

# **ENVIRONMENTAL IMPACT OF ZEBRA MUSSEL CONTROLS IN NUCLEAR POWER PLANTS**

by

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## THESIS EXAMINATION INFORMATION

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An oral defense of this thesis took place on April 1, 2020 in front of the following examining committee:

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The above committee determined that the thesis is acceptable in form and content and that a satisfactory knowledge of the field covered by the thesis was demonstrated by the candidate during an oral examination. A signed copy of the Certificate of Approval is available from the School of Graduate and Postdoctoral Studies.

## **ABSTRACT**

Industries that rely on the Great Lakes for cooling have battled the zebra mussel infestation for years. With increasing emphasis on environmental sustainability, decision-makers need to consider more than just monetary cost. This work compares two methods of zebra mussel control that are used in Nuclear Power Plants (NPP), chlorine and ozone, through life cycle assessment. The GHGenius model was used to estimate greenhouse gas (GHG) emissions from each life cycle stage, from control agent production, through delivery, to end use of each method. The goal of the study is to estimate the amount of GHG produced per unit of water treated. While GHG analysis does not portray the entire picture for environmental impacts, it can be used to help future operators select a more environmentally friendly solution to zebra mussel control. For large NPPs, chlorination was found to perform better. Other considerations need to be considered for smaller reactors.

**Keywords:** nuclear; environment; mussel; control; LCA

## **AUTHOR'S DECLARATION**

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## **STATEMENT OF CONTRIBUTIONS**

The creative works and/or inventive knowledge described in this thesis was performed under the supervision and guidance of Dr. Jennifer McKellar and Dr. Glenn Harvel. Both supervisors provided critical feedback and helped shape the research, analysis, and manuscript.

I hereby certify that no part of this thesis has been published or submitted for publication. I have used standard referencing practices to acknowledge ideas, research techniques, or other materials that belong to others.

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## LIST OF ABBREVIATIONS AND SYMBOLS

AMRs	Advanced Modular Reactors
BWR	Boiling Water Reactor
CaCO <sub>3</sub>	Calcium Carbonate
CANDU	Canada Deuterium Uranium
CCS	Carbon Capture and Sequestration
CH <sub>4</sub>	Methane
ClO <sub>2</sub>	Chlorine Dioxide
CNSC	Canadian Nuclear Safety Commission
CO <sub>2</sub>	Carbon Dioxide
CO <sub>2</sub> e	Carbon Dioxide Equivalent
COG	CANDU Owners Group
DDMAC	Didecyl Dimethyl Ammonium Chloride
DNGS	Darlington Nuclear Generating Station
EPRI	Electric Power Research Institute
GHG	Greenhouse Gas
GWP	Global Warming Potential
H <sup>+</sup>	Hydrogen Ion
H <sub>2</sub>	Hydrogen Gas
H <sub>2</sub> O	Water
H <sub>2</sub> O <sub>2</sub>	Hydrogen Peroxide
HAA	Haloacetic Acids
HO <sub>2</sub> <sup>-</sup>	Hydroperoxyl Radical
HOCl	Hypochlorous Acid
ICAIS	International Conference on Aquatic Invasive Species
IESO	Independent Electricity System Operator
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
LEM	Lifecycle Emissions Model
LNG	Liquefied Natural Gas
MF	Microfiltration

MWh	Megawatt Hour
N <sub>2</sub> O	Nitrous Oxide
NaCl	Sodium Chloride (salt)
NaOCl	Sodium Hypochlorite
NaOH	Sodium Hydroxide
NPP	Nuclear Power Plant
NRCan	Natural Resources Canada
O <sub>2</sub>	Oxygen
O <sub>3</sub>	Ozone
OCl <sup>-</sup>	Hypochlorite Ion
OCS	Octachlorostyrene
OH <sup>-</sup>	Hydroxyl Radical
OPEX	Operating Experience
OPG	Ontario Power Generation
PHWR	Pressurized Heavy Water Reactor
PWR	Pressurized Water Reactor
QAC	Quaternary Ammonium Compound
SMRs	Small Modular Reactors
t CO <sub>2</sub> e/m <sup>3</sup>	Tonne Carbon Dioxide Equivalent per Cubic Meter
THM	Trihalomethane
TOC	Total Organic Carbon
TRC	Total Residual Chlorine
TRO	Total Residual Oxidants
UF	Ultrafiltration
UV	Ultraviolet
WTP	Water Treatment Plant

# 1. INTRODUCTION

## 1.1 BACKGROUND

Industries that rely on lake water for cooling, such as nuclear power plants (NPPs), have battled the zebra mussel infestation of the Great Lakes for many years.<sup>1,2</sup> In the past, monetary cost was one of the major factors in decision making with respect to the method of zebra mussel control.<sup>2-5</sup> However, with increasing emphasis on environmental sustainability, would the decisions of the past be different if they were made today? The decisions made for adopting certain technologies were driven by the information and requirements at the time, which for the nuclear industry were the principles of safety and cost. Environmental protection was a major factor in nuclear design in the early years from the point of view of addressing the radiological impact of a release upon the environment. Hence, design decisions were made for protection systems such as containment to address such an impact. Environmental considerations, such as non-radiological contamination, were considered to be addressed through standard industry practices at the time. Thus, the nuclear industry would address environmental problems in much the same way as any other industry would with the added constraints of protecting the public and environment from radiation release.

As zebra mussels first emerged in the Great Lakes in the 1980s, the main concern was for providing adequate cooling water to ensure safe operation of the facility. This required the mitigation or removal of the zebra mussels from the water intakes and the preventing of the zebra mussels from entering deeper into the water

environments of the plant. Due to the significant growth rate of zebra mussels, the potential for a significant impact on cooling capability was possible and this resulted in the need to act quickly to adopt solutions. Also, at this time, many of the environmental concerns that are considered today, specifically climate change and the impact of CO<sub>2</sub> emissions, were not well understood, and in some cases, not even believed. Thus, solutions were adopted without the detailed considerations that might occur today in the decision making process.

#### 1.1.1 Zebra Mussels: What are they, their origins, why are they a problem?

Dreissenid Mussels (zebra and quagga mussels) are invasive species of mussels which can foul virtually all solid substrate within an aquatic system.<sup>1</sup> For industrial plants, this includes external structures associated with water intakes along with internal surfaces of most pipes.<sup>6</sup> If left uncontrolled, clumps of zebra mussels can cause restriction to flow, plugging of the condenser, reduced heat transfer, damage to equipment, and potential under deposit degradation of both metal and concrete.<sup>6,7</sup> Generally, attachment is observed in flows less than 2m/s.<sup>8</sup>

Zebra mussels were first introduced in 1986 and by 1990, they were found in all the Great Lakes.<sup>1,9,10</sup> A second species of invasive mussels, quagga, was first spotted in 1989 in Lake Erie, but was not recognized until 1991, and was established in all the Great Lakes by 2005.<sup>9,10</sup> Quagga mussels have since replaced zebra mussels as the dominant species in Lake Ontario. General differences include: ability to attach to soft substrates, found in greater depths and colder water temperatures, high

population density (55000/m<sup>2</sup> vs 32000/m<sup>2</sup>), requiring less force to dislodge.<sup>9-11</sup>

Today, the term *zebra mussels* encompasses both zebra and quagga mussels.<sup>1,10-12</sup>

### 1.1.2 Relevance to the Canadian Nuclear Industry

Today, with the issues of zebra mussels, and other potential macrobiological species, along with the need to be more proactive in dealing with environmental issues including climate change, the Canadian nuclear industry needs to re-examine some of the decisions made in the past. In some cases, such as Pickering, the remaining plant life is too short to justify a change in systems. In other cases, such as the Bruce or Darlington units, an additional 30 years of operating life after refurbishment means that there will be an on-going need to protect the water systems from zebra mussels and other types of fouling material. Thus, the control systems could be changed or updated for more optimal control and a reduced impact on the environment.

Further, Canada is experiencing a strong interest in small modular reactors (SMRs) and advanced modular reactors (AMRs) for near future deployment.<sup>13</sup> SMRs are light water type reactors usually of an integral design, and AMRs are non-light water reactors (molten salt, liquid metal coolants).<sup>14</sup> These reactor designs will all require cooling, albeit on a lower scale per unit than a full plant, but the requirement is still there and hence the potential for zebra mussels to cause problems will remain. In fact, it is possible that the zebra mussel problem may be more severe for SMRs since the water intake flow rates are much lower and the

lower velocity and smaller diameter in the intake pipe might encourage faster adherence and growth of the zebra mussels. Thus, the new designs will need protective systems and it is an opportune time to consider the environmental impact of those protective systems.

## 1.2 OBJECTIVE

This research compares two different methods of zebra mussel control that are widely used today (i.e., chlorine and ozone)<sup>2</sup> through life cycle assessment (LCA). The goal of the study is to estimate the amount of greenhouse gas (GHG) produced by zebra mussel control per unit of water treated. It is recognized that the measuring and reporting of GHG emissions is only one of the contributors to the overall environmental impact and thus, does not paint a complete picture. GHG and LCA will be elaborated further in Section 3.2.2.3 and Section 3.2.2.4. Completion of this study is expected to help future NPP operators select a more environmentally friendly solution to zebra mussel control.

## 1.3 LAYOUT OF THESIS

This thesis will first explore the history and biology of zebra mussels, how it came to be a problem in the Great Lakes, and what industries have been doing about the zebra mussel infestation problem, along with some discussion on the pros and cons for each method (Chapter 2). Then the thesis will do a brief overview on life cycle assessment (Chapter 3) before getting into performing a life cycle assessment on two zebra mussel control methods, chlorination and ozonation. The results will then

be presented along with a detailed discussion (Chapter 4). Important factors will then be studied in detail for sensitivity analysis. The thesis will conclude with a few parting thoughts on zebra mussel controls, how it impacts the environment and the nuclear industry, and highlight some suggestions for future work (Chapter 5).

## 2. DETAILED BACKGROUND

### 2.1 ZEBRA MUSSELS (HISTORY AND BIOLOGY)

Zebra mussels were first introduced to North American Great Lakes in the mid 1980s by the ballast of transoceanic ships travelling to and from the Black, Caspian, and Azov Seas of Eastern Europe.<sup>9</sup> A related species, the Quagga mussel, was introduced in a similar fashion in the late 1980s from the Dneiper River area of Ukraine<sup>9</sup>. Biologically, these two species are very similar and the control methods are identical.<sup>11</sup> As of 2012, Quagga mussels represent more than 95% of the Dreissenid mussel population in Lake Ontario.<sup>6</sup> A summary of the biological differences between zebra and quagga mussels can be found in Table 1.

*Table 1 – Biological difference between Zebra and Quagga Mussels<sup>9</sup>:*

	<b>Zebra</b>	<b>Quagga</b>
Length	Up to 15mm	Up to 4cm
Attachment	Hard substrate	Hard and soft substrates
Depth	8m to 110m	Up to 130m
Time Between Veliger and Pediveliger* Stages	6-9 weeks	Similar
Time to Adult	12 week	Similar
Reproductive Peak	Spring	Spring
Temperature Range	12-30°C	9 to <30°C. Can be as low as 6°C. High mortality at 30°C.

\*Pediveliger is defined as when the shell starts to form

While Dreissenid mussels cannot survive in saline conditions, they are well adapted to the water conditions (see Table 2), and turbidity levels that are found in the Great Lakes, St. Lawrence River, Rideau River, and many freshwater lakes and canals across Canada.<sup>10</sup>

*Table 2 – Water Conditions of the Great Lakes (May to October) <sup>10</sup>*

<b>Property</b>	<b>Range</b>
Water Temperature	6-25°C
pH	6.5 to 8.0
Hardness	50 to 100mg/L as CaCO <sub>3</sub>

Spawning typically occurs in spring when water temperatures rise above 12°C and can continue into October. Females can release more than 30,000 planktonic (free-swimming) larvae (veligers) that can move with water currents and grow up to 1.3cm in the first half-year. Veligers settle into colonies and attach to firm surfaces through secreted byssal thread strands. Densities can reach up to 500,000 per square meter and individual life spans are three to five years. Figure 1 below is an example of a boating component covered in zebra mussels.



*Figure 1 - Zebra Mussels Encrust Bumper. Photo: Dave Britton<sup>10</sup>*

While Dreissenid mussels are filter feeders that open up their shells to allow ingestion of particulates, sensitive chemoreceptors alert them to certain toxins (e.g., some molluscicides and oxidizing agents) in the environment and cause shell closure that can be maintained for up to two weeks. Note, not all molluscicides evoke this response (e.g., Quaternary ammonium compounds (QACs); see Sec 2.2.2.2). Therefore, QACs are deemed as 'instant' molluscicides even when applied over a short term.<sup>9,15</sup>

### 2.1.1 Zebra Mussels and Their Impact

Dreissenid mussels can foul virtually all solid substrates within an aquatic system and cause wide spreading impacts environmentally, socially, and across multiple industries.<sup>12</sup> As an invasive species to North America, local aquatic ecosystems of lakes and rivers are disrupted. Two such disruptions include making lakes more susceptible to deleterious algal blooms and altering/destroying fisheries.<sup>7</sup> These disruptions spill over to social aspects such as reducing recreational and aesthetic

value of lakes and beaches. Users of the waterfront become susceptible to cuts caused by the shells of mussels that have attached onto any available surface, natural or man-made.<sup>7</sup> Restriction of flow, reduction of heat transfer, fouling and corrosion of metal and concrete, can all be detrimental to industries that uses water from the lake (e.g., water treatment plants, paper mills, manufacturing plants, and power plants)<sup>3,12,16</sup>. If left uncontrolled, zebra mussel infestation can lead to complete restriction of flow and blockage to intakes of water conveyance systems. For an industry that requires a lot of water, like NPPs, the effects can be devastating.

#### 2.1.2 Requirements of Nuclear Power Plant Operators

In general, the requirement is to have a zebra mussel control system that ensures continued safety of operations of the NPP by protecting station assets from zebra mussel infestation.<sup>4</sup> This is achieved by minimizing the risk of: plugging of service water lines in critical and supporting systems by zebra mussel shells, decreased cooling water flow, and increased degradation of materials of construction.<sup>4</sup> This is done by ensuring that all systems in contact with lake water have adequate protection.<sup>4</sup>

When determining the best solution for NPPs, the following is a set of critical factors to be considered<sup>15,17</sup>:

- Effectiveness (i.e., ability to prevent zebra mussel from entering the water system and/or ability to exterminate zebra mussel once they have entered),

- Applicability to the specific conditions faced by the NPP,
- Environmental impact (effect on ecosystem and human health), and
- Economic viability.

Note, effectiveness is typically measured as the action required to achieve a 99.9% kill rate, which is the industry standard for zebra mussel control.<sup>4</sup>

It is recognized that these are not the only factors that go into the decision-making process, but rather, a guideline for decision-making. Other factors such as laws and regulations, employee safety, and social responsibility will also need to be considered.

### 2.1.3 Principles in Control

In the earliest period of veliger stage, the mussels are free-swimming, very small in size, can pass through the piping systems without causing damage, and do not pose a threat to nuclear facilities. At the pediveliger stage, the mussels begin to form a shell and become dense enough to settle due to gravity. Shortly after, byssal threads will form and the mussels will begin to attach to the substrate materials. Once a hard shell is formed, the mussels are considered adults. While veligers are very sensitive to control chemicals, adults are difficult to kill and can survive up to 14 days (in a chlorinated environment) due to their protective shells. The control strategy for Dreissenid mussels is therefore: 1) Prevent zebra mussels from entering

the facility or attaching to the piping network, and 2) Minimize the settlement of pediveligers before a hard shell is formed.<sup>4,15</sup>

## 2.2 CONTROL METHODS

Control methods are generally broken down into two major types: Front End Control Methods and System Wide Control Methods. The difference between the two is the duration of impact for zebra mussel control and the ability to eradicate the mussels upon entering the system.<sup>15</sup>

Front End Control Methods are typically single point controls that aim to prevent zebra mussels from entering or attaching to the piping network. Examples of Front End Control methods include: antifouling coatings, cathodic/electrolytic protection, mechanical filtration, UV radiation, and judicious application of water velocities (greater than 1.4m/s at 1mm from pipe wall surface).<sup>2</sup> Note, antifouling coatings, cathodic/electrolytic protection, and judicious application of water velocities above 1.4m/s is usually only applied over a limited portion of the systems due to practical limitations such as costs.<sup>4</sup> Thus, it is considered a front end control in the industry.

System Wide Controls, once employed/implemented, stay in the system (residue effect) and aim to eradicate zebra mussels that have entered into the piping network. System Wide Controls typically inject a chemical agent into the water system at the intake and disperse the treated water throughout the system. Chemical agents are separated into two categories: oxidizing agents and non-oxidizing

agents. Examples of oxidizing agents include: bromine, chlorine, hydrogen peroxide, and ozone. Examples of non-oxidizing agents include ammonium compounds and biological molluscicides (bio-pesticides).<sup>15</sup>

In practice, multiple types of zebra mussel controls are employed by NPP operators to increase the efficacy of limiting zebra mussel infestation.<sup>18</sup> This study will focus on the impact of single control strategies in isolation of others for simplification. This will eliminate potential overlap between different control strategies.

### 2.2.1 Control Methods – Front End Control Methods

Front End Control methods act as the first line of defense in preventing zebra mussels from entering the facility and can be employed throughout the year. These are generally simple techniques, but are limited in the sense that if the zebra mussels get past the barrier, they are free to proliferate.

#### Microfiltration and Strainers:

This control method uses mechanical systems as a filtration barrier that will physically separate zebra mussels and other debris (e.g., silt, algae, and other micro-organisms) from raw water entering water systems. This can then be augmented by relatively small doses of microbial biocide (e.g., chlorine/bromine or non-oxidizing biocides) to control microbial growth and bio-fouling films. In order to achieve the objective of removing veligers and larvae from service water,

microfiltration (MF) or ultrafiltration (UF) membrane systems (40 $\mu$ m and 25 $\mu$ m absolute screens, respectively) would need to be used.<sup>17</sup>

MF and UF membranes do not perform well in large plants due to the high pressure drop given the large flow (up to 6m<sup>3</sup>/s per Unit)<sup>19,20</sup>. This is further complicated by the severe fouling and loss of flow due to deposit of silt, natural organic matter and biological contaminants. A backwash (flushing backwards through the filters' media) system would need to be installed as part of the filtration system. Other factors that would need to be considered include: volume of water for backwash, pressure differential for effective backwash, pressure drop, and power consumption.<sup>21</sup>

#### UV irradiation:

UV irradiation disinfects by damaging nucleic acids (DNA and RNA) of bacterial cells and viruses. Use of UV for effluent treatment in sewage plants and lake water intakes in cottage country is well established. UVB and UVC are most effective for disinfection purposes. UV performance is affected by light intensity and contact time. Maximum efficiency is achieved in closed systems where water is passed parallel to UV light tubes. UV may be used in conjunction with injection of hydrogen peroxide to oxidize organic matter (e.g., algae, microbes, etc.).<sup>22</sup>

UV irradiation is effective for single cell or simple organisms, but less so for multi-cell organisms, such as zebra mussels.<sup>22</sup> As mentioned, UV is dependent on ease of penetration and duration of contact time. Suspended solids shield and disperse UV

light while iron absorbs UV light.<sup>22</sup> This will prevent the UV light from coming into contact with the zebra mussels.

