middle River (n=6×3)</th>
<th>Cedar Creek (n=6×3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AOC (µg/L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>S.D.</td>
</tr>
<tr>
<td>Raw</td>
<td>17.46</td>
<td>1.93</td>
</tr>
<tr>
<td>5</td>
<td>29.29</td>
<td>1.76</td>
</tr>
<tr>
<td>10</td>
<td>35.81</td>
<td>2.99</td>
</tr>
<tr>
<td>20</td>
<td>43.34</td>
<td>4.99</td>
</tr>
<tr>
<td>40</td>
<td>57.51</td>
<td>6.45</td>
</tr>
</tbody>
</table>

*S.D. is the standard deviation, C.V. is the coefficient of variation and 95% interval represents two tailed interval.

Data plotted in *Figure 5.9*. 

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C3. VUV Pilot Testing

Table C.4 lists the data for the AOC formations (Figure 5.16) during VUV AOP pilot study (performed in triplicates) at increased flow rates (upto 20 L/min), as discussed in Section 5.3.1. Since, any AOC concentration is reported as an average of six values, the total samples (n) from triplicate experiments for each AOC data point was 18. The ‘t’ value obtained from the t-distribution (two tailed) for 95% confidence interval was ‘2.11’.

Table C.4: AOC formations during VUV AOP pilot study at different residence time.

<table>
<thead>
<tr>
<th>Residence time (sec)</th>
<th>AOC (µg/L)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Van Anda Piloting (n=6×3)</td>
<td>Mean</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
<td>37.88</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>58.22</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>80.06</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>84.45</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td>107.21</td>
</tr>
</tbody>
</table>

*S.D. is the standard deviation, C.V. is the coefficient of variation and 95% interval represents two tailed interval.

Data plotted in Figure 5.16.
C4. Combined VUV and BAC

*Table C.5* lists the data for the AOC concentrations (*Figure 6.3*) for integrated VUV and BAC treatment (performed in triplicates, as discussed in *Section 6.2*. The experiments were performed with Jericho Pond surface water. Since, any AOC concentration is reported as an average of six values, the total samples (n) from triplicate experiments for each AOC data point was 18. The ‘t’ value obtained from the t-distribution (two tailed) for 95% confidence interval was ‘2.11’.

*Table C. 5: AOC concentration change for combined VUV and BAC treatment.*

<table>
<thead>
<tr>
<th>Treatment Processes</th>
<th>AOC (µg/L)</th>
<th>Jericho Pond Surface Water (n=6×3)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>S.D.</td>
<td>C.V.</td>
<td>95% interval</td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>300.94</td>
<td>33.37</td>
<td>11</td>
<td>16.60</td>
<td></td>
</tr>
<tr>
<td>VUV</td>
<td>342.04</td>
<td>33.04</td>
<td>10</td>
<td>16.43</td>
<td></td>
</tr>
<tr>
<td>VUV + BAC</td>
<td>110.94</td>
<td>13.22</td>
<td>12</td>
<td>6.57</td>
<td></td>
</tr>
<tr>
<td>BAC</td>
<td>100.52</td>
<td>10.85</td>
<td>11</td>
<td>5.40</td>
<td></td>
</tr>
</tbody>
</table>

*S.D. is the standard deviation, C.V. is the coefficient of variation and 95% interval represents two tailed interval. Data plotted in *Figure 6.3*. 


D: FEEM Analysis

The fluorescence intensities along the unique excited-emission wavelengths typical to NOM components (i.e., P1, P2, P3, T1, & T2, from Tables 5.1 & 5.2) were extracted using the MATLAB code developed as described below.

clear all; clc;
data=xlsread('C:\backup\my work\file.xlsx');

% fluorescence intensity file: file.xlsx

% P1 (275/<300)
u1=275;
u2=300;

idx_emission_min=2;
idx_emission_max=find(data(2:end,1) > nu2,1)-1;
u3=data(idx_emission_max,1);

idx_excitation=find(data(1,2:end)==nu1,1);

figure(1);
plot(data(idx_emission_min:idx_emission_max,1),data(idx_emission_min:idx_emission_max,idx_excitation))

emit_val_P1=trapz(data(idx_emission_min:idx_emission_max,1),data(idx_emission_min:idx_emission_max,idx_excitation))

% P2 (275/310)
u1=310;
u2=275;

idx_emission_min=idx_excitation;
idx_emission_max=find(data(2:end,1)>nu2,1);
val1=data(idx_emission-1,idx_excitation);
val2=data(idx_emission,idx_excitation);
diff=data(idx_emission,1)-data(idx_emission-1,1);

emit_val_P2=val1+(val2-val1)/diff*(nu2-data(idx_emission-1,1))

% P3 (275/340)
u1=340;
u2=275;

idx_emission_min=idx_excitation;
idx_emission_max=find(data(2:end,1)>nu2,1);
val1=data(idx_emission-1,idx_excitation);
val2=data(idx_emission,idx_excitation);
diff=data(idx_emission,1)-data(idx_emission-1,1);

emit_val_P3=val1+(val2-val1)/diff*(nu2-data(idx_emission-1,1))

% T1 (260/380-460)
u1=260;
u2=380;
u3=460;
idx_emission_min=find(data(2:end,1) >= nu_emit_min,1);
idx_emission_max=find(data(2:end,1) > nu_emit_max,1)-1;

idx_excitation=find(data(1,2:end)==nu_excit,1);
figure(2);
plot(data(idx_emission_min:idx_emission_max,1),data(idx_emission_min:idx_emission_max,idx_excitation))

emit_val_T1=trapz(data(idx_emission_min:idx_emission_max,1),data(idx_emission_min:idx_emission_max,idx_excitation))

%T2 (350/420-480)
nu_excit=350;
nu_emit_min=420;
nu_emit_max=480;

idx_emission_min=find(data(2:end,1) >= nu_emit_min,1);
idx_emission_max=find(data(2:end,1) > nu_emit_max,1)-1;

idx_excitation=find(data(1,2:end)==nu_excit,1);
figure(3);
plot(data(idx_emission_min:idx_emission_max,1),data(idx_emission_min:idx_emission_max,idx_excitation))

emit_val_T2=trapz(data(idx_emission_min:idx_emission_max,1),data(idx_emission_min:idx_emission_max,idx_excitation))

%T3 (300-370/400-500)
nu_excit_min=300;
nu_excit_max=370;
nu_emit_min=400;
nu_emit_max=500;

idx_emission_min=find(data(2:end,1) >= nu_emit_min,1);
idx_emission_max=find(data(2:end,1) > nu_emit_max,1)-1;

idx_excit_min=find(data(1,2:end)<nu_excit_min,1)-1;
idx_excit_max=find(data(1,2:end)<=nu_excit_max,1);

x=data(idx_emission_min:idx_emission_max,idx_excit_max:idx_excit_min);
y=data(1,idx_excit_max:idx_excit_min);
F=data(idx_emission_min:idx_emission_max,idx_excit_max,idx_excit_min);
emit_val_T3=trapz(y,trapz(x,F,1))

[X,Y] = meshgrid(x,y);figure(4);surf(X,Y,F)