Additional factors that should be considered for UV irradiation include: power usage, heat dissipation, and end of life disposal of the mercury lamps.<sup>15,22,23</sup>

#### Antifouling and Cathodic/Electrolytic Protection:

Antifouling and Cathodic/Electrolytic protection work on the same principle: creating a surface that is prohibitive for zebra mussels' settlement. Antifouling uses chemical properties of materials to prevent attachment while cathodic/electrolytic protection uses electric currents to protect metal surfaces. A limitation for both of these methods is that equipment is only protected in areas that are covered by the antifouling coating or electric current. With the large network of piping inside an industrial plant, the cost of material (for antifouling) and electricity (for electrolytic protection) would be substantial. Thus, antifouling coating and/or cathodic/electrolytic protection is typically only applied in a limited region of the system. Furthermore, antifouling coating would need to be replaced over time due to wear. As such, neither of these methods have gained traction in large industrial plants.<sup>4</sup>

#### 2.2.2 Control Methods – System Wide Control Methods

System Wide Controls create environments hostile to the settlement stage of the pediveliger and maintain inviable conditions that prevent adult mussel translocation

and settlement. Control compounds include oxidizing biocides (such as chlorine gas or hypochlorite (bleach) solutions, bromine, ozone, chlorine dioxide) and non-oxidizing biocides (e.g., quaternary ammonium compounds, molluscicides, and bio-pesticides). Chemical application can be either pro-active (before fouling occurs) or reactive (after fouling occurs). Proactive treatments are more commonly used for systems with a history of fouling.<sup>1,3,4,15</sup>

Industry experience has shown that veligers can be present year-round. During winter, veligers are unlikely to grow at a significant rate. This is due to the cold temperatures and scarce food supplies that are detrimental (or rather, not supportive) to high rates of metabolism. Hence, veligers that enter during winter pose little risk to the facility and can be controlled in the spring by the initiation of a rigorous chemical deployment program. This is especially important throughout the breeding season where lapses in treatment should be avoided when possible to prevent veligers from settling and becoming adults.<sup>4,15</sup>

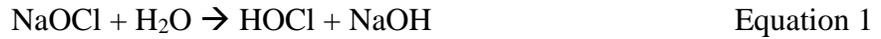
#### 2.2.2.1 Oxidizing Molluscicides

In general, oxidizing molluscicides have the following advantages: environmental effects and requirements for safe discharge are well understood by users and regulators, effective for Dreissenid mussels and other organics (biofilm and slime), and relatively low cost. Negatives include: corrosive effect on metals and adverse impact to environment.<sup>4,15</sup>

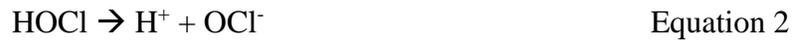
## Chlorination:

Chlorine is a strong oxidizing chemical that attacks and reacts with cells (i.e. soft tissues). Toxic and lethal effect for zebra mussels is produced at total residual oxidizer (TRO) range of 0.2-0.5mg/L.<sup>4,18,23,24</sup> Effective control requires total residue chlorine (TRC) above 0.3mg/L within any location in treated service water systems.<sup>4,18,23,24</sup> Chlorine is poisonous as a gas or a liquid. In addition, disinfection by-products from the reaction of chlorine with organic matter, such as trihalomethane (THM), haloacetic acids (HAA), and chloroform, have been shown to have harmful effects to humans and other aquatic life. As such, the Government of Ontario has mandated minimizing the use of hypochlorite to the extent possible.<sup>25</sup> Organizations such as International Conference on Aquatic Invasive Species (ICAIS)<sup>26</sup> and Electric Power Research Institute (EPRI)<sup>27</sup> have dedicated resources over the years to look at alternatives. The Canadian Water Quality Guidelines for the Protection of Aquatic Life and the Government of Ontario recommend chlorine concentration levels below 0.2mg/L at the outfall.<sup>25,28</sup> This is typically achieved by diluting the flow prior to the outfall.<sup>4,18</sup> Note, while a wide range of chlorine de-activation products are available, this study will only consider dilution as it is the most common method. That is, concentration will be diluted prior to the outfall to below 0.2mg/L. As multiple water systems collect at the outfall, it is assumed dilution is properly met as such. Future studies may consider looking further into the impact of such downstream activities.

Chlorine can be applied both as a gas and, more commonly, as a 12% solution of sodium hypochlorite (NaOCl).<sup>29</sup> When sodium hypochlorite is added to water, hypochlorous acid (HOCl) and sodium hydroxide (NaOH) are formed:



Hypochlorous acid undergoes partial dissociation to produce a hydrogen ion (H<sup>+</sup>) and a hypochlorite ion (OCl<sup>-</sup>).



In water, the so-called ‘active chlorine’ or ‘free-chlorine’ is represented by the hypochlorite ion. This ‘free-chlorine’ disinfects in the same manner as chlorine gas in terms of the required concentration for zebra mussel control.<sup>4,15</sup> For the purposes of this thesis, unless specified otherwise, free-chlorine/active chlorine and chlorine will be used interchangeably.

Continuous application at 0.5mg/L TRO for 2-4 weeks can eliminate established colonies.<sup>4,18,23,24</sup> Time and concentration is dependent on temperature, pH, availability of food in water, and the physiological state of the mussel (i.e. whether the mussel shells are open or closed).<sup>4,18,23,24</sup> As noted earlier, adult mussels can remain closed in their shells for up to 2 weeks.<sup>1</sup> In order for oxidizing agents to be effective, mussel shells must be opened to expose the agent to the mussels’ organic tissue.

Note, EPRI findings show that continuous low-dose may have similar environmental impact (i.e. chlorine released) as intermittent high dose application.<sup>23</sup> Intermittent dose application of 2.5-3.0mg/L TRO for one hour every eight hours is required to sustain a hostile environment for zebra mussels.<sup>23</sup> Food availability is an important factor for intermittent chlorination as mussels can open and feed minutes after chlorination stops. This means intermittent chlorination must be sustained beyond the limit in which zebra mussels can remain closed (i.e. two weeks).<sup>4,18,23,24</sup> This will either starve the zebra mussels to death and/or force them to open their shells and be exposed to the chemical agents.

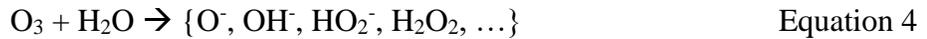
#### Ozone:

Ozone is a strong oxidizing chemical that has a long history of being used in municipal water/waste water treatment plants and power stations. Continuous application at 1.5mg/L is typically required to eliminate established colonies.<sup>15,18</sup> Ozone is generated when energy is added to a system, which will split the oxygen double bond, producing atomic oxygen. These oxygen atoms will then react with diatomic oxygen molecules to form ozone.



When ozone is added to water, ozone will dissociate in water resulting in a complex chain of reactions that causes the formation of radicals. Some examples include: hydroxyl radical ( $\text{OH}^\cdot$ ), hydroperoxyl radical ( $\text{HO}_2^\cdot$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The type and amount of radicals formed varies depending on

water quality parameters such as pH and total organic carbon (TOC). Oxidation occurs in two ways, directly via ozone and indirectly via free radicals.<sup>30</sup>



Ozone is generally deemed to be more environmentally friendly than chlorine as it does not produce harmful by-products such as trihalomethane and chloroform. However, ozone and its radicals can produce free bromine or bromate by-products in its reaction with bromine containing halogen compounds in water. This restriction makes it more ideal in closed loop cooling water applications rather than once through cooling. Manganese oxides may also be produced. Due to its higher redox potential, the rate of metal corrosion with ozone is higher when compared to chlorination. Additionally, ozone in the troposphere represents a health hazard with potential to also damage crops and forests. Free ozone must be captured for re-use or be destroyed.<sup>18,24,30</sup>

Ozone must be generated on-site due to a relatively ‘short’ half-life of approximately 25hrs in air.<sup>31</sup> Additionally, ozone has a half-life of about 30 minutes in 15°C water.<sup>18,30</sup> Multiple injection points across the plant are required to ensure consistent concentration of ozone throughout the system in the NPP.

<sup>18,30,32,33</sup>

Production of ozone involves use of equipment such as a compressor, ozone generator/destructor, dry air supply, and a safety system. Use of bottled oxygen

eliminates the need of a compressor and air dryer, but an ozone absorption column and a chiller are still required. The power draw required to generate ozone is comparable to that of UV systems. In total, ozone is about four times more costly to produce than chlorine.<sup>18,30,32,33</sup>

Intermittent ozonation mitigates some of the issues around power draw and large footprint (for the generation equipment) as less ozone is required. Furthermore, designs for intermittent ozonation are modular and standardized, which mitigates issues of multiple injection points such as reducing the footprint for the equipment and reducing the amount of ozone off-gas.<sup>18,30,32,33</sup>

#### Other Oxidizing Chemicals/ Biocides:

##### Bromine:

Bromine is used for antifouling purposes in forms such as activated bromine, sodium bromide, bromine chloride, and mixtures of other chemicals.<sup>4</sup> In the past, bromine was thought to be less toxic than chlorine for non-target species. However, this has been shown not to be the case as the total amount of oxidant required is approximately the same as chlorine.<sup>4</sup> Furthermore, bromine is most effective as an oxidizing agent when water pH is above 8.0.<sup>15</sup> Since the water pH of the Great Lakes is below 8.0 (see Table 2), bromine is not effective for zebra mussel control.

EPRI has recognized the benefits of using bromine in parallel with chlorine as a more effective treatment than chlorine alone when pH is greater than 8 and/or when ammonia concentration in water is about 2mg/L.<sup>23</sup> However, use of bromine will be

subjected to further environmental approvals for use in addition to the chlorination.<sup>23</sup> The use of multi-chemical treatment will not be looked at in this study as mentioned above. This will eliminate potential overlap between the effectiveness of different chemicals.

#### Chlorine Dioxide (ClO<sub>2</sub>):

Chlorine Dioxide is an oxidizing chemical that has a long history of being used as a drinking water disinfectant, in paper bleaching, in food processing, and as an airborne virus killer. Industry experience has shown that there is no significant zebra mussel mortality observed at concentrations of 2mg/L at up to 6hrs exposure. In contrast, 95% mortality was observed when zebra mussels were exposed for four days at concentrations of 40mg/L. Considering the high concentrations and long exposure time required, ClO<sub>2</sub> is not an effective control agent for zebra mussels. Chlorine dioxide is also an explosive/flammable substance that is a hazard for personnel handling the chemical.<sup>15,18,24</sup>

#### Potassium permanganate:

Potassium permanganate is a chemical that is commonly used in the water treatment industry to disinfect drinking water. Industry testing has shown that it is not effective at controlling zebra mussels.<sup>15,18,24</sup>

#### Hydrogen peroxide:

Hydrogen peroxide is a chemical that is used in conjunction with other chemicals and processes in the water treatment industry. It is not effective as a stand alone

control chemical. Industry testing has shown that it is not effective on veligers although there is some success on adult mussels. <sup>15,18,24</sup>

#### Ferrate:

Ferrate has been used for small scale water treatment applications. However, no significant mortality was observed during mussel exposure in industry testing.

<sup>15,18,24</sup>

#### 2.2.2.2 Non-Oxidizing Molluscicides

Non-oxidizing molluscicides are a diverse group of organic compounds that include aromatic hydrocarbons, quaternary ammonium compounds (QACs), and bio-pesticides. <sup>15,16,21</sup>

Examples of QACs include: Bulab 6002, Nalco H-130M, Nalco H-150M, ClamTrol, MacroTrol 9210, VelicGon.

Examples of aromatic hydrocarbons include: Bulab 6009, Mexel 432, Endothall (EVAC) herbicide.

Examples of bio-pesticides include: *Pseudomonas fluorescens* (such as ZEQUANOX, MBI, and BioBullet).

In general, these non-oxidizing molluscicides are applied in two large doses during the year. Once in the fall after water temperatures drop below 15°C to remove the mussels that have settled during the summer and once in early to mid-summer to rid

the system of mussels that survived the winter and/or have settled in the spring. During the spawning season between the two large doses, periodic treatment is used. <sup>15,16,21</sup>

Two types of periodic treatment are available: 1) a high dose short application period of 16-48hr followed by detoxification (i.e. de-activation) with clay, or 2) continuous application of lower dosage for 5-14days until a near 100% kill is achieved. <sup>15,16,21</sup>

A major benefit to molluscicides is that Dreissenid mussel's chemoreceptors do not sense the presence of these toxins unlike oxidizing agents such as chlorine, which causes the mussels to immediately close their shells. As such, these products are considered a more effective 'instant' molluscicide. QACs are generally also highly compatible with materials and metallurgies typically found in water systems. Being non-corrosive, non-volatile, and non-flammable, molluscicides are relatively easy to transport and safe to handle compared to oxidizing agents. Furthermore, as treatment is periodic rather than continuous (compared to oxidizing chemicals), there is a potential to reduce the quantity of chemicals used and in theory, save costs. <sup>15,16,21</sup>

Aside from Zequanox, H-130M, H-150M, and EVAC, most of the non-oxidizing molluscicides are not commonly used commercially due to issues such as lack of long term effectiveness based on test data, lack of environmental acceptability, and

lack of registration in Canada. Actual testing has shown that non-oxidizing molluscicides have higher costs compared to more traditional molluscicides.<sup>15,16,21</sup>

Nalco's H-130M and H-150M:

H-130M is a non-oxidizing ethanol-based solution of poly-quaternary alkyl ammonium compound (didecyl dimethyl ammonium chloride, DDMAC) that has been registered for use in Canada as a molluscicide in industrial cooling towers and once through freshwater cooling water systems. The H-150M is a more desirable water-based product, rather than an ethanol-based product (which is a flammability hazard).<sup>15</sup>

These compounds work as a coating and surfactant that coagulates the mucous membrane on the gills of the mussels to restrict oxygen transfer and cause rapid mortality. Note, these compounds are toxic to fish if not deactivated and are therefore prohibited where discharge is within one quarter mile from public/municipal potable/drinking water intake in the United States. Deactivation is done by injection of bentonite clay and must be done prior to discharge at a minimum ratio of 5:1.<sup>15</sup>

As H-130M results in an instant kill, detachment and removal of mussels may generate a significant amount of debris that may clog water system lines and ducts. Another concern is the likelihood that the suspended solids from the deactivant clay suspension may cause an environmental problem and have an adverse impact on fish habitat.<sup>15</sup>

Endothall (EVAC):

No detoxification is required for this product. <sup>15</sup> A 100% kill rate was achieved with 0.5mg/L dose rate in various plants on Lake Ontario. However, this product is not approved for use in Canada.<sup>15</sup>

Zequanox MBI:

Zequanox MBI is a naturally occurring bacterium (*Pseudomonas fluorescens* strain CL0145A) that produces a toxin which attacks the digestive system when ingested by Dreissenid mussels. Testing by Zequanox indicates mortality rates of greater than 90%. As a naturally occurring bacterium, this bio-pesticide is environmentally compatible, has low toxicity (to humans), presents little risk to non-target organisms (i.e. other aquatic species), and is non-corrosive to plant equipment.<sup>15</sup>

In COG Technical Note TN-08-3044, it was noted that the cost of Zequanox MBI is roughly eight times that of chlorine treatment due to the high dose concentrations (as high as 80mg/L) required to achieve good kill rates. However, this cost may be offset by the savings from reduced equipment and piping maintenance due to corrosion.<sup>34</sup>

While this technology (bio-pesticide) represents a very desirable trend that places emphasis on environmental protection and safety as key criteria, there are concerns/issues that must be worked out prior to it being recommended as a large scale solution. A concern for this product is the possible adaptation of the mussels

to the bacterium.<sup>15</sup> This is typically mitigated by applying high doses to reduce the possibility of adaptation. Also as a targeted treatment, it is not clear that application of Zequanox will mitigate bio-fouling and concomitant microbially induced corrosion due to naturally occurring organic and biological matter.<sup>15</sup>

## 2.3 RELATED RESEARCH

Industrial and academic organizations, such as the International Conference on Aquatic Invasive Species (ICAIS), have spent millions on research and technologies for prevention, monitoring, and control of aquatic invasive species.<sup>26</sup> This also includes discussion on policy, legislation, education, and outreach to prevent the spread of aquatic invasive species.<sup>26</sup> Most of the research has been directed at developing and/or testing new oxidizing molluscicides, non-oxidizing molluscicides and bio-pesticides, with the objective of uncovering an environmentally friendly/compatible, high efficacy, and cost-effective molluscicide that specifically targets zebra and quagga mussels to replace the use of chlorine.<sup>26</sup> While chlorine has not yet been replaced, there have been studies that looked at minimizing the amount that is used. This includes using a combined cooling and stripping tower for coastal power plants.<sup>35</sup>

In terms of LCA of zebra mussel control, there have been a few studies that looked at the environmental impact of water treatment processes. An economic input-output life cycle assessment was done for the City of Toronto municipal water treatment system.<sup>36</sup> The processes considered in that life cycle analysis included:

chemical production, transportation of materials, and water treatment plant operation.<sup>36</sup> They concluded operational burdens, such as on-site pumping, accounted for 94% of the total energy usage and 90% of the GHG emissions.<sup>36</sup> This thesis focuses specifically on zebra mussel controls and assumes plant operation (e.g., on-site pumping) is the same for each zebra mussel control method. It is also worth noting that the referenced study<sup>36</sup> was done in 2007 when Ontario's coal plants were still operational. The current distribution of emission contributors is likely quite different as coal plants in Ontario have since been shut down.

There have been studies that compared the results of a LCA for UV disinfection with chlorination for waste water treatment.<sup>37,38</sup> This approach differs from this study since a front end control (UV) was compared with a system wide control (chlorination). As discussed above, the effectiveness for front end controls like UV irradiation differs from that of system wide controls. Furthermore, there are studies completed for drinking water treatment and electric power generation facilities on the economic impact of various zebra mussel control methods.<sup>39,40</sup>

Considering the research that has been done in this field, this thesis offers additional insight on the environmental impact of various zebra mussel controls for NPP operators. This will help provide decision makers a more complete picture when evaluating options.

### **3 METHODOLOGY**

As mentioned earlier, zebra mussel infestation is a widespread problem for many industries, such as NPPs, which use water from the Great Lakes. Zebra mussel controls are split into two main categories, as discussed in Chapter 2: 1) Front End Control and 2) System Wide Control. The main difference between the two categories is the ability to eradicate the mussels upon entering the system. This thesis examines two zebra mussel control methods used in NPPs (chlorination and ozonation<sup>4,18,23</sup>), through LCA, with the goal of evaluating the environmental impact of each control method so that future plant operators can make a more informed decision when selecting zebra mussel controls.

This chapter covers theory for LCA and a short discussion on the analytical tool used to perform the LCA. This will be followed by discussion on the life cycle assessment scope and inventory analysis. Equations and calculation of the inputs will also be discussed in this chapter. Results, in terms of GHGs, will be discussed in Chapter 4 along with sensitivity analysis of important variables.

#### **3.1 THEORY (LIFE CYCLE ASSESSMENT) AND OBJECTIVES**

Life cycle assessment is a technique/method that assesses the environmental impacts associated with all stages of a product or process. This typically includes extraction/processing of the raw materials, manufacturing, distribution, use, and disposal/recycling. The four steps involved with LCA are: Goal and Scope Definition, Inventory Analysis, Impact Assessment, and Interpretation. The first

stage defines the boundaries and the goals of the assessment. The second stage looks at the environmental inputs and outputs of the product or service. The third stage evaluates the environmental impacts of the inventoried flows. The final stage summarizes the results and produces a set of conclusions and recommendations from the study. Further details on the procedures for LCAs are outlined and described in the ISO 14040 and ISO 14044 standards.<sup>41-43</sup> ISO 14040 is the overarching standard that describes the “principles and framework” for LCA.<sup>41</sup> ISO 14044 describes the requirements in more detail and provides guidelines for LCA including: all four phases of LCA, “limitations of the LCA”, and “the conditions for use of value choices and optional elements”.<sup>42</sup>

## 3.2 LIFE CYCLE ASSESSMENT SCOPE

### 3.2.1 Functional Unit

Discussion of the functional unit, per the ISO 14040 series standards,<sup>41,42</sup> requires discussion of the function of the product system. As defined in ISO 14040:2006,<sup>41</sup> a product system is a collection of processes, which provide a certain function. The function represents the performance characteristics of the product system. In other words, function represents ‘what does it do’. The product system, in this thesis, is the zebra mussel control process at a nuclear power plant. The function of this product system is to treat water for zebra mussels.

The functional unit is a clear and quantitative defined measure relating the function to the inputs and outputs to be studied. The functional unit for this thesis is billion

cubic meters of water treated ( $10^9 \text{ m}^3$ ). The volume of water is based on the amount of water treated annually for once-through use in a large scale nuclear power plant situated on the shore of Lake Ontario e.g. Class 1A power nuclear reactors as defined by the Canadian Nuclear Safety Commission (CNSC) regulations.<sup>44</sup> This was calculated using estimates of how much water is required to produce 1MWh and the annual capacity of a NPP situated on Lake Ontario. EPRI estimates that for every MWh produced, 25000 to 60000 gallons of water are used (i.e. 95-227m<sup>3</sup>/MWh).<sup>20,45</sup> For example, Ontario Power Generation (OPG) estimates the output of Darlington Nuclear Power Plant to be 25791GWh in 2016, before the start of the Refurbishment Project.<sup>46</sup> For context, below is the summary of Ontario’s transmission-connected generator output broken down by fuel type. Data is from the Independent Electricity System Operator (IESO).<sup>47</sup>

*Table 3 – Ontario Grid Make-up in 2016 from IESO <sup>47</sup>*

	Nuclear	Hydro	Coal	Gas/Oil	Wind	Biofuel	Solar/Other
2016 [TWh]	91.7	35.7	0	12.7	9.3	0.49	0.46
2016 (% of total)	61	24	0	9	6	<1	<1

With cubic metres as the denominator, one can multiply the volume of water treated and scale the impacts. For example, one of the impacts of adding sodium hypochlorite into water systems is the increased amount of salt being added to lakes. For the purpose of this thesis, salt is assumed to be in the form of NaCl. By

calculating the equivalent amount of salt (NaCl) being added from chlorination, it is possible to compare such impact to other processes that add salt into lakes (e.g., road salting).

Since water usage has year-to-year variations due to a variety of factors (e.g., lake temperature, grid demand)<sup>45</sup>, sensitivity analysis was used to study the effects of varying the parameters. The base case examines the average annual amount of water treated. Calculations were replicated using the upper and lower bounds for comparison. From the amount of water treated, the chemical usage was estimated based on the concentration required to achieve 99.9% kill rate. From there, further upstream activities like delivery and chemical production were analyzed.

Note, zebra mussel controls are only applicable/employed during spawning season when waters are between 6°C to 25°C.<sup>9,15,24</sup> For Lake Ontario, the zebra mussel spawning season is during May to October.<sup>24</sup> In other bodies of water, the reproductive periods will change based on the temperature profile of that body of water. This will change the length of time zebra mussel controls are deployed, which will change the amount of control chemicals used.

### 3.2.2 Boundaries, Assumptions, and Limitations

This analysis was done to compare environmental impacts of zebra mussel control for a large NPP (e.g., Class 1A reactor<sup>44</sup>) that employs once-through cooling, as a point of consideration for future decisions; the results are not intended to be a

recommendation/direction. Environmental impact is only one of many factors that need to be considered when deciding which method of zebra mussel control is implemented. Examples include, but are not limited to, costs of implementation, cost of equipment/technology, upkeep costs, impact to supporting systems and equipment, availability of the technology, knowledge and ability of the workforce, schedule, laws and regulations, maintainability, constructability, opportunity costs, support from local community, etc. Future decision-makers would need to consider all of the above aspects as well before making a decision.

#### 3.2.2.1 Location of Power Plant

A theoretical NPP that draws cooling water from Lake Ontario through a once-through cooling loop is used as a reference model for this work. Lake Ontario was selected as the cooling source as it currently supplies cooling water to two of the three existing NPPs in Ontario and has been identified as having zebra mussel infestation. Should a different water source be chosen as the cooling source, the water conditions would need to be re-assessed for the possibility of zebra mussels' livability and infestation i.e., if zebra mussels cannot survive in the body of water, no zebra mussel control would be required. Different bodies of cooling water may also have different challenges that need to be addressed (e.g., water usage, cooling capacity, etc.). Along the same lines, if a different mode of cooling was selected for a theoretical NPP (e.g., air cooling via cooling fins, cooling using closed loop water circuit and cooling tower, etc.), issues caused by zebra mussel infestation can be engineered out entirely.<sup>35</sup>

### 3.2.2.2 Selection of Chemical Agents/Control Methods for Comparison

Of the wide range of chemicals that can be used for zebra mussel controls, chlorination and ozonation are the two oxidizing agents being studied. Chlorine and ozone are both system wide oxidizing agents that have a long history of being used for water treatment purposes.<sup>15</sup> Both agents have proven to be effective at controlling zebra mussels. Both being oxidizing agents, the analysis allows for a fair comparison of similar control methods. As both oxidizing agents are chemicals, it is assumed that the manufacturing of the equipment used to produce these chemicals, per unit of chemical agent used for zebra mussel control, is similar in nature. A chemical manufacturing plant would not solely produce chemicals for zebra mussel controls. As such, the environmental impact for both is excluded in the analysis. Furthermore, emissions associated with the infrastructure for chlorination and ozonation are excluded as it is assumed to be part of the NPP.

Should another oxidizing agent be selected, impacts from all life cycle stages (e.g., manufacturing, transport, delivery, application, post-treatment, etc.) would need to be assessed. Relatively new control agents, such as molluscicides, were not considered. At this time, there is insufficient data / operating experience (OPEX) from commercial facilities available to do a meaningful comparison e.g., manufacturing method(s), comparison of efficiency year over year, zebra mussel adaptation over time, etc.<sup>15</sup> While it may not be viable to compare the use of new control agents to existing control agents at this time, this could be considered in

future work when more data becomes available. If this work was taken on, it should be noted that the mechanism for oxidizing agents is different from non-oxidizing agents as discussed in Chapter 2. That said, the life cycle stages for non-oxidizing agents would need to be studied as they were for the oxidizing agents.

### 3.2.2.3 Environmental Impact Indicator

GHG emissions (tonnes CO<sub>2</sub> equivalent in particular) were selected as the indicator for environmental impact. It is recognized that there are many other methods of measuring environmental impact both quantitatively and qualitatively. Other environmental impacts include, but are not limited to, increasing temperature of the water body, increasing salinity of lakes, impact to wildlife (habitat, changing of local ecosystem), smog, chlorine and ozone releases, etc.

Reporting GHG emissions is a method for reporting contribution to global warming. GHG emissions also have a monetary implication associated with them (e.g., Carbon tax). Depending on the processes that release GHGs, one may be able to infer other environmental impacts. For example, if the source of the GHG emission is from the combustion of fuels, one may be able to infer similarly high potential for air pollutant emissions. Furthermore, the nuclear industry strives for the image of being socially responsible and environmentally sustainable<sup>46</sup>.

Minimizing GHG emissions aligns with that vision.

Conversion to tonnes of CO<sub>2</sub> equivalent is based on global warming potentials (GWP), which is defined as a measure of the amount of heat a greenhouse gas traps in the atmosphere relative to carbon dioxide. Specifically, the GHGs included by GHGenius model are: <sup>48,49</sup>

- Carbon dioxide (CO<sub>2</sub>),
- Methane (CH<sub>4</sub>),
- Nitrous oxide (N<sub>2</sub>O),
- Chlorofluorocarbons (CFC-12),
- Hydrofluorocarbons (HFC-134a)

Other emissions modelled into GHGenius include: <sup>48,49</sup>

- Carbon monoxide (CO),
- Nitrogen oxides (NO<sub>x</sub>),
- Non-methane organic compounds (NMOCs),
- Sulphur dioxide (SO<sub>2</sub>), and
- Total particulate matter

In this thesis, emissions of GHG, such as CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>, are converted to CO<sub>2</sub>e using GWP. The emissions from each process stage are then normalized to the functional unit (10<sup>9</sup> m<sup>3</sup>). This normalization to the functional unit allows one to compare the results across the project stages.

### 3.2.2.4 Tools Used and How They Work

GHGenius 4.03a was the primary tool used to estimate greenhouse gas (GHG) emissions from each life cycle stage of each zebra mussel control method. i.e. From the production of the control agent, through delivery to the NPP, and the end use of injecting the control agent into the water system. GHGenius is a spreadsheet-based model that was developed based on the 1999 version of Dr. Mark Delucchi's Lifecycle Emissions Model (LEM) which focuses on the LCA of current and future fuels.<sup>48,49</sup> The model was constructed to predict emissions for past, present, and future years using historical data or correlations for changes in energy and process parameters with time or government forecasts.<sup>48,49</sup> The model data is applicable to North American regions (Canada, US, and Mexico), India, and four regions in the European Union.<sup>48,49</sup> This tool is primarily for estimating life cycle emissions of primary GHGs, and other pollutants from combustion sources such as fossil fuels in transportation. Information pertaining to vehicle and fuel combination scenarios have been used to estimate GHG emissions from various life cycle stages. GHGenius considers the energy required to manufacture capital equipment associated with equipment and transport.<sup>48,49</sup> Screenshots of the model and some of the data from the model are shown in Appendix A. Further details to the models used in GHGenius can be found in the User Manuals.<sup>48,49</sup>

There is other software available to perform impact assessment, such as GaBi, SimaPro, openLCA, and Umberto.<sup>50-53</sup> GHGenius was selected based on availability of the software, transparency regarding information on the software's

model, and applicability. Specifically, GHGenius<sup>48,49</sup> uses data from Canada (going as far back as 1995), which is valuable while performing a Canadian case study. Furthermore, the Canadian data within GHGenius is regional specific, which allows the model to be tailored for Ontario. GHGenius 4.03a<sup>54</sup> was obtained from NRCan and is applicable for this thesis.

### 3.2.3 Chlorination – Overall Process

The life cycle stages for chlorination are: Salt (NaCl) mining, water processing, delivery of salt and processed water for sodium hypochlorite (NaOCl) brine production, delivery of brine to the facility for zebra mussel control,<sup>55</sup> addition of the brine to the water intake, and outflow of the treated water to the lake. The life cycle stages for chlorination, along with the relationships between them, are shown in Figure 2. Further details on the production of NaOCl are discussed in Sec 3.2.3.1.

Eradication of the zebra mussels occurs when sodium hypochlorite brine is mixed with water at the water intake to release free chlorine. Once deployed and cycled through the water system, it is assumed that the remaining chlorine in the water is diluted at the outfall and dissipated into the lake.<sup>15,55</sup>

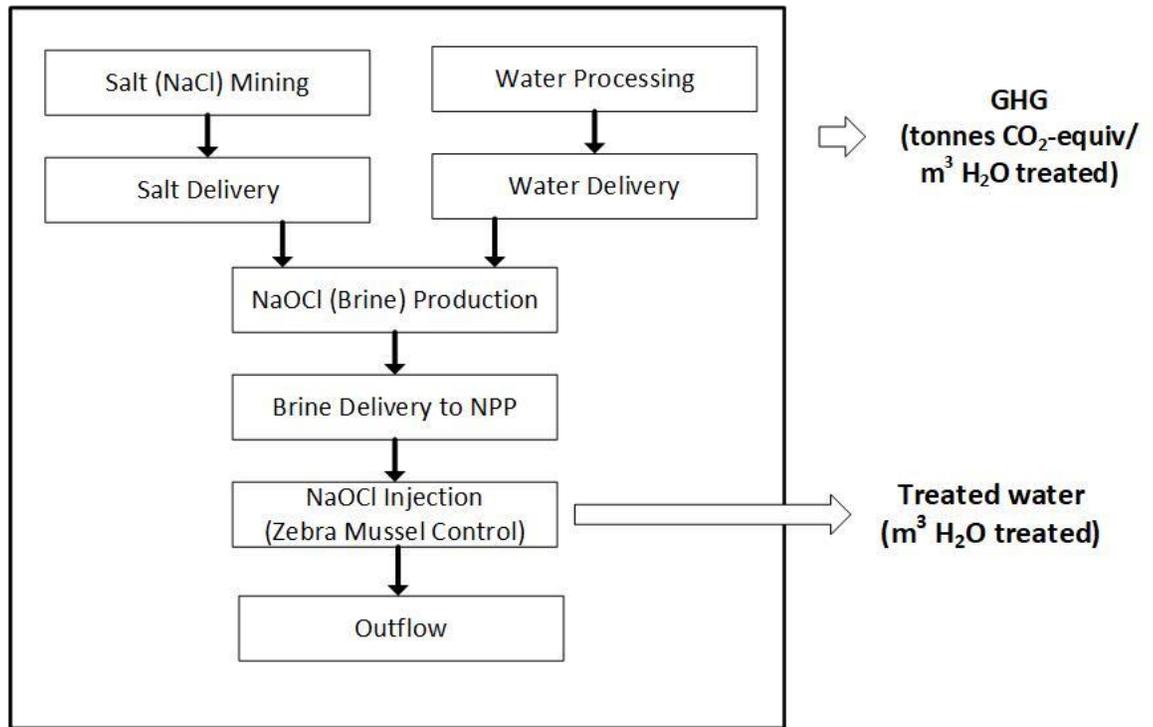


Figure 2 – LCA Scope Definition: Overall Process for Chlorination

### 3.2.3.1 Chlorination – Sodium Hypochlorite Production

Sodium hypochlorite is the control agent used for chlorination. In this study, NaOCl is assumed to be manufactured via electrolysis since it is the most common method of NaOCl production commercially.<sup>15,29,55</sup> The upstream inputs to the process include salt (NaCl from salt mining), water (via local, municipal water treatment facilities/network), and electricity (from the local electricity grid, Ontario in this case). The outputs from this process include NaOCl brine (pure NaOCl) and hydrogen. The inputs and outputs to sodium hypochlorite production are illustrated in Figure 3.

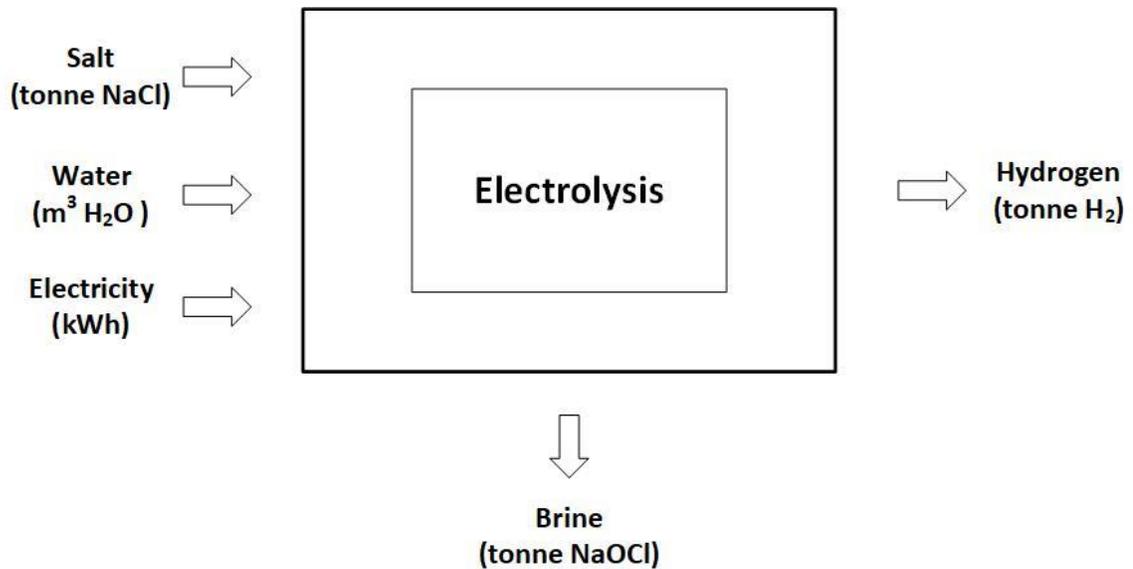


Figure 3 – LCA Scope Definition: Process for Sodium Hypochlorite Production

This work assumes the NaOCl production plant is on the same site as the salt mines and is connected to the local electrical grid and water network. The brine is then delivered to the NPP for use. In this study, brine is delivered using tanker trucks. Hydrogen, a co-product from NaOCl production, is used to replace hydrogen which would have otherwise been produced via other methods. Note, per ISO 14040 and 14044, a “co-product” is “any of two or more products coming from the same unit process or product system”.<sup>41,42</sup> Since hydrogen is sold, hydrogen is identified as a co-product instead of a by-product. To be conservative, all of the emissions associated with the NaOCl production process is assigned to the production of NaOCl.

The impacts of these assumptions are discussed in the inventory analysis in Section 3.3 and in the sensitivity analysis in Section 4.1.

### 3.2.4 Ozonation – Overall Process

The life cycle stages for ozonation are: Ozone ( $O_3$ ) production, addition of the ozone to the water intake, and outflow of the treated water to the lake. The life cycle stages for ozonation, along with the relationships between them, are shown in Figure 4.

Ozone is dissolved into the water at a holding tank before it is mixed in the water intake. Undissolved ozone is captured for re-use or is destroyed. For this study, it is assumed that any undissolved ozone is recycled and re-used at the holding tank. Once deployed and cycled through the water system, it is assumed that the remaining ozone in the water is dissipated into the lake and eventually into the atmosphere as oxygen ( $O_2$ ) gas.<sup>15</sup>

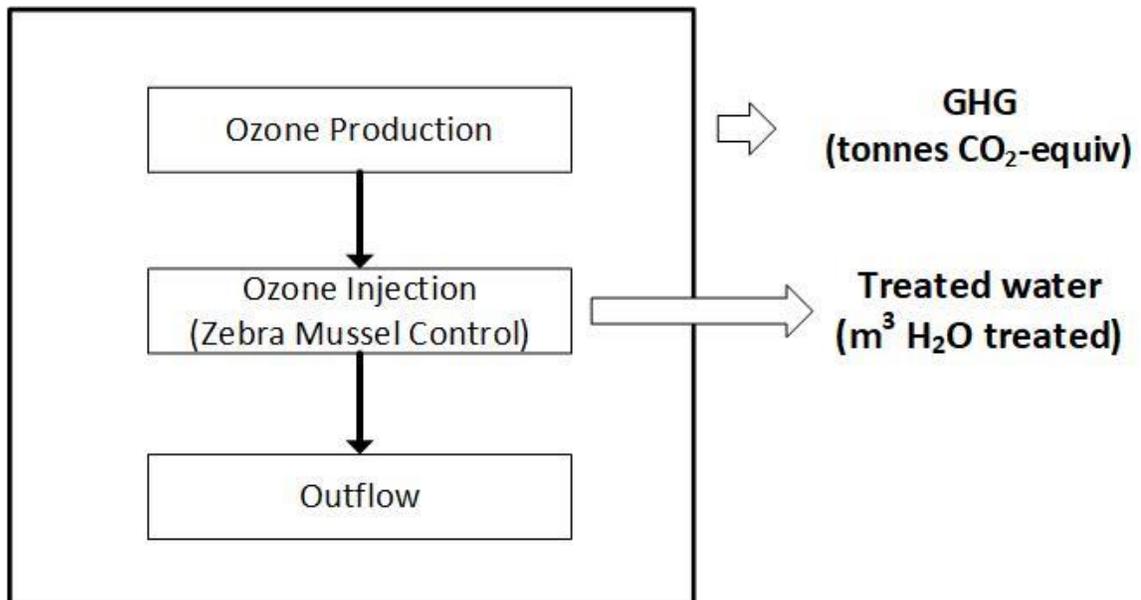


Figure 4 – LCA Scope Definition: Overall Process for Ozonation

### 3.2.4.1 Ozonation – Ozone Production

The main product used for controlling zebra mussels in this case is ozone. Oxygen and electricity are the only inputs required to generate ozone. The upstream inputs to the process are oxygen (from ambient air or oxygen gas) and electricity (from the local electricity grid, Ontario in this case). The output from this process is ozone and is directly dissolved into the water in a storage tank, which will then be mixed into the station water system. The inputs and outputs to the production of ozone are shown in Figure 5.

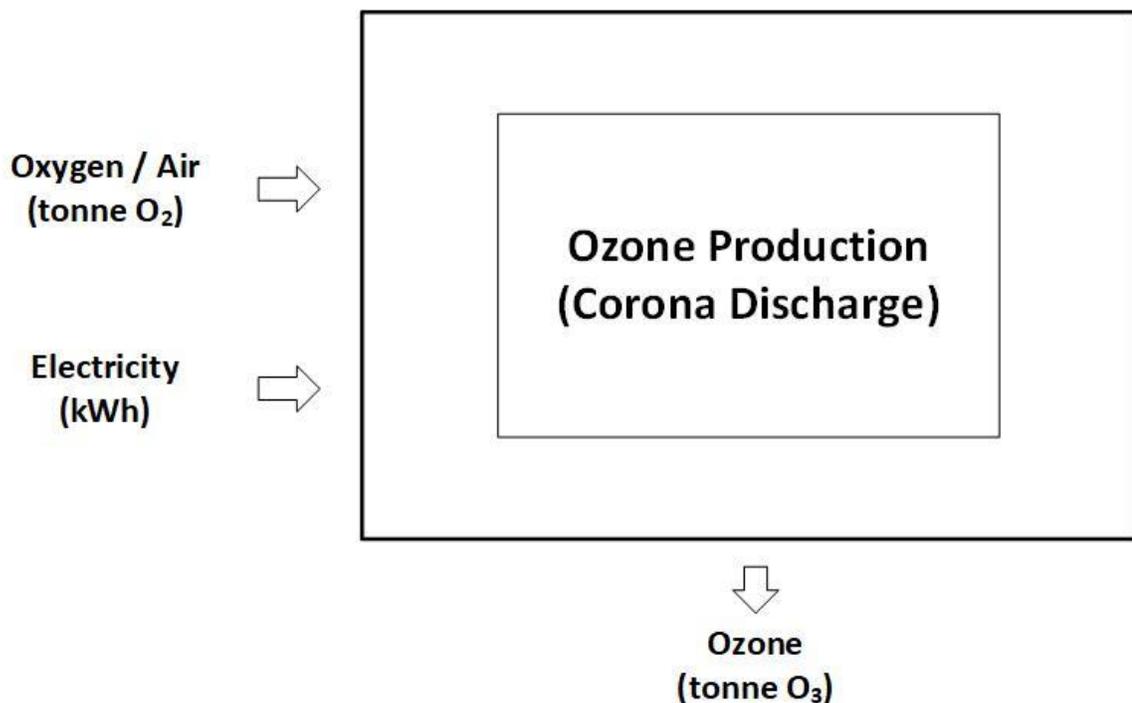


Figure 5 – LCA Scope Definition: Ozone Production

In this study, O<sub>3</sub> is manufactured via the corona discharge process since it is the most common method for ozone production commercially available.<sup>18,30,32,33,56</sup> This process mimics the action of lightning on oxygen found in the atmosphere. Electricity is used to split oxygen molecules into oxygen atoms. These oxygen atoms will then react with oxygen molecules to form ozone.<sup>56</sup>

The oxygen source used is assumed to be ambient air. Using pure oxygen in corona discharge would result in higher and more efficient yields for ozone. However, there are additional steps that need to be considered if pure oxygen is used e.g., energy costs, source material, maintenance, and construction costs of facilities and machinery required to distill pure oxygen.<sup>18,30,56</sup>

Ozone is assumed to be produced on site due to its relatively short half life (25hrs in air<sup>31</sup> and 30 minutes in 15°C water<sup>18,30</sup>). With the large amounts of ozone used, producing ozone off-site would pose practical problems that would need to be overcome e.g., investing in a steady supply/delivery of ozone to site, leaks during delivery of a gaseous chemical, chemical handling, etc.<sup>18,30</sup> Having ozone produced onsite eliminates the transport component, half-life issue, and transport costs amongst other factors as well as reduce possible GHG contribution.

### 3.3 INVENTORY ANALYSIS

The inventory analysis phase is the phase where data is collected and documented to meet the stated goal and scope. For this thesis, this means gathering the data to

determine the GHG emissions for chlorination and ozonation. In general, the total GHG emissions are the summation of GHG emissions from all the life cycle stages involved with the process.

$$[\text{GHG}]_{\text{Total}} = \sum \text{Life Cycle Stages } [\text{GHG}] \quad \text{Equation 5}$$

As described in the previous section, chlorination and ozonation are made up of multiple life cycle stages. In order to determine the total GHG emissions for the two processes, the GHG emissions for each stage are added up.

For chlorination, the total GHG emission is calculated by:

$$\begin{aligned} [\text{GHG}]_{\text{Chlorination}} = & [\text{GHG}]_{\text{NaCl Mining}} + [\text{GHG}]_{\text{Water Processing}} + \\ & [\text{GHG}]_{\text{NaOCl Production}} + [\text{GHG}]_{\text{NaOCl Delivery}} - [\text{GHG}]_{\text{H}_2 \text{ Production}} \end{aligned} \quad \text{Equation 6}$$

For ozonation, the total GHG emission is calculated by:

$$[\text{GHG}]_{\text{Ozonation}} = [\text{GHG}]_{\text{O}_2 \text{ Production}} + [\text{GHG}]_{\text{Ozone Production}} \quad \text{Equation 7}$$

Note, if ambient air was used as the oxygen source,  $([\text{GHG}]_{\text{O}_2 \text{ Production}})$  would be zero as no additional processing is required.

### 3.3.1 NPP Water Usage

As described in Section 3.2, water usage is calculated by multiplying the annual output of a reactor by the amount of water used to generate 1 MWh, which is estimated to be between 25000 to 60000 gal per MWh (94.635 to 227.12m<sup>3</sup>/MWh<sup>19,20,57</sup>). The ratio of water use to electricity generated is based on studies of NPPs from the United States. It is noted that water usage varies across different types of NPP technologies (e.g., molten salt, Boiling Water Reactor (BWR), Pressurized Water Reactor (PWR), Pressurized Heavy Water Reactor (PHWR), etc.).

Facilities, such as SMRs, would have different cooling requirements which may lead to lower water usage. A change in water usage would change the amount of control chemicals required. The effects of varying water usage were looked at using sensitivity analysis. With lower flows, other types of zebra mussel controls may become viable (e.g., UV irradiation).<sup>4,15</sup>

Water usage is calculated by multiplying the water required to generate 1 MWh with the generating capacity of the NPP.

$$\text{Water Usage (Annual)} = \text{Water Required/MWh} * \text{Generating Capacity} \quad \text{Equation 8}$$

While the capacity of Darlington Nuclear Generating Station (DNFS) was used (25791GWh)<sup>46</sup>, it can be replaced with any reactor with a capacity of # GWh/year.

As water requirement is in a range, calculations were repeated using the low end of the range, upper end of the range, and the middle of the range. Recall from earlier, zebra mussel controls are only required when water temperatures allow zebra mussels to be reproductive. For Lake Ontario, this is typically between May to October (i.e. 6 months).

$$\begin{aligned} \text{Water Usage For Zebra Mussel Control} &= \text{Water Usage} && \text{Equation 9} \\ &(\text{Annual}) * \text{Number of Months Zebra Mussel Control is Active} \\ &/12 \text{ months per year} \end{aligned}$$

Recall in Section 3.2.1, the functional unit is billion cubic meter of water treated. Water usage is the amount of water that requires treatment. Water usage becomes an input to calculating the amount of oxidizing agent required. The results of the water usage calculations are shown in Table 4.

*Table 4 – Input Variable: Water Usage for Large Scale NPP*

<b>Input Variable</b>	<b>Base</b>	<b>Range</b>
Water Usage per Megawatt-hour [m <sup>3</sup> /MWh]	1.6 x10 <sup>2</sup>	0.95x10 <sup>2</sup> to 2.3x10 <sup>2</sup>
Water Usage (Annual) [m <sup>3</sup> ]	4.1x10 <sup>9</sup>	2.4x10 <sup>9</sup> to 5.9x10 <sup>9</sup>
Water Usage For Zebra Mussel Control (6 months) [billion m <sup>3</sup> ]	2.1	1.2 to 2.9

### 3.3.2 Chemical Usage

Chemical usage is estimated based on the concentration required to achieve 99.9% kill rate, which is the typical standard for zebra mussel control.<sup>4</sup> Concentration is multiplied by the flow/water usage (from Table 4) to yield the amount of chemical (chlorine and ozone) required.

$$\text{Chemical Usage} = [\text{Water Usage}] * [\text{concentration required for 99.9\% kill rate}] \quad \text{Equation 10}$$

Recall from Section 2.2.2, the concentration of chlorine required to achieve 99.9% kill rate is 0.5ppm (5.0g/m<sup>3</sup>). Similarly, the concentration of ozone required to achieve the same result is 1.5ppm (15g/m<sup>3</sup>).

It is important to note that, for chlorination, the results of Equation 10 identifies the amount of chlorine required to achieve the required 99.9% kill rate. The weight of chlorine is not equal to the weight of NaOCl. Thus, the calculated chlorine required from Equation 10 must be converted to obtain the amount of NaOCl required.

Multiple industry sources have shown that the amount of NaOCl required is equal to 1.05 times the amount of chlorine required.<sup>29,58</sup> This is represented by Equation 11.

$$\text{Mass NaOCl} = 1.05 * \text{Mass Active Chlorine} \quad \text{Equation 11}$$

Combining Equation 10 and Equation 11, NaOCl usage is determined by using Equation 12.

$$\text{NaOCl Usage [kg/y]} = 1.05 [\text{kg NaOCl/kg Chlorine}] * \text{Concentration [kg Chlorine/m}^3] * \text{Flow [m}^3/\text{y}] \quad \text{Equation 12}$$

Using Equation 12 above, the amount of NaOCl required is shown in Table 5.

Volume is calculated using the specific gravity of NaOCl (1.04).<sup>18,29</sup> For ozonation, the amount of ozone required is calculated by using Equation 10 and the results shown in Table 6.

The results from Table 5 and Table 6 will be used as an input to calculate the energy requirement for producing these chemicals.

*Table 5 – Input Variable: Annual NaOCl Usage*

	<b>Base</b>	<b>Range</b>
NaOCl Usage [kg]	1.1x10 <sup>6</sup>	6.4x10 <sup>5</sup> to 1.5x10 <sup>6</sup>
NaOCl Usage [m <sup>3</sup> ]	1.0x10 <sup>3</sup>	6.2x10 <sup>2</sup> to 1.5x10 <sup>3</sup>

\*Numbers based on 6 months deployment of zebra mussels control

Table 6 – Input Variable: Annual Ozone Usage

	<b>Base</b>	<b>Range</b>
O <sub>3</sub> Usage [kg]	3.1x10 <sup>6</sup>	1.8x10 <sup>6</sup> to 4.4x10 <sup>6</sup>

\*Numbers based on 6 months deployment of zebra mussels control

### 3.3.3 Chemical Injection Methods

Sodium hypochlorite, that is produced off-site and trucked to the NPP, is stored in tanks and would need to be mixed with water into a solution prior to being added into the water system (see Section 3.2.3). The storage tanks and mixing apparatus are typically all connected via piping connections to minimize exposure to workers.<sup>15,58</sup> As shown in Table 4, the amount of water circulated through the NPP is in the order of billion cubic meters, whereas the amount of NaOCl from Table 5 is in the order of thousand cubic meters. Since the difference is over several orders of magnitude, it is assumed that the additional power required to dilute, mix, and circulate the chlorine through the NPP is negligible. The additional power used to dissolve and inject ozone into the water systems is also assumed to be negligible for the same reason.

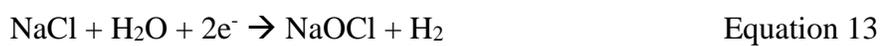
Similarly, ozone, after being generated, is dissolved/injected into water inside a holding tank. The ozonated water will then be added to the water system to achieve the concentration required. Again, due to the limited half-life of ozone in water of approximately 30 minutes, multiple injection points are required throughout the system to maintain the hostile environment for zebra mussels. For simplicity, it is

assumed that in one dose, the treated water will make its way around the entire system within 30 minutes. I.e. A single dose of ozone will be sufficient to meet the requirements for effective zebra mussel control with ozone. This is a low-end estimate as multiple doses would result in using multiple times the amount of ozone so increasing the calculated baseline.

### 3.3.4 Chemical Production Methods

#### 3.3.4.1 Sodium Hypochlorite (NaOCl)

The method of NaOCl production studied in this thesis is electrolysis, as mentioned in Section 3.2.3.1. The chemical reaction of producing NaOCl from electrolysis is shown in Equation 13. Factors such as efficiency (stoichiometric conversion and electrical), energy usage, and impact of upstream and downstream activities will need to be considered for the LCA.



Stoichiometry was used to determine the amount of each compound used. That is, 1kg NaOCl requires 0.785kg NaCl, 0.242kg H<sub>2</sub>O, and produces 0.027kg H<sub>2</sub>. To calculate the chemical production impact, one needs to determine the amount of energy required to produce the chemical using the following equation:

Energy Required for Chemical Production = Energy

Intensity \* Chemical Usage

Equation 14

Three different energy intensities were studied as part of sensitivity analysis. The three different energy intensities include:

- 1) An industrial source (2.5kWh/kg),<sup>18</sup>
- 2) A low end estimate from a lab / controlled environment (1.7kWh/kg),<sup>59</sup> and
- 3) A high end estimate (4.8kWh/kg)<sup>60</sup>.

It is expected that the electricity required to produce NaOCl will scale with energy intensity. Thus, the resultant amount of CO<sub>2</sub>e produced during the production of NaOCl also scales with the energy intensity. Using Equation 14, the three different energy intensities, and the amount of NaOCl required from Table 5, the amount of electricity required to produce NaOCl is shown in Table 7.

*Table 7 – Input Variable: Electricity Required to Produce NaOCl*

	<b>Base</b>	<b>Range</b>
Electricity required in producing NaOCl [GWh] (Industrial Source)	2.7	1.6 to 3.8
Electricity required in producing NaOCl [GWh] (Low Estimate)	1.9	1.1 to 2.6
Electricity required in producing NaOCl [GWh] (High Estimate)	5.2	3.1 to 7.4

To calculate the equivalent GHG emissions from chemical production, the amount of electricity required is multiplied by the grid GHG intensity; this is shown in Equation 15. The grid GHG intensity value is obtained from GHGenius and is shown in Appendix A. The resultant GHG produced is discussed in Chapter 4.

$$\text{GHG Emission From Chemical Production} = \text{Energy Required for Chemical Production} * \text{Grid GHG Intensity} \quad \text{Equation 15}$$

As discussed in Section 3.2.3.1, the NaOCl production plant is assumed to be co-located with the mining site. This is comparable to existing chemical production facilities in Ontario. Sifto Canada is an example of this set-up.<sup>61</sup> This eliminates trucking distance between the mining site and NaOCl production facility and relative emissions. Separating the chemical production site from the salt mine would add a transport element into manufacturing of NaOCl. The impact of separating the NaOCl production facility and mining site will be looked at in the sensitivity analysis (Section 4.1).

#### 3.3.4.2 Ozone

The method of ozone production studied in this work is the corona discharge method. As with NaOCl production, factors such as efficiency, energy usage, and impact of upstream and downstream activities need to be considered for the LCA.

As with chlorination, the energy required is equal to the product between energy intensity and amount of chemical agent required. This is calculated using Equation 14.

Two different energy intensities were studied as part of sensitivity analysis. The two energy intensities correlate to the source of oxygen. These energy intensities are shown in Table 8.

*Table 8 – Energy Intensity in Producing Ozone* <sup>56</sup>

	Base	Range
Energy Intensity of Producing O <sub>3</sub> (Air source) [kWh/kg]	16.5	15 to 18
Energy Intensity of Producing O <sub>3</sub> (O <sub>2</sub> source) [kWh/kg]	6.5	5.0 to 8.0

It is expected that the electricity required to produce ozone will scale with energy intensity. Thus, the resultant amount of CO<sub>2</sub>e produced during the production of ozone also will scale with the energy intensity. Using Equation 14, the energy intensities in Table 8, and the amount of ozone required from Table 6, the amount of electricity required to produce ozone is shown in Table 9.

Note, when using pure oxygen, the additional electricity required to generate pure O<sub>2</sub> need to be accounted for. The amount of electricity required to generate pure O<sub>2</sub> is approximately 0.2kWh/kg O<sub>2</sub>.<sup>56,62</sup> The above process is repeated to calculate the amount of electricity required to generate pure O<sub>2</sub> and the results are shown in Table 10.

Table 9 – Input Variable: Electricity Required in Producing Ozone

	Base	Range
Electricity Required in Producing O <sub>3</sub> [GWh] (Air Source)	51	30 to 73
Electricity Required in Producing O <sub>3</sub> [GWh] (O <sub>2</sub> source)	20	12 to 29

Table 10 – Input Variable: Electricity Required in Producing O<sub>2</sub>

	Base	Range
O <sub>2</sub> Usage [kg]	3.1x10 <sup>6</sup>	1.8x10 <sup>6</sup> to 4.4x10 <sup>6</sup>
Electricity Required in Producing O <sub>2</sub> [GWh]	0.62	0.37 to 0.88

As with NaOCl, to calculate the equivalent GHG emissions from ozone production, the amount of electricity required is multiplied by the grid GHG intensity (See Equation 15). The grid GHG intensity value is obtained from GHGenius and is shown in Appendix A. The resultant GHG produced is discussed in Chapter 4.

### 3.3.4.3 Hydrogen

Hydrogen is produced as a co-product from NaOCl production. This hydrogen could be used to replace hydrogen in the marketplace, which would have otherwise been produced via other methods. As such, there is a potential GHG credit that needs to be accounted for during the production of NaOCl. This GHG credit will be referred to as the Hydrogen credit going forward.

The most common method of commercial H<sub>2</sub> production is steam methane reforming.<sup>63</sup> For this study, the Hydrogen credit is equal to the emissions of producing an equivalent amount of hydrogen through steam methane reforming.

A life cycle analysis was completed on the GHG emissions from hydrogen fuel production in the US from LNG and Coal<sup>63</sup>. While coal is still a popular energy source in the US, it has been phased out in Ontario. If the process was replicated in Ontario, the numbers would likely be lower than those from the US study because the source of electricity in Ontario is mostly from nuclear or hydroelectric. The US study included GHG intensities for both including and excluding Carbon Capture and Sequestration (CCS). The values of the GHG intensities are as follows:

- 1) With CCS (4.9 kg CO<sub>2</sub>e/kgH<sub>2</sub>), and
- 2) Without CCS (8.9 kg CO<sub>2</sub>e/kgH<sub>2</sub>).

Sensitivity analysis was performed to look at the impact of CCS. Assuming more efficient processes in manufacturing hydrogen would reduce the hydrogen credit. The opposite would be true for less efficient processes in manufacturing hydrogen.

The amount of hydrogen produced is calculated using Equation 16, which is based on stoichiometry assuming 100% conversion, as above.

$$\text{Amount of H}_2 \text{ Produced} = \text{NaOCl Usage} * 0.027$$

Equation 16

The amount of H<sub>2</sub> produced as a co-product of NaOCl production, based on stoichiometry, is shown in Table 11. In practice, not all of the initial compounds will be converted into the end products. As such, it is possible that less H<sub>2</sub> is produced from the same quantities of material, which would decrease the size of the hydrogen credit.

*Table 11 – Input Variable: Annual H<sub>2</sub> Production from NaOCl Production Process:*

	Base	Range
H <sub>2</sub> Produced [tonne]	3.5	2.1 to 5.0

\*Numbers based on 6 months deployment of zebra mussels control

The equivalent GHG emissions from H<sub>2</sub> production are calculated as the product between the amount of hydrogen produced and the GHG intensity of hydrogen production (see Equation 17). The resultant GHG emissions from H<sub>2</sub> production are discussed in Chapter 4.

$$\text{GHG Emission From H}_2 \text{ Production} = \text{Amount of H}_2$$

$$\text{Produced} * \text{GHG Intensity}$$

Equation 17

### 3.3.5 Sources of Primary Materials

#### 3.3.5.1 Salt (NaCl)

This work assumes that salt is mined in Sarnia, Ontario (Windsor mines). Windsor mines is an existing and active salt mine. It is also one of the largest salt mines in the world.<sup>61,64</sup> This assumption was made to keep production local. If salt import is required, transportation of salt to the chemical production plant would need to be considered, which would increase the environmental impact. The impact of transporting salt to the chemical production plant is looked at in the sensitivity analysis.

Salt is assumed to be from open mines. Underground mines would typically have higher GHG emissions as it requires more specialized machinery to mine the salt.<sup>64,65</sup> Drawing a comparison with coal mining, the impact of surface mining is approximately an order of magnitude less than the impact of underground mining (0.84gCO<sub>2</sub>e/MJ vs 4.5gCO<sub>2</sub>e/MJ).<sup>63</sup>

Note, this work only considered GHG emissions for environmental impact. Other factors such as aesthetics/visual pollution, noise pollution, wastewater run-off, groundwater contamination, impact on wildlife, etc. would need to be considered when looking at the overall environmental impact.

The impacts of salt mining are taken from the Government of Canada website, which estimates energy usage from the mining sector and assigns a GHG intensity

for the mining activity for a given year. Per Natural Resources Canada (NRCan), there is a level of uncertainty that could be due to the numbers reported.<sup>65,66</sup> Since uncertainty exists in data collection, thus a level of uncertainty in the analysis is added. Furthermore, it is noted that the GHG intensity provided by NRCan is not specifically for salt mining, but for mining in general. In spite of the uncertainty, the calculations will provide a general sense of the impact. The Energy Intensity for Mining given by NRCan is 216.5MJ/tonne of salt mined, which was converted to GHG Intensity by NRCan based on the fossil fuels used.<sup>65,66</sup>

The amount of salt required was determined using stoichiometry: i.e. 1kg NaOCl requires 0.785kg NaCl, 0.242kg H<sub>2</sub>O, and produces 0.027kg H<sub>2</sub>. In practice, not all of the initial compounds will be converted into the end products. As such, it is possible that more compounds are required to produce the quantities of material needed, which would increase the GHG emissions associated with the process. This will be studied further in the Results and Discussion (Chapter 4).

$$\text{Amount of NaCl Required} = \text{NaOCl Usage} * 0.785 \quad \text{Equation 18}$$

The energy required for salt mining was determined by multiplying the amount of salt required by the mining energy intensity reported from NRCan.

$$\text{Energy Required for Mining} = \text{NaCl Required} * \text{Energy Intensity for Mining} \quad \text{Equation 19}$$

The calculated amount of salt required and energy required to mine it, can be found in Table 12 and Table 13, respectively.

*Table 12 – Input Variable: Annual Salt (NaCl) Used:*

	Base	Range
NaOCl Usage [tonnes]	1100	640 to 1500
Salt (NaCl) used [tonne]	$1.0 \times 10^2$	$6.0 \times 10^2$ to $1.5 \times 10^2$

\*Numbers based on 6 months deployment of zebra mussels control

*Table 13 – Input Variable: Energy Required for Mining Salt*

	Base	Range
Energy Required in Mining Salt [TJ]	0.022	0.013 to 0.031

\*Numbers based on 6 months deployment of zebra mussels control

The equivalent GHG emissions from salt mining is calculated as the product between the energy required in mining salt and the GHG intensity of salt mining (see Equation 20). The GHG intensity, as reported by Stat Can, is 62.8 tonne CO<sub>2</sub>e/TJ.<sup>66</sup> The resultant GHG produced from salt mining is discussed in Chapter 4.

GHG Emission From Salt Mining = Energy Required for

Mining Salt \* GHG Intensity

Equation 20

### 3.3.5.2 Electricity / Grid

This study considers electricity from the Ontario grid i.e., electricity used during the manufacturing of the chemicals comes from the Ontario grid. The Ontario grid is supplied by multiple sources. Furthermore, this assumes the grid average, which averages out variances such as overnight and daily/seasonal peaks. As such, the grid is assumed to be made up of all sources that supply the grid. Organizations such as the IESO have real-time data showing which power station is supplying the grid and how much electricity it is supplying.<sup>47</sup> GHGenius has taken this into consideration in its software model.<sup>48,49</sup> Should the mix/composition of the grid change, the equivalent GHG emissions would change accordingly i.e., if the grid is made up of more lower emission sources, the overall amount of GHG equivalent generated per kWh would be lower and vice versa. The life cycle contribution of the grid, as modeled in GHGenius, is approximately 137g CO<sub>2</sub>e/kWh delivered. Note, GHGenius also incorporates electricity distribution in its assumptions.<sup>48,49</sup>

### 3.3.5.3 Water for NaOCl Production

Water used for NaOCl production (i.e., electrolysis) is assumed to be processed/treated and supplied by the local municipal system. A study on Energy Intensity of Water Treatment Plants in Ontario concludes that the electricity used to power the equipment within the facility to be the largest contributor to GHG emissions.<sup>67</sup> The study considered drawing water from various sources (e.g., open surface, underground, etc.) and for large and small facilities. For this thesis, the effects for a large capacity open-surface water treatment facility was used to

estimate the environmental impact of processing water. Note, the referenced study is from 2009 before coal was phased out in Ontario. Without coal, the impact from the grid would be arguably smaller. However, since the impact from water processing is very small, the final conclusions of this thesis are not changed.

Water usage is determined based on stoichiometry where 1kg of NaOCl requires 0.242kg of H<sub>2</sub>O. (1kg NaOCl requires 0.785kg NaCl, 0.242kg H<sub>2</sub>O, and produces 0.027kg H<sub>2</sub>). The calculated amount of water required for NaOCl production is shown in Table 14

$$\text{Water Required for NaOCl Production} = \text{NaOCl Usage} * 0.242 \quad \text{Equation 21}$$

*Table 14 – Input Variable: Annual Water Required for Producing NaOCl:*

	Base	Range
H <sub>2</sub> O Required [m <sup>3</sup> ]	25	15 to 35

\*Numbers based on 6 months deployment of zebra mussels control

The energy required to process water is shown in Table 15. The amount of energy required to process water for NaOCl production is shown in Table 16.

Table 15 – Water Conservation Indirect Energy Intensities<sup>68</sup>

Water Use Component	Mean Energy Intensity (kWh/m <sup>3</sup> )			
	Surface Supply (WTPs)		Groundwater Supply (Wells)	
	Small Capacity (< 5,000 m <sup>3</sup> /d)	Large Capacity (> 5,000 m <sup>3</sup> /d)	Small Capacity (< 1,000 m <sup>3</sup> /d)	Large Capacity (> 5,000 m <sup>3</sup> /d)
<b>Total Indirect Energy Intensity</b>	1.11	0.68	1.05	0.74

Table 16 – Input Variable: Electricity Required in Processing Water for NaOCl Production

	Base	Range
Electricity Required for Treating Water [kWh]	17	9.9 to 24

\*Numbers based on 6 months deployment of zebra mussels control

To calculate the equivalent GHG emissions from water processing in NaOCl production, the amount of electricity required is multiplied by the grid GHG intensity, as shown in Equation 22. The grid GHG intensity value is obtained from GHGenius and is shown in Appendix A. The resultant GHG produced is discussed in Chapter 4.

$$\text{GHG Emission From Water Processing} = \text{Energy Required}$$

$$\text{for Processing H}_2\text{O} * \text{Grid GHG Intensity}$$

$$\text{Equation 22}$$

### 3.3.6 Delivery of Chemicals to Site

Sodium hypochlorite is delivered by tanker truck, which is between 4000-6000 US gal (15.14-22.71m<sup>3</sup>).<sup>18,29</sup> This thesis uses the average volume (i.e. 5000 US gal or 18.93m<sup>3</sup>) for the base case. Tanker truck is a reasonable mode of transport for NaOCl. Marine shipping or rail would be better suited for much larger volumes.

Recall, it was assumed that the theoretical NPP is situated on the site that is on the shores of Lake Ontario. An example of such a plant that is currently in operation is DNGS. Delivery emissions was calculated using the distance between Sarnia and DNGS. Delivery emissions was calculated using the distance between Sarnia and DNGS, which is the furthest amongst the three operating NPP in Ontario from Sarnia at 349km per Google Maps (See Figure 6). Sensitivity analysis was done to study the effects of increasing/decreasing the transport distance. This will be discussed further in Chapter 4.

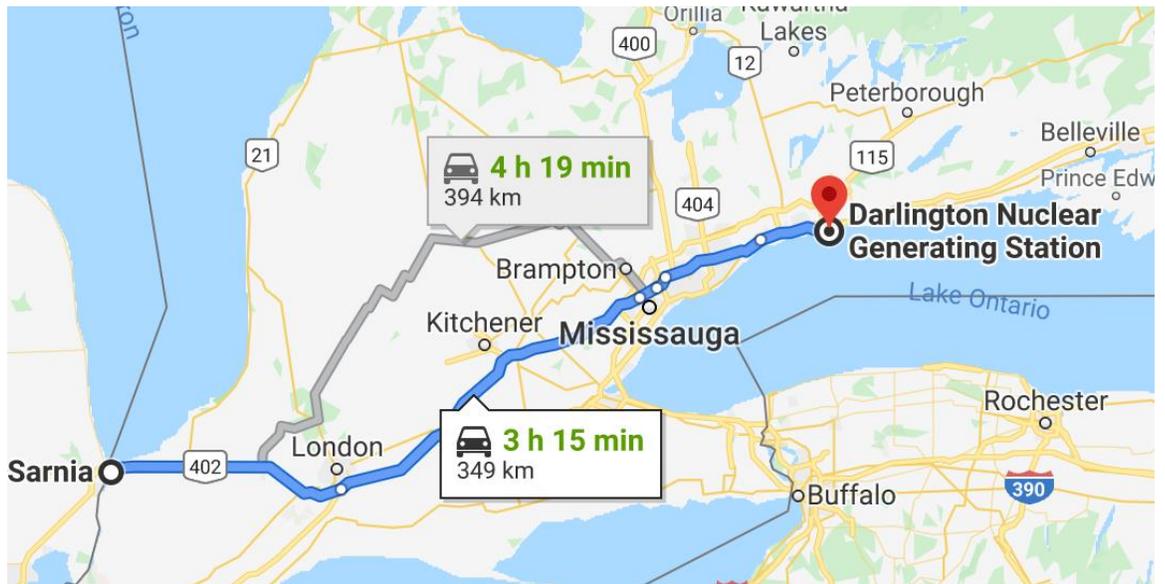


Figure 6 – Sarnia to Darlington Nuclear Generating Station<sup>69</sup>

GHGenius provides the GHG production from heavy truck delivery is calculated. Empty backload, that is the return trip of the truck once the chemical has been delivered, is factored in the GHGenius model.<sup>70</sup> The number of truck deliveries required is calculated by dividing the total amount of NaOCl used by the average volume of a tanker truck, rounded to the next whole number.

$$\text{Number of Truckloads} = \text{Amount of NaOCl} / \text{Volume of Truck} \quad \text{Equation 23}$$

The distance travelled by the delivery vehicle is the product between the number of truckloads and the distance between the chemical plant and NPP.

$$\text{Total Distance Travelled} = \text{Number of Truckloads} * \text{Distance} \quad \text{Equation 24}$$

Between Chemical Plant and NPP

The total number of deliveries required and total distance travelled for chemical delivery are shown in Table 17 and Table 18, respectively.

*Table 17 – Input Variable: Annual Number of Deliveries*

	Base	Range
Number of Truck Loads (Rounded Up)	56	33 to 79

*Table 18 – Input Variable: Annual Distance Travelled by Delivery Truck*

	Base	Range
Total Distance Travelled [km]	2.0x10 <sup>4</sup>	1.2x10 <sup>4</sup> to 2.8x10 <sup>4</sup>

To calculate the equivalent GHG emissions from chemical delivery, the total distance travelled is multiplied by the GHG intensity for heavy duty vehicle, as shown in Equation 25. The GHG intensity value (1.455kg CO<sub>2</sub>e/km) is obtained from GHGenius and it is shown in Appendix A. The resultant GHG produced is discussed in Chapter 4.

$$\text{GHG Emission From Chemical Delivery} = \text{Total Distance}$$

$$\text{Travelled} * \text{GHG Intensity}$$

$$\text{Equation 25}$$

### 3.4 SUMMARY OF TEST VARIABLES AND PARAMETERS

Before going into discussion of the results, it is useful to recall the variables and parameters that were used for the calculations. Table 19 below lists out the parameters. Table 20 and Table 21 are the test matrices for chlorination and ozonation.

*Table 19 – Summary of Test Variables and Parameters*

	<b>Variable/Parameter</b>	<b>Values</b>	<b>Notes</b>
A	NPP Water Usage	94.63 to 227.1 m <sup>3</sup> /MWh	Per <sup>19,20,57</sup>
B	NPP Capacity	25791 GWh	Per <sup>46</sup>
C	Oxidizing Agent Concentration	5.0g/m <sup>3</sup> 15g/m <sup>3</sup>	For chlorination (C <sub>Cl</sub> ) For ozonation (C <sub>O3</sub> )

D	Ontario Grid GHG Intensity	137kg CO <sub>2</sub> e/MWh	From GHGenius
E	Electricity Intensity for NaOCl Production	1.7 kWh/kg 4.8 kWh/kg 2.5 kWh/kg	Low Estimate <sup>59</sup> (E <sub>L</sub> ) High Estimate <sup>60</sup> (E <sub>H</sub> ) Industrial Source <sup>18</sup> (E <sub>I</sub> )
F	Electricity Intensity for Ozone Production	5.0 to 8.0 kWh/kg 15 to 18 kWh/kg	O <sub>2</sub> Source <sup>56</sup> (F <sub>O2</sub> ) Air Source <sup>56</sup> (F <sub>Air</sub> )
G	Energy Intensity for O <sub>2</sub> Production	0.2 kWh/kg	Per <sup>56,62</sup>
H	H <sub>2</sub> Production	0.027kg per kg NaOCl	Calculated based on stoichiometry
I	GHG Intensity for H <sub>2</sub> Production	4.9 kg CO <sub>2</sub> e/kg H <sub>2</sub> 8.9 kg CO <sub>2</sub> e/kg H <sub>2</sub>	With CCS <sup>63</sup> (I <sub>1</sub> ) Without CCS <sup>63</sup> (I <sub>2</sub> )
J	NaCl Usage	0.785kg per kg NaOCl	Calculated based on stoichiometry
K	Energy Requirement for NaCl Mining	216.5 MJ/tonne	From NRCan <sup>65,66</sup>
L	GHG Intensity for Mining	62.8 tonne CO <sub>2</sub> e/TJ	From NRCan <sup>65,66</sup>
M	Water Required for NaOCl Production	0.242kg per kg NaOCl	Calculated based on stoichiometry
N	Energy Intensity for H <sub>2</sub> O Processing	0.68kWh/m <sup>3</sup>	For Large Capacity Surface Supply WTP <sup>68</sup>
O	Tanker Size	15.14 to 22.71m <sup>3</sup>	Average tanker size per 18,29
P	Distance Between Chemical Plant and NPP	349km	Per Google Maps <sup>69</sup>
Q	GHG Intensity for Heavy Duty Vehicle Delivery	1.455kg CO <sub>2</sub> e/km	From GHGenius

Table 20 – Test Matrix for Chlorination

		Parameter															
	Case	A	B	C	D	E	H	I	J	K	L	M	N	O	P	Q	
1	Electricity Intensity for NaOCl Production	A	B	C <sub>Cl</sub>	D	E <sub>LR</sub>	H	0	J	K	L	M	N	O	P	Q	
2	Electricity Intensity for NaOCl Production (Base Case)	A	B	C <sub>Cl</sub>	D	E <sub>I</sub>	H	0	J	K	L	M	N	O	P	Q	
3	Electricity Intensity for NaOCl Production	A	B	C <sub>Cl</sub>	D	E <sub>HR</sub>	H	0	J	K	L	M	N	O	P	Q	
4	With H <sub>2</sub> credit	A	B	C <sub>Cl</sub>	D	E <sub>I</sub>	H	I <sub>1</sub>	J	K	L	M	N	O	P	Q	
5	With H <sub>2</sub> credit	A	B	C <sub>Cl</sub>	D	E <sub>I</sub>	H	I <sub>2</sub>	J	K	L	M	N	O	P	Q	
6	With H <sub>2</sub> credit	A	B	C <sub>Cl</sub>	D	E <sub>LR</sub>	H	I <sub>1</sub>	J	K	L	M	N	O	P	Q	
7	With H <sub>2</sub> credit	A	B	C <sub>Cl</sub>	D	E <sub>LR</sub>	H	I <sub>2</sub>	J	K	L	M	N	O	P	Q	
8	With H <sub>2</sub> credit	A	B	C <sub>Cl</sub>	D	E <sub>HR</sub>	H	I <sub>1</sub>	J	K	L	M	N	O	P	Q	
9	With H <sub>2</sub> credit	A	B	C <sub>Cl</sub>	D	E <sub>HR</sub>	H	I <sub>2</sub>	J	K	L	M	N	O	P	Q	

\* LR denotes Low Range, HR denotes High Range

Table 21 – Test Matrix for Ozonation

		Parameter					
	Case	A	B	C	D	F	G
1	Air Source (Base Case)	A	B	C <sub>O3</sub>	D	F <sub>Air</sub>	0
2	Oxygen Source	A	B	C <sub>O3</sub>	D	F <sub>O2</sub>	G

## 4 RESULTS AND DISCUSSION

Table 22 provides the GHG emissions for each major life cycle stage in a chlorination zebra mussel control system per billion cubic meters of water treated. The initial stages of salt mining and water processing have low GHG emissions and play no significant role in the overall GHG emissions for the chlorination process. Chemical delivery has moderate impact at approximately 14 tonnes of CO<sub>2</sub>e per billion cubic meters of water treated. The chemical production process has the highest impact at between 120 to 350 tonnes of CO<sub>2</sub>e per billion cubic meters of water treated. Note, the credit from the hydrogen co-product has a moderate impact and is estimated in the range of 8.5 to 15 tonnes of CO<sub>2</sub>e per billion cubic meters of water treated. This is likely due to the large environmental impact that comes with generating hydrogen from steam methane reforming.

*Table 22 – Summary of GHG Emissions Each Stage (Chlorination)*

<b><u>Life Cycle Stage</u></b>	<b><u>GHG Emissions [t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup>]</u></b>
NaOCl Delivery	<b>14</b>
Salt Mining	<b>0.67</b>
Water Processing	<b>0.0011</b>
NaOCl Production (Low Source)	<b>120</b>
NaOCl Production (High Source)	<b>350</b>
NaOCl Production (Industrial Source)	<b>180</b>
H <sub>2</sub> Production (without CCS)	<b>15</b>
H <sub>2</sub> Production (with CCS)	<b>8.3</b>

As described above, the largest contribution to GHG emissions from chlorination comes from NaOCl production. While there are many processes to generate NaOCl, electrolysis is the most commonly used method commercially.<sup>18,59,60</sup> Given the large amounts of NaOCl used, it makes sense that this stage is the largest contributor. Since the main input for this process is electricity, the amount of GHG generated in this stage is directly related to the output from the grid.

Figure 7 compares the GHG emissions from chlorination cases, as described in Table 20, with the GHG emissions from ozonation cases, as described in Table 21. The graph shows that the amount of GHGs generated using ozone is much higher than that from using chlorine. For comparison, per billion cubic meters of water treated, chlorination produces on the order of hundreds of tonnes (120 to 350 tonnes of CO<sub>2</sub>e). In contrast, ozonation produces on the order of thousands of tonnes (1300 to 3400 tonnes of CO<sub>2</sub>e) per billion cubic meters of water treated. Figure 8 and Figure 9 breaks out the comparison for chlorination cases 1, 2, and 3 and ozonation cases 1 and 2 respectively.

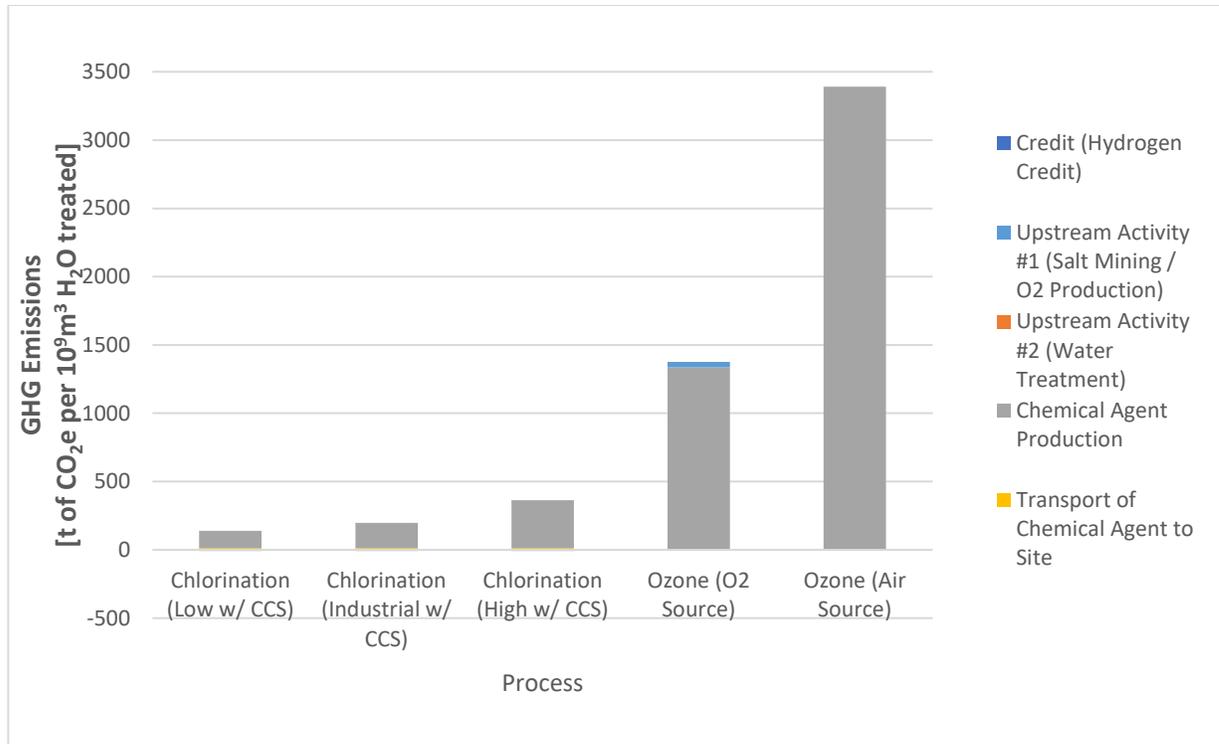


Figure 7 – Comparison of GHG Emission From Chlorination and Ozonation (per 10<sup>9</sup> m<sup>3</sup> Water Treated). From Left to Right (Chlorination Case 1, 2, 3 and Ozonation Case 1, 2).

There are a few factors of note based on the calculated results:

- 1) The largest contributor for GHG emissions for either process is the chemical production. All other factors are at least an order of magnitude less.
- 2) For both processes, the impact due to electricity usage is linear. That is, the more efficient the process, the fewer tonnes of GHG it will generate.
- 3) The concentration required to achieve 99.9% kill rate is three times higher for ozone (1.5ppm vs 0.5ppm).<sup>15,18</sup> This results in requiring larger amounts of ozone to control zebra mussels when compared to NaOCl.
- 4) The amount of electricity required to generate the oxidizing agent is much higher for ozone when compared with NaOCl (5-8kWh/kg using O<sub>2</sub> or 15-

18kWh/kg using air for ozone<sup>56</sup> vs 1.7-4.9kWh/kg for NaOCl<sup>18,59,60</sup>). Along with the higher amounts of oxidizing agent required, this factor makes the GHG emissions for ozone much higher than the GHG emissions for chlorination.

5) The hydrogen credit is in the same order of magnitude as chemical delivery. Inclusion of the hydrogen credit makes chlorination even more favourable compared to ozonation.

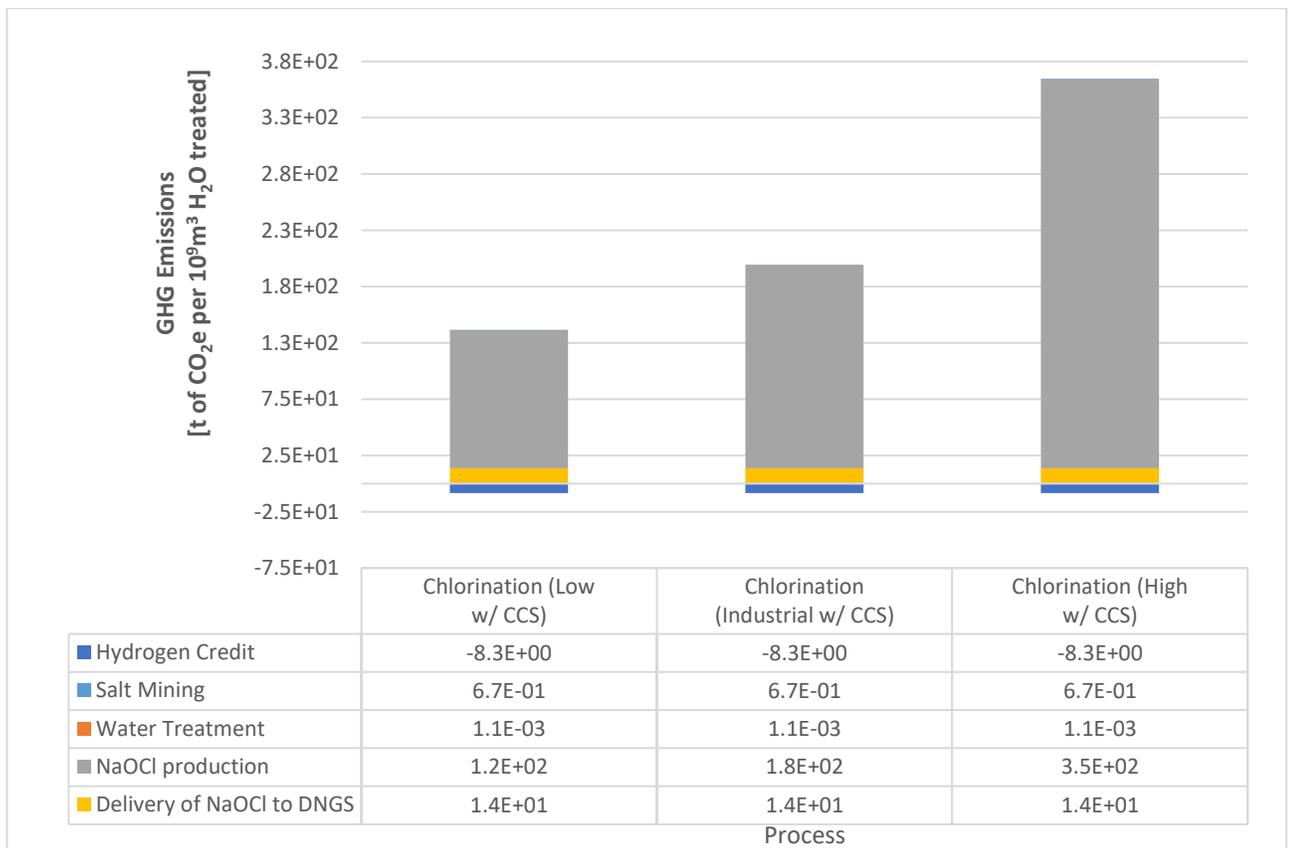


Figure 8 – Comparison of GHG Emission From Chlorination (per 10<sup>9</sup> m<sup>3</sup> Water Treated). From Left to Right (Chlorination Case 1, 2, 3)

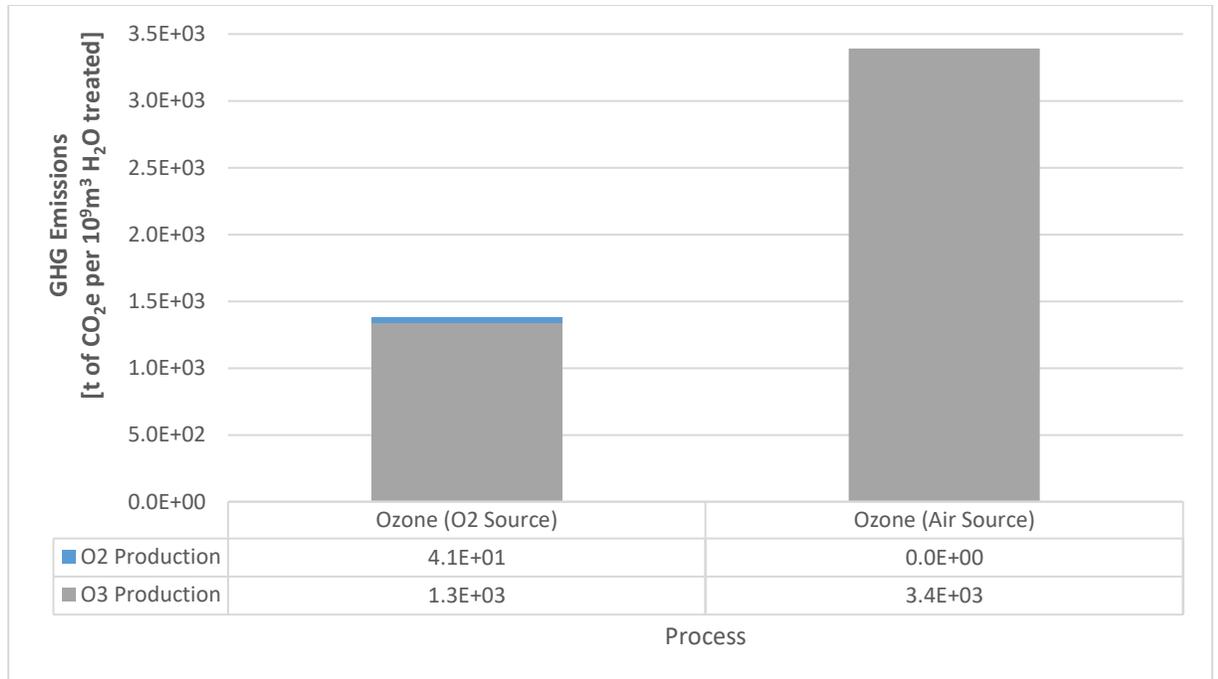


Figure 9 – Comparison of GHG Emission From Ozonation (per 10<sup>9</sup> m<sup>3</sup> Water Treated). From Left to Right (Ozonation Case 1, 2).

For ozonation, the only contributor to GHG emissions is the generation of ozone in the base case. In this work, the major variable is the oxygen source: Case 1 - Pure O<sub>2</sub> and Case 2 - Air. With the large volume of ozone required, it is assumed ozone is produced on site and the transport of oxygen to site was omitted in the case of using pure oxygen. These factors will be further discussed in Section 4.1.2.

As noted earlier, this work assumed ozonated water will make its way through the system within the half-life of ozone in water. In reality, the same dose will need to be applied over multiple injection points to ensure the concentration of ozone within the water system is over the required concentration for effective zebra mussel control. With multiple injections, the impact of ozone will be multiple times

higher than what is presented in the results. As such, the overall conclusion was not affected by this assumption.

A common factor between both chlorination and ozonation is that one of the main inputs to producing the control chemical is electricity. Electricity, or contribution from the grid, is the largest contributor to GHG emissions for control methods. GHGenius models the GHG intensity of the grid as a weighted average by considering the major electricity sources that make-up the grid. This also accounts for the fluctuations in terms of grid make-up. The grid make-up used in thesis can be found in Appendix A.

The contribution of the grid is approximately 137g CO<sub>2</sub>e/kWh delivered (Variable D from Table 19). A large portion of the grid's emissions comes from natural gas/boilers (~107g CO<sub>2</sub>e/kWh delivered), despite natural gas/boilers only making up about 18% of the grid.<sup>48,49</sup> For ozone to be more comparable with chlorination, in terms of GHGs produced, the difference between the production of NaOCl and O<sub>3</sub> must be reduced so that O<sub>3</sub> production emissions are about equal to or less than those of the delivery of NaOCl.

The emissions from delivery are about two orders of magnitude smaller than the emissions from ozone production. This means, for ozonation to be comparable with chlorination, the GHG emissions for the total process needs to drop down two

orders of magnitude from  $1.0 \times 10^3$  tonnes of  $\text{CO}_2\text{e}/10^9 \text{ m}^3$  treated to the order of  $1.0 \times 10$  tonnes of  $\text{CO}_2\text{e}/10^9 \text{ m}^3$  treated.

Based on the data from the GHGenius model, solar and wind energy are the only electricity sources that are about two orders of magnitude lower than natural gas at  $5.3 \text{ g CO}_2\text{e}/\text{kWh}$  delivered.<sup>48,49</sup> Nuclear, biomass, and hydro are one order of magnitude lower than natural gas at  $31.9 \text{ g CO}_2\text{e}/\text{kWh}$  delivered,  $30.9 \text{ g CO}_2\text{e}/\text{kWh}$  delivered, and  $46.0 \text{ g CO}_2\text{e}/\text{kWh}$  delivered, respectively.<sup>48,49</sup>

Therefore, in order for ozonation to be comparable with chlorination, the Ontario grid would need to be made up of 100% solar and wind energy. This would bring Variable D - Ontario Grid GHG intensity down from  $137 \text{ g CO}_2\text{e}/\text{kWh}$  to  $5.3 \text{ g CO}_2\text{e}/\text{kWh}$ . This will bring the GHG contribution from ozone production to approximately  $50 \text{ t CO}_2\text{e}/10^9 \text{ m}^3$  treated to  $130 \text{ t CO}_2\text{e}/10^9 \text{ m}^3$  treated. In such a scenario, the emissions associated with  $\text{NaOCl}$  production would also be reduced. This means that other aspects of the process, such as chemical delivery, would contribute to a higher percentage of the overall GHG emissions. Other factors, such as the potential of spills during transport and storage requirements may play a bigger role in the final decision.

Canada is experiencing a strong interest in SMRs and AMRs for near future deployment. These reactor designs, while smaller in scale compared to a full NPP, require cooling and hence the potential for zebra mussels to cause problems

remains. It is possible that the zebra mussel problem may be more severe for the smaller reactors as water intake flow rates are much lower and the lower velocity and smaller diameter intake pipe might encourage faster adherence and growth of the zebra mussels. These new designs will need protective systems and the environmental impact of those protective systems would need to be studied. For example, chemical releases may be more impactful with the possibility of SMRs and AMRs being situated on smaller bodies of water. Chlorination and ozonation were studied in this paper, but with lower flows, other methods of control, such as UV irradiation, could be considered viable.

For the base case in chlorination (Case 2 from Table 20) and ozonation (Case 1 from Table 21), the total GHG emissions are  $1.9 \times 10^2$  t CO<sub>2</sub>e/10<sup>9</sup> m<sup>3</sup> treated and  $3.4 \times 10^3$  t CO<sub>2</sub>e/10<sup>9</sup> m<sup>3</sup> treated. That is, chlorination is the preferred method for large scale reactors. The major contributor is from the production of chemical agents as shown in Figure 7, Figure 8, and Figure 9. The impact from chemical delivery does not influence the results for any appreciable distance. This result remains true for SMRs that are located near the highway using the same evaluation criteria and assumptions as the delivery effects by truck are too small. This result may not remain true if alternate methods of delivery are chosen which may be the case if the SMR is not located along a highway.

For SMRs that do not require water cooling, zebra mussel controls will not be needed and hence, no environmental impact from zebra mussel controls. However,

under certain conditions, alternatives to chlorination could be considered viable as alluded to above. In such scenarios, consideration to other business factors such as practicality, cost, operation/maintenance burden, and legal/regulatory implications, may be prioritized ahead of environmental impact in the decision-making process.

An example of this is a SMR located in a remote location such as Ontario's Far North. In such scenario, the reactor is not connected to a grid. Conventional modes of transport, such as road and rail, are not available. Control agents, if required, would need to be manufactured on-site. Under these conditions, alternatives to chlorination such as ozonation and UV irradiation may be considered more viable. This is because the inputs to generate ozone and UV rays are readily available and do not need to be delivered and/or stored on-site. For ozone, an oxygen source and electricity are required. For UV rays, only electricity is required.

#### 4.1 SENSITIVITY ANALYSIS

With the uncertainty surrounding the data, sensitivity analysis was done to illustrate the range of results when accounting for changes in key variables. One factor looked at was varying the amounts of water used for the NPP (Variable A from Table 19). That is, calculations were repeated using the upper and lower bounds of the range for water required to produce 1MWh ( $95\text{m}^3/\text{MWh}$  and  $227\text{m}^3/\text{MWh}$ ). Since a fixed concentration of oxidizing agents (Variable C from Table 19) is required to control zebra mussels (1.5ppm for ozone and 0.5ppm for chlorine), the amount of oxidizing agents required scales proportionally with the amount of water

treated for use by the NPP. That is, the lower the volume of water treated, the lower the volume of oxidizing agent required, and the fewer tonnes of GHGs generated. It is important to note that there are other variables which would affect how much water is required. One of the factors is lake temperature. Higher lake temperatures would result in lower efficiency in power generation. Thus, if the same MWh output is required during periods of higher lake temperatures, higher volumes of water would be required, resulting in higher amounts of oxidizing agents (see Table 5 and Table 6 in Section 3.3.2). With higher amounts of oxidizing agents used, higher amounts of GHGs will be generated as a result.

Earlier, it was assumed that the efficiency of converting chemicals is 100%. In practice, the conversion factor (or yield) will not be 100% due to factors such as incomplete reactions and losses through the system.<sup>71</sup> The chemical reactions mentioned in this thesis all have different yields of less than 100%. This would equate to more source material, or reactants being required to produce the same amount of products. Therefore, the calculated GHG emissions are likely lower than it would be in practice.

For example, if the yield for the NaOCl production is at 50%, the overall impact from NaOCl production would be doubled. That is, the impact from salt mining and water treatment would double. The impact from those stages would still be negligible even if doubled. For salt mining, the emissions would go from 0.67 t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup> to 1.3 t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup>. For water processing, the emissions would go

from 0.0011 t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup> to 0.0022 t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup>. The current difference between ozonation and chlorination, in terms of GHG emissions, is about a factor of 10. Factoring in the reduced efficiency would still show ozonation performing worse than chlorination. Hence, this factor was not studied further.

#### 4.1.1 Chlorination Specific

A couple of factors that influence the GHG contribution for the chemical production life cycle stage were varied to see the effects: Variable E - Electricity Intensity for NaOCl Production and Variable H - H<sub>2</sub> Production Credit. Table 23 shows the totals for chlorination cases 1 through 9. Effects of chemical production and chemical delivery will be discussed further in their respective sections below. Factors associated with Water Processing and Salt Mining were not looked at since they are several orders of magnitude below the overall impact and any changes would be negligible when looking at the overall picture.

*Table 23 – Cases for Chlorination With Total GHGs Released*

Case	Variable		Totals [t CO <sub>2</sub> e/10 <sup>9</sup> m <sup>3</sup> ]
	Electricity Intensity for NaOCl Production	H <sub>2</sub> Production Credit	
1	Low Estimate	No Credit	1.4 x10 <sup>2</sup>
2	Industrial Source (Base Case)	No Credit	1.9 x10 <sup>2</sup>
3	High Estimate	No Credit	3.6 x10 <sup>2</sup>
4	Industrial Source	With CCS	1.9 x10 <sup>2</sup>
5	Industrial Source	Without CCS	1.8 x10 <sup>2</sup>
6	Low Estimate	With CCS	1.3 x10 <sup>2</sup>
7	Low Estimate	Without CCS	1.2 x10 <sup>2</sup>
8	High Estimate	With CCS	3.5 x10 <sup>2</sup>
9	High Estimate	Without CCS	3.4 x10 <sup>2</sup>

#### 4.1.1.1 Energy Intensity for NaOCl Production

The study looked at varying the energy intensity of NaOCl production (Variable E), using different data sources. This included an industrial source (2.5kWh/kg),<sup>18</sup> a low end estimate from a lab / controlled environment (1.7kWh/kg)<sup>59</sup>, and a high end estimate based off a study from 1996 (4.8kWh/kg)<sup>60</sup>. Table 23 from above shows the results of varying energy intensity.

As expected, the GHG emissions correlate with the energy intensity (i.e., electricity usage) required to generate NaOCl via electrolysis. The higher the energy intensity, the higher the amounts of GHGs produced. As the largest contributor to GHG emissions for chlorination, significant changes to GHG production at this stage are reflected in the overall results. That is, the lower the energy intensity required to generate NaOCl, the lower the impact of using chlorine to control zebra mussels. Figure 10 below illustrates this relationship in terms of the absolute impact rather than the functional unit.

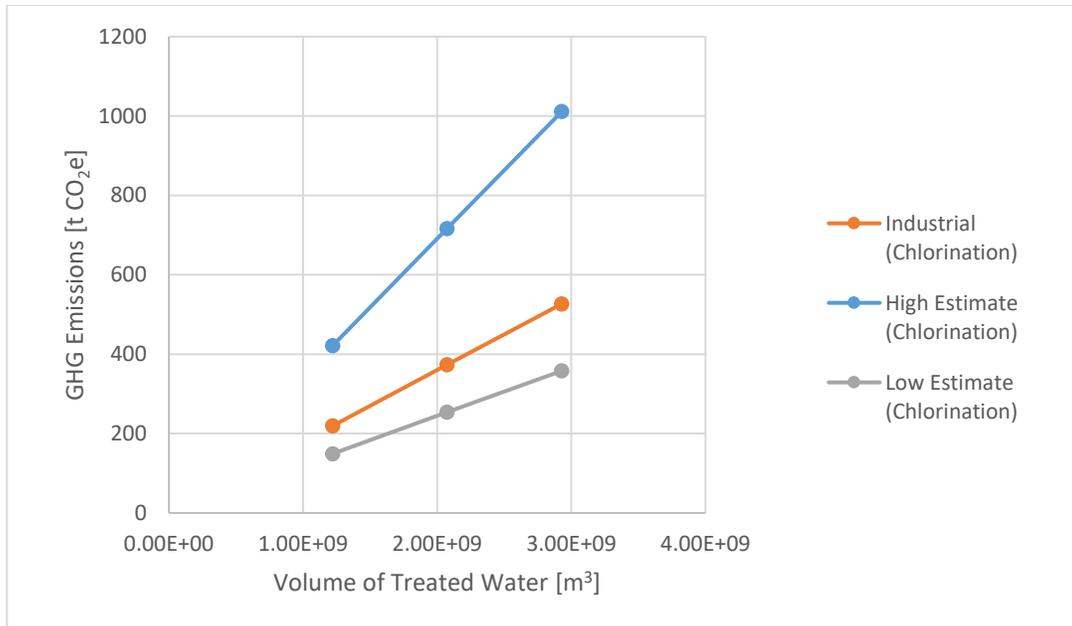


Figure 10 – Impact of NaOCl Production per Volume of Treated Water. Results of Chlorination Cases 1, 2, 3 Changing with Variable A – NPP Water Usage.

#### 4.1.1.2 Hydrogen Credit

Hydrogen is a co-product of NaOCl manufacturing. If the hydrogen generated from NaOCl manufacturing is used to replace hydrogen which would have been generated from other processes, GHG credit can be considered. Again, the size of the hydrogen credit correlates with the GHG intensity for hydrogen production (Variable I): the higher the GHG intensity, the higher the hydrogen credit.

Figure 11 below shows the size of the hydrogen credit, from two hydrogen production processes, with respect to the amount of water treated. The process with higher GHG intensity (i.e. hydrogen produced without CCS) will generate more GHGs, resulting in a larger hydrogen credit. Again, this is shown in terms of the absolute impact rather than the functional unit.

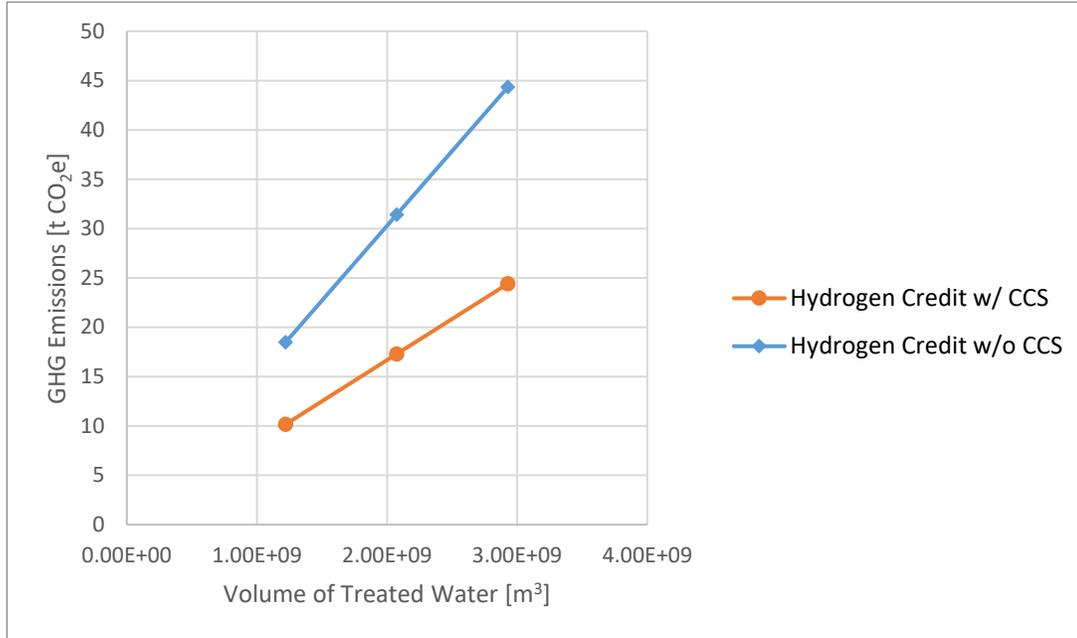


Figure 11 – Hydrogen Credit per Volume of Treated Water. Based on Chlorination Cases 4 and 5.

Figure 12 and Figure 13 illustrates the totals between the cases without and with CCS. As discussed in the previous section, chlorination performs better than ozonation. Inclusion of the hydrogen credit does not change that. In fact, inclusion of the hydrogen credit would result in chlorination performing even better compared to ozonation. Table 24 presents the size of the hydrogen credit relative to the overall emissions.

Table 24 – Percentage of Hydrogen Credit Relative to Overall Emissions (Chlorination)

<b>Electricity Intensity for NaOCl Production</b>	<b>Percentage of Total Emissions (w/ CCS)</b>	<b>Percentage of Total Emissions (w/o CCS)</b>
Low Estimate (1.7 kWh/kg)	<b>6.2%</b>	<b>11%</b>
High Estimate (4.8 kWh/kg)	<b>2.3 %</b>	<b>4.1%</b>
Industrial Source (2.5 kWh/kg)	<b>4.3 %</b>	<b>7.7%</b>

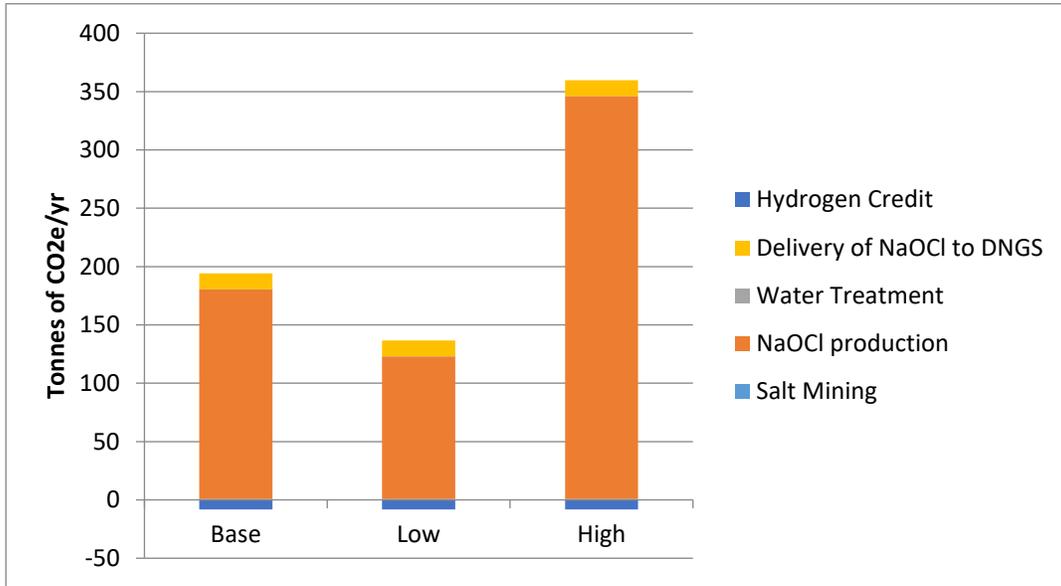


Figure 12 – Comparison of GHG Emission From Chlorination With CCS (per  $10^9$  m<sup>3</sup> Water Treated). From Left to Right (Chlorination Case 4, 6, and 8).

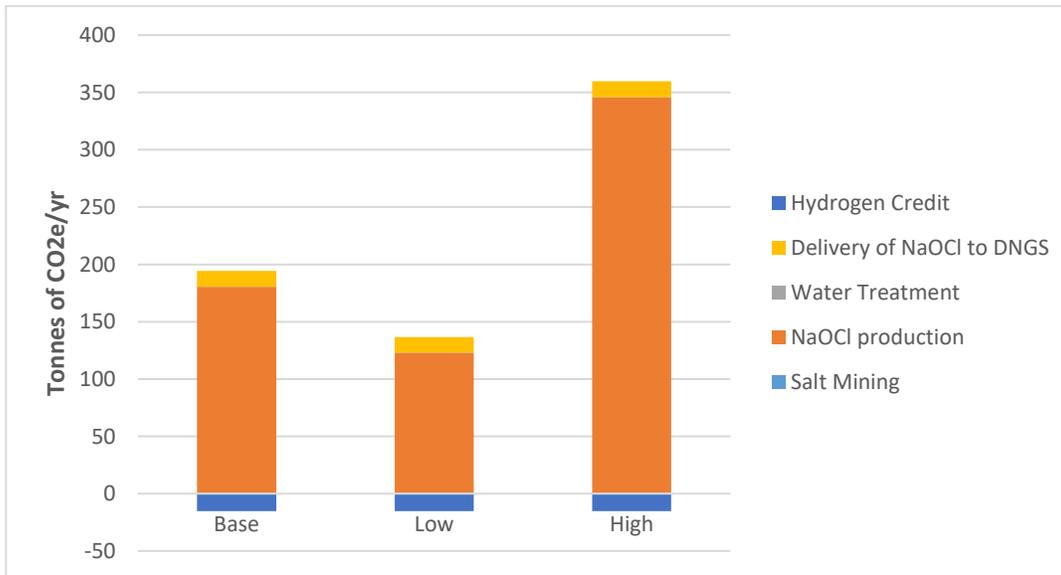


Figure 13 – Comparison of GHG Emission From Chlorination Without CCS (per  $10^9$  m<sup>3</sup> Water Treated). From Left to Right (Chlorination Case 5, 7, and 9)

#### 4.1.1.3 Distance Between Sites

Another factor studied is the distance between the salt mine / NaOCl production plant to the NPP (Variable P). According to GHGenius, the emission factor from delivery by truck (Variable Q) is 1.455kg CO<sub>2</sub>e/km<sup>70</sup>. Therefore, the impact from delivery is linear in this analysis. This means, the larger the distance, the larger the amount of GHGs produced. GHGenius takes the effects of empty backhauls into consideration in its model. A couple interesting discussion points that stem from this observation include, the limitation on the distance between the salt mine/NaOCl production plant to the NPP and the number of chemical deliveries (and by extension, the amount of NaOCl used) before ozonation is considered as a less impactful zebra mussel control method.

Using the base cases for chlorination and ozonation, the annual GHG emissions are 1.9x10<sup>2</sup> t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup> for chlorination and 3.4x10<sup>3</sup> t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup> for ozonation (see Table 20 and Table 21 from Section 3.4). The difference is approximately 3.2x10<sup>3</sup> t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup>. The impact of NaOCl delivery is approximately 14 t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup> (from Table 22). This means the impact from delivery will need to be about 229 times higher for ozone to be more favourable. For chemical delivery by tanker truck, the one-way distance would have to be approximately 8.0x10<sup>4</sup> km. This is roughly equivalent to twice the circumference of Earth<sup>72</sup> and it would be unreasonable to deliver chemicals across such distance. Figure 14 below illustrates the impact of chemical delivery based on the volume of water treated.

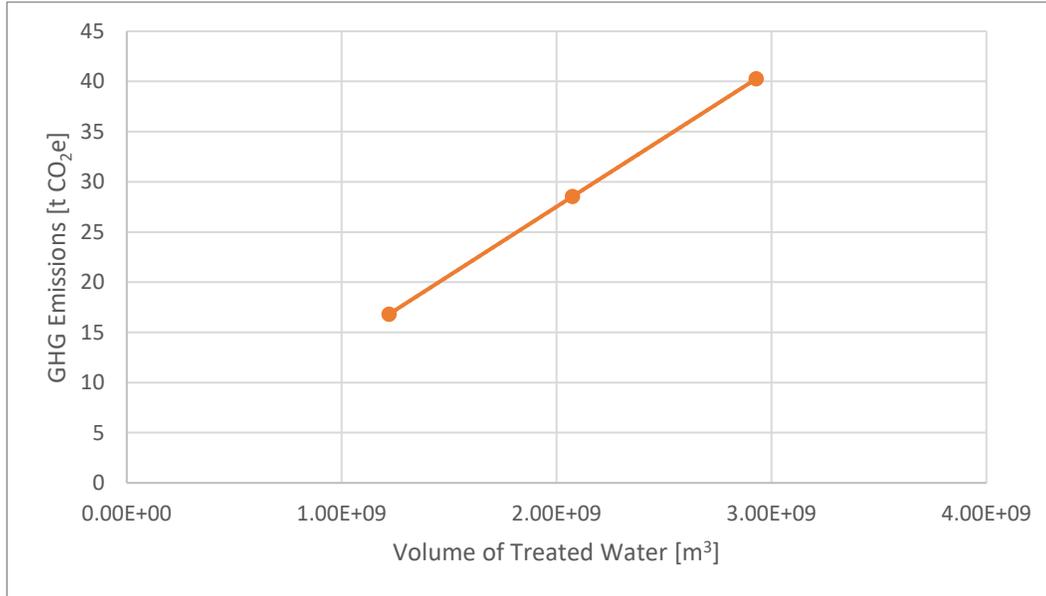


Figure 14 – Impact of Delivery per Volume of Treated Water (Variable A).

An extension of the above discussion point is introducing distance between the salt mining facility and the chemical production facility. That is, increase the impact of source material delivery due to the need of transporting salt between the mining site and the production facility. The introduction of this upstream stage could be interesting based on the number of truckloads of salt required to produce NaOCl brine. As noted earlier, GHGenius has a linear model for truck emissions.<sup>70</sup> Because of the linear model for truck emissions, the impact from transport between mining site and production facility is not expected to change the order of magnitude of impact from this stage.

One way of considering this is to figure out the distance salt would need to be transported to make up the difference between ozonation and chlorination. Taking

the density of NaCl ( $2.16 \text{ t/m}^3$ )<sup>18,29</sup>, average amount of NaCl used ( $1.0 \times 10^2 \text{ t}$  from Table 12), and the average volume of a tanker truck ( $18.93 \text{ m}^3$ )<sup>18,29</sup>, 3 truckloads of salt would be required to produce the amount of NaOCl in the base case.

The difference between base case chlorination and base case ozonation is approximately  $3.2 \times 10^3 \text{ t CO}_2\text{e}/10^9 \text{ m}^3$ . For each base case, the volume of water treated is 2.07 billion cubic meters. Using the emission factor of  $1.455 \text{ kg CO}_2\text{e}/\text{km}$  for delivery by truck, the one way distance between the NaCl mine to NaOCl production facility would need to be in the order of  $1.5 \times 10^6 \text{ km}$  to make up the difference between chlorination and ozonation.

Another factor that could be considered is varying the mode of chemical delivery/transport. That is, switch from delivery by tanker truck to delivery by rail or barge. Such analysis would need to consider several assumptions. This includes, but is not limited to, assuming the necessary infrastructure is in place (e.g., rail connected to manufacturing site/NPP, port available at chemical manufacturing site/NPP), and that there is sufficient storage capacity for the chemicals at the end use site (for larger deliveries; a barge has an average carrying capacity of  $1716 \text{ m}^3$  (453500 gallons)<sup>73</sup> vs tanker of  $15.1$  to  $22.7 \text{ m}^3$  (4000-6000 gallons)<sup>18,29</sup>). Because of the larger carrying capacity of rail/barge, one could consider them carrying other products in the payload. The impact would then be a percentage of the trip.

Considering that the impact from chemical delivery by truck would need to be approximately 229 times higher for ozone to be more favourable, the mode of chemical delivery is not likely going to impact the overall conclusions. As such, this was not looked at in this thesis.

#### 4.1.1.4 Water Processing for NaOCl Production

Another factor studied is the variable related to water processing (Variable M). The study assumes the control agent production plant draws water from an open surface for a large capacity facility. The GHG intensity factor between surface water source and underground water source differ slightly (about 10%) while the GHG intensity difference between a large capacity and small capacity facility is between about 30 and 40%. Depending on the size of the NPP facility, the type/technology of the NPP, and the heat sink for the NPP, the amount of control agent will vary. As the amount of control agent varies, so would the amount of water required for producing the control agent. Based on the calculated results, the impact from water processing is negligible and was not studied further in detail.

#### 4.1.2 Ozonation Specific

Since the ozone is generated on-site, the major, and only, contributor to GHG emissions for using ozone to control zebra mussels is the energy intensity for ozone production (Variable F). The major factor, other than the contribution from the grid, is the oxygen source: pure O<sub>2</sub> versus ambient air. Table 25 shows the total

GHG from ozonation cases 1 and 2. Even considering the impact of generating pure O<sub>2</sub> (i.e. Variable G at ~200kWh/tonne of O<sub>2</sub> or 0.2kWh/kg O<sub>2</sub>)<sup>56,62</sup>, using pure oxygen would produce less GHGs compared to using an air source. This is due to the much lower electricity intensity in generating ozone from pure oxygen when compared to air.

Note, in the case of using pure oxygen, the transport of oxygen to site was omitted in this thesis. Due to the large volume of ozone required, it would not be reasonable to transport oxygen to site. This will be further discussed below.

*Table 25 – Cases for Ozonation With Total GHG Emissions*

<b>Case</b>	<b>Oxygen Source</b>	<b>Totals [t CO<sub>2</sub>e/10<sup>9</sup>m<sup>3</sup> ]</b>
1	Air	<b>3.4 x10<sup>3</sup></b>
2	O <sub>2</sub>	<b>1.3 x10<sup>3</sup></b>

#### 4.1.2.1 Energy Intensity for Ozone Production

The amount of GHGs emitted from generating ozone via Corona Discharge Method is correlated to the amount of electricity used (i.e. Variable F – Electricity Intensity for Ozone Production). Based on commercial numbers from Water Tec Engineering, electricity required when using a pure O<sub>2</sub> source is 5-8kWh/kgO<sub>3</sub> while electricity required when using an air source is 15-18kWh/kgO<sub>3</sub>.<sup>18,56</sup> By using purer sources of oxygen, less electricity would be required to generate the same amount of ozone. And by extension, using purer forms of oxygen will result in less

GHG produced from O<sub>3</sub> production. This is evident from the figures in Table 25 and illustrated in Figure 15 below.

As discussed in Section 3.3.4.2, the electricity intensity for O<sub>2</sub> production (Variable I) is approximately 0.2kWh/kg O<sub>2</sub>.<sup>56,62</sup> In comparison to the electricity intensity for ozone production from air, the electricity intensity for O<sub>2</sub> production is a couple orders of magnitude smaller. As such, inclusion of the effects from generating pure O<sub>2</sub> does not have a significant impact to the overall results.

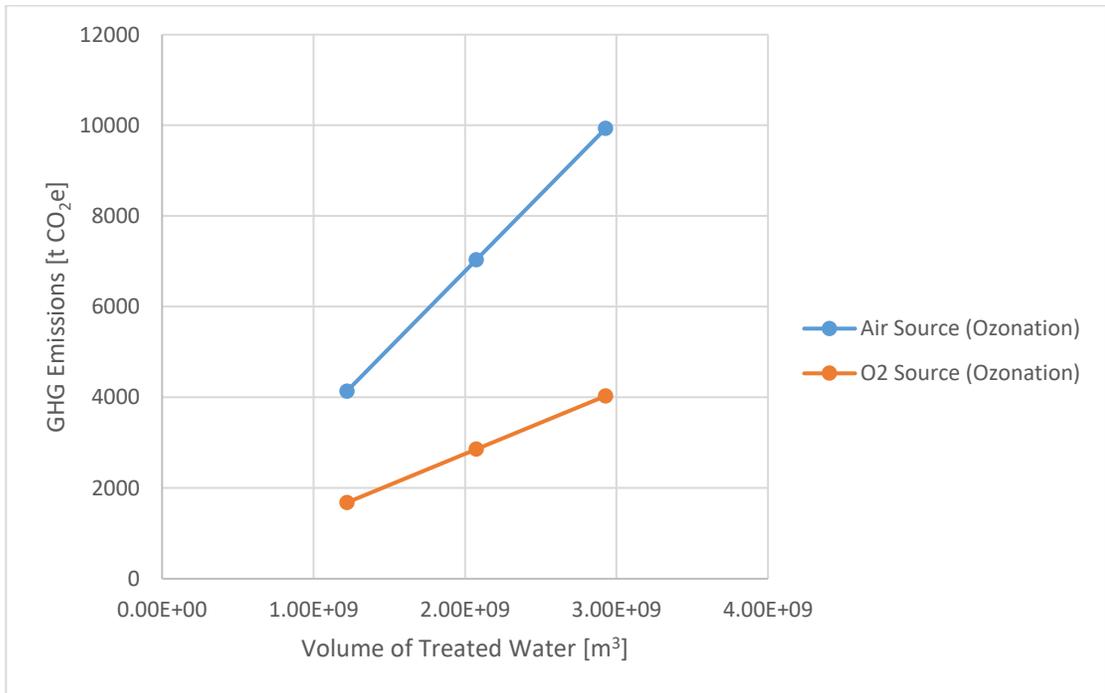


Figure 15 – Impact of Ozone Production per Volume of Treated Water. Results of Ozonation Cases 1 and 2 with Changing Variable A – NPP Water Usage.

#### 4.1.2.2 Distance Between Sites

Another factor that could be considered is introducing distance between the ozone production site and the end use facility. This would introduce an upstream stage with impact similar to that of NaOCl delivery. Based on the annual consumption of ozone for zebra mussel control (1.8kt to 4.4kt), the number of truckloads could be significant. Combined with the challenges of transporting a gas and the limited half life of ozone (25.4hrs in air),<sup>31</sup> this option may not be realistic from a practical point of view. Assuming that it is practical to transport ozone, another factor that could be looked at is varying the mode of transport/delivery. This would involve similar considerations as varying the mode of transport/delivery of sodium hypochlorite. This variable was not considered in this thesis as it does not change the overall conclusions. However, this could be another point of interest for a case study where ozonation is the preferred method based on a criterion other than GHGs and where ozone could not be produced on site.

#### 4.2 OVERALL OBSERVATIONS

In October 2016, Prime Minister Trudeau announced a carbon price plan, starting at \$10/tonne CO<sub>2</sub>e in 2018 to a target of \$50/tonne CO<sub>2</sub>e in 2022.<sup>74</sup> Using the 2018 and 2022 targets, the carbon tax associated with chlorination would be between approximately \$1500 and \$10000 (based on 2018 target), and \$7400 and \$50000 per year (based on 2022 target). For ozonation, that figure would be between approximately \$16000 and \$99000 (based on 2018 targets) and \$82000 and \$500000 per year (based on 2022 targets). Table 26 shows the comparison of

estimated carbon tax between chlorination and ozonation. While the financial aspect for zebra mussel control is out of the scope of this paper, these estimates would be of interest for NPP operators in determining which method of control would best serve their interest.

*Table 26 – Estimated Carbon Tax Associated with Zebra Mussel Control*

<b>Process</b>	<b>Estimated Carbon Tax (2018 Figures)</b>	<b>Estimated Carbon Tax (2022 Figures)</b>
Chlorination	\$1500 to \$7400	\$10000 to \$50000
Ozonation	\$16000 to \$82000	\$99000 to \$500000

The purpose of this study was to investigate the environmental impact of two types of zebra mussel controls. Greenhouse gas (GHG) emissions are only one element of consideration for environmental impact. A side effect of using chlorine to control zebra mussels is the salinization of freshwater lakes. The extent to which lake salinity is changing due to urbanization and associated chloride runoff remains unknown.<sup>75</sup> Salt application for de-icing roadways has been recognized as a major contributor to chloride in groundwater, streams, rivers, and lakes.<sup>75</sup> In Canada, an average of five million tonnes of road salt was applied per year between 1995 and 2001.<sup>75</sup> In 2009, Environment and Climate Change Canada reported that Ontario used around 2.2 million tonnes of road salt each year.<sup>76</sup> By comparison, between 60 to 145 tonnes of salt are required to produce the annual amount of NaOCl needed for zebra mussel control. This is very small (approximately 0.005%) compared to the annual amount of road salt used. Even accounting for the fact that not all road

salt ends up in freshwater lakes, there is still a large disparity between the amount of road salt used and amount of salt added from using NaOCl. Note, this thesis only considered the impact from a single NPP. The impact would be multiple times larger with more NPPs.

Despite the amount of salt added to Lake Ontario from chlorination being many orders of magnitude smaller than the amount of road salt used in Ontario, the residual free chlorine cannot simply be ignored. Dilution is the most common means of detoxifying treated water. Another potential solution is to add a neutralizer, such as sodium metabisulfite and sodium thiosulfate, at the outfall to capture residual free chlorine before the water is discharged back into the lake.<sup>15</sup>

The addition of a chlorine neutralizer would introduce an additional GHG contributor to the chlorination process, which may make ozone more attractive. The GHG emissions from producing a chlorine neutralizer would need to be in the order of  $1.0 \times 10^3 \text{ t CO}_2\text{e}/10^9 \text{ m}^3$  water treated for ozonation to be comparable based on the results of this thesis.

On the other hand, it is important to note that off-gas from ozone presents a hazard to both personnel and the environment. Off-gas from ozone must be captured and destroyed. Common methods of ozone destruction, if recycle/re-use is not available, include: thermal, chemical, catalytic, and ultraviolet.<sup>15,18</sup> Each ozone destruction method would introduce an additional life cycle stage for ozonation.

This would further increase the overall GHG emissions for ozonation for large scale NPP.

Another environmental impact to consider for chlorination is the by-products from the production of chlorine. The study assumed free chlorine was derived from NaOCl, which is made using electrolysis. There is the potential for harmful by-products from other chlorine production methods. Octachlorostyrene (OCS) is a waste product from production of chlorine gas from the electrolysis of NaOCl (electrolytic chlorine production).<sup>77</sup> OCS is of concern due to its possible toxicity, persistence in the environment, and ability to accumulate in wildlife.<sup>77</sup> There has been a general trend of decline of OCS concentration in the Great Lakes in all environmental media (air, water, and sediments) along with no fish advisories as of 2012.<sup>77</sup> OCS is just one example of harmful by-products in the manufacturing process for zebra mussel control agents. In this study, GHG was the focus for a few reasons mentioned earlier: its association with financial aspect (e.g., carbon tax), industry image, and other environmental impacts (e.g., combustion products from fossil fuels). GHGs is by no means all encompassing when looking at the overall environmental impact. Future decision makers would need to be mindful of this and consider environmental impacts beyond GHGs in their decisions.

One option for mitigating environmental impact is exploring alternative cooling methods. The CANDU 6 design has most of the cooling systems as closed loop water systems.<sup>78</sup> This limits the number of water systems that are exposed to zebra

mussel infestation. While this significantly reduces fouling of the internal piping systems, a large once through cooling loop is still required to remove heat from the reactor. An alternative design is to employ air cooled heat exchangers and cooling towers for the closed loop water systems.<sup>35</sup> This would eliminate the possibility of zebra mussel infestation and the environmental impact from zebra mussel control since the NPP will not be drawing water with zebra mussels. However, air cooled heat exchangers have issues of their own, such as requiring large footprints, inconsistent air quality, and fouling.<sup>79</sup> Overall, large scale cooling by water is still the preferred method of cooling for large reactors.<sup>80</sup> Hence, controls for macro-biological fouling, such as from zebra mussels, are still required.

## 5 CONCLUDING REMARKS

### 5.1 CONCLUDING REMARKS

From this life cycle assessment, chlorination has a lower environmental impact based on the amount of GHG produced when compared to ozonation. This is due to the higher electricity requirement of generating ozone and the higher concentration of ozone required to achieve the desired kill rate when compared to chlorination.

The main contributor to GHG emissions for both processes is the generation of electricity used to produce the control chemicals. The overall make-up of the grid plays a large part in the GHG intensity of both processes. Higher contribution from sources that emit less GHGs, such as wind, hydro, and nuclear, would lower the GHG intensity. For large scale reactors, the chemical usage is significant. Under such circumstances, chlorination is better than ozonation in terms of GHG emissions.

For instances such as SMRs and AMRs deployed in off-grid locations that are not connected by conventional modes of transport, other factors such as practicality, implications for spills during transport, and storage requirements may play a bigger role in the final decision. Alternatives to chlorination, such as ozonation and UV irradiation may be more viable.

In this study, GHG emissions were the focus for a few reasons mentioned earlier: their association with the financial aspect (e.g., carbon tax), public image, and other

environmental impacts (e.g., combustion products from fossil fuels). This is by no means all encompassing when considering the overall environmental impact for zebra mussel controls.

Based on the estimated annual consumption of NaOCl, the amount of salt added to Lake Ontario is many orders of magnitude smaller than the amount of road salt used to de-ice roads in Ontario. While it is recognized that not all the road salt ends up in the lake, salt from chlorination is only approximately 0.005% of the amount of road salt. This makes it unlikely that the amount of salt added from chlorination to be in the same order of magnitude as road salt.

Both oxidizing agents (chlorine and ozone) need to be neutralized. Residual free-chlorine needs to be dealt with before it is discharged back into the lake to minimize the impact to the environment. This is typically done by dilution at the outfall. On the other hand, off-gas from ozone presents a hazard to personnel and must be recycled or captured and destroyed. Each oxidizing agent neutralization technique would create additional GHG emissions that need to be considered.

Ultimately, future decision-makers would need to determine the method of zebra mussel control(s) to implement at their NPP. Decision-makers would not be limited to just one type of control. For each control method, the environmental impact would need to be considered, alone and in relationship with others. Other factors such as cost, operation/maintenance burden, and legal/regulatory implications

would need to be considered in addition to environmental impact. For an operator of an existing plant, it may not be practical or financially feasible to make large scale changes. However, a new constructor would have a clean slate to work with and may find the conclusions of this paper useful. It is also entirely possible that a constructor of a new NPP would be able to engineer out the issue with zebra mussel infestation all together by removing the need of cooling via an open water loop. However, such endeavours would face a set of challenges of their own and would need to be further evaluated.

## 5.2 FUTURE WORK

As alluded to throughout this thesis, the work completed here does not represent a complete picture. There are several variables which could be analyzed in further detail. The first is varying the production methods of the control agents for zebra mussels. In this study, electrolysis and corona discharge were the processes analysed for the production of sodium hypochlorite and ozone, respectively. These are the most common commercial production methods of these control agents. Other methods of producing sodium hypochlorite include, but are not limited to: chlorination of soda ( $\text{NaOH}$ ), reaction from calcium hypochlorite, reaction between hypochlorous acid and sodium hydroxide, and reaction between ozone and salt ( $\text{NaCl}$ ). For ozone, other production methods include, but are not limited to: ultraviolet light, cold plasma, and electrolysis. Additionally, oxygen source can be varied in the production of ozone. Each production method has their individual pros and cons. Factors such as efficiency and electricity usage could impact the overall

GHG emissions for each process. Furthermore, these processes could have additional upstream and downstream activities to consider, which would further add to the overall GHG emissions.

A second variable that could be studied further is the transport/delivery of control agents and source materials for upstream activities. One aspect discussed earlier is the mode of transport for the control agent. Instead of using tanker trucks, the impact of delivery using rail and/or water could be considered. Such studies would need to include and assess the viability and practicality of each. For example, ozone has a limited half life. In such case, it may not be practical to select a transport method which would exceed the half life of ozone. Additionally, if source material (e.g., salt) is required to be transported from the mining site to the control agent production facility, GHG emissions from this stage should be captured for a more complete picture. For a large scale NPP that relies on conventional modes of transport for chemical deliveries (e.g. highway, rail, water), these variables are likely to remain negligible. However, this may not be true for NPPs that does not have access to conventional modes of transport.

Lastly, future studies could look into the environmental impact of other control agents that were not studied in this thesis. This thesis considered two oxidizing agents, chlorine and ozone, that operate on the same mechanics for fair comparison. It would be interesting to compare the environmental impact, from a GHG generated point of view, of various non-oxidizing agents and compare the results

with those from the oxidizing agent. This would bring further perspectives when selecting a control agent for future NPP.

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## APPENDICES

### Appendix A. GHGenius 4.03a Input Data<sup>48,49</sup>

#### A1. Selection Criteria

Below is a screenshot of the 'Input' tab of GHGenius. Target year of 2016 was selected along with Ontario as the Regional Defaults. To run the simulation/calculation, click on the top left 'Run Program' button. Results can be saved using the 'Save' button.

#### Year (2016), Regional Defaults (Ontario)

The screenshot displays the 'Input' tab of the GHGenius software. At the top, there are two main buttons: 'Run Program' (green) and 'Save' (white). Below these are two green banners with instructions: 'Click here to run program for values on input sheet' and 'Click here to create files of results for saving'.

The main interface is divided into several sections:

- Regional Defaults:** A grid of buttons for selecting regions. 'Ontario' is selected under 'Canada'. Other options include Canada East, Canada Central, Canada West, Quebec, Saskatchewan, Alberta, Manitoba, BC, US East, US, and US West.
- TARGET YEAR, COUNTRY, CO2-EQUIVALENCY FACTORS (CEF<sub>s</sub>) (Sheet: GWP):**
  - Target Year: 2016
  - Country/Region: Ontario
  - Country Weight Factor: Can Avg
  - GWP Selector: 2
- VEHICULAR ENERGY USE (Sheet: Vehicular Energy):**
  - Buttons for Canada, US, Mexico, and India.
  - Vehicle Class: (Use default values or enter own data)
- CANADA FUEL CONSUMPTION PARAMETERS:** A table showing fuel consumption (L/100km) for various vehicle classes (LDGV, LDDV, HDGV, Buses, Trucks) across different regions (Canada East, Central, West, US East, Central, West, Mexico East, Central, West).

#### A2. Index of Tabs:

Below is the index to the sheets in the GHGenius spreadsheet. A couple tabs of note include: 'Lifecycle Results' – for calculation of Delivery Impact, 'Power Generation' – for grid make-up, 'Elec Emissions' – for emissions from electricity generation.

List of sheets is copy/pasted from GHGenius. <sup>48,49</sup>

<a href="#">Index</a>	INDEX TO SHEETS IN THE SPREADSHEET
<a href="#">Input</a>	INPUT SHEET FOR RUNNING MODEL
<a href="#">Input Cost</a>	INPUT SHEET FOR ALL COST DATA NEEDED TO CALCULATE COST EFFECTIVENESS
<a href="#">Output Summary</a>	A TOOL TO DYNAMICALLY COMPARE OUTPUT DATA
<a href="#">Energy Balance</a>	PRIMARY ENERGY BALANCE AND BREAKDOWN OF SECONDARY ENERGY
<a href="#">Elec Emissions</a>	COMPLETE FUELCYCLE EMISSIONS FROM ELECTRICITY GENERATION
<a href="#">Upstream Results HHV</a>	GRAMS/GJ FUELCYCLE EMISSIONS (HHV), EXCLUDING END USE (CALCULATED RESULTS)
<a href="#">Upstream Results LHV</a>	GRAMS/GJ FUELCYCLE EMISSIONS (LHV), EXCLUDING END USE (CALCULATED RESULTS)
<a href="#">Lifecycle Results</a>	CO2-EQUIVALENT EMISSIONS, BY VEHICLE/FUEL AND STAGE
<a href="#">Lifecycle Results 2</a>	CO2-EQUIVALENT EMISSIONS, BY VEHICLE/FUEL AND STAGE
<a href="#">Percent Changes</a>	SUMMARY OF PERCENTAGE CHANGES
<a href="#">LDV Summ</a>	LIGHT DUTY VEHICLES: SUMMARY OF GREENHOUSE AND NON-GREENHOUSE GAS EMISSIONS, g/km
<a href="#">HDV Summ</a>	HEAVY DUTY VEHICLES: SUMMARY OF GREENHOUSE AND NON-GREENHOUSE GAS EMISSIONS, g/km
<a href="#">Freight Emissions</a>	FREIGHT CO2-EQUIVALENT EMISSIONS, BY MODE/FUEL AND STAGE
<a href="#">Feedstock Emissions</a>	FEEDSTOCK EMISSIONS
<a href="#">CostLDV</a>	COST-EFFECTIVENESS FOR LIGHT-DUTY VEHICLE ALTERNATIVES
<a href="#">CostHDV</a>	COST-EFFECTIVENESS FOR HEAVY-DUTY VEHICLE ALTERNATIVES
<a href="#">Sensitivity Solver</a>	SENSITIVITY SOLVER
<a href="#">Monte Carlo</a>	MONTE CARLO
<a href="#">Printing</a>	PRINTING
<a href="#">GWP</a>	TARGET YEAR, COUNTRY, CO2-EQUIVALENCY FACTORS (CEFs)
<a href="#">Power Gen</a>	ELECTRICITY GENERATION: EFFICIENCY, AND TYPES OF FUEL USED
<a href="#">Fuel Char</a>	CHARACTERISTICS OF FUELS, GASES, AND FEEDSTOCKS
<a href="#">Misc Fuel</a>	MISCELLANEOUS FUEL, FEEDSTOCK, AND FUELCYCLE INPUT DATA
<a href="#">Crude Production</a>	CRUDE OIL PRODUCTION AND OWN USE
<a href="#">Venting &amp; Flares</a>	VENTING AND FLARING OF ASSOCIATED GAS
<a href="#">US Petroleum Supply</a>	U. S. PETROLEUM SUPPLY AND DISPOSITION 1990-2050
<a href="#">Petroleum Flow</a>	FLOW OF PETROLEUM (CALCULATION OF TONNE-KM)
<a href="#">Refineries</a>	REFINERY ENERGY USE and EMISSIONS
<a href="#">Natural Gas Supply</a>	NATURAL GAS AND NATURAL GAS LIQUIDS SUPPLY AND DISPOSITION

<a href="#">Coal Mining</a>	COAL MINING AND OWN USE; METHANE FROM COAL MINES
<a href="#">Uranium</a>	URANIUM AND NUCLEAR POWER
<a href="#">Feedstock Adj</a>	ADJUSTMENTS TO CALCULATION OF ENERGY USED TO RECOVER FEEDSTOCKS AND RAIL TRANSIT
<a href="#">Biomass Prod</a>	PRODUCTION OF BIOMASS
<a href="#">Fertilizer</a>	FERTILIZER MANUFACTURE, APPLICATION; NUTRIENT LOSS; LAND USE
<a href="#">Coprods</a>	EMISSIONS DISPLACED BY CO PRODUCTS OF FUEL PRODUCTION PROCESSES
<a href="#">Sequestration</a>	SEQUESTRATION INPUTS
<a href="#">Alt Fuel Prod</a>	PRODUCTION OF ALTERNATIVE FUELS
<a href="#">Energy Use</a>	SECONDARY ENERGY-USE INTENSITY AND SECONDARY ENERGY-USE BY TYPE OF FUEL
<a href="#">Transport</a>	TRANSPORT OF FEEDSTOCKS, FUELS, VEHICLES, ETC.
<a href="#">Equip Emis Factors</a>	EMISSION FACTORS FOR TRAINS, TANKERS, REFINERIES, METHANOL PLANTS, GAS COMPRESSORS, ETC.
<a href="#">Service Stations</a>	ENERGY USE AND EMISSIONS AT SERVICE STATIONS, INCLUDING ENERGY TO COMPRESS OR LIQUEFY GASEOUS FUELS
<a href="#">Vehicular Energy</a>	VEHICULAR ENERGY USE
<a href="#">Exhaust Emissions</a>	MOTOR-VEHICLE EMISSIONS: INPUT DATA AND RESULTS FOR: Ontario
<a href="#">Materials</a>	MATERIALS USED IN VEHICLES
<a href="#">Vehicle Assembly</a>	EMISSIONS FROM VEHICLE ASSEMBLY AND MATERIALS MANUFACTURE; INDIRECT ENERGY USE FOR TRAINS, SHIPS, TRUCKS, ETC.
<a href="#">Macros</a>	MACROS
<a href="#">MenuSheet</a>	SHEET USED TO SETUP THE MENU
<a href="#">Glossary</a>	GLOSSARY OF ABBREVIATIONS
<a href="#">Defaults</a>	DEFAULT VALUES USED TO INITIATE MODEL INPUT SHEET (**DO NOT INPUT SCENARIO DATA INTO THIS SHEET**)

### A3. Inputs

Table A1 below is the installed capacity (make-up) of the grid from GHGenius. Sum of the sources add up to 1.

Coal	Oil	Gas Boiler	Gas Turbine	Nuclear	Wind	Other Carbon	Biomass	Hydro	Other	Fossil
0.00	0.00	0.18	0.00	0.46	0.04	0.00	0.04	0.27	0.00	0.00

Table A1 – Installed Capacity (GHGenius)<sup>48,49</sup>

Table A2 below is the source of electricity used for electrolysis from GHGenius. Again, sum of the sources add up to 1. Note, the difference between the grid make-up (table above) and the sources for electricity (table below) is due to rounding.

Coal	Oil	Gas Boiler	Gas Turbine	Nuclear	Wind	Other Carbon	Biomass	Hydro	Other	Fossil
0.000721	0.000322	0.17979	0	0.46172	0.04496	0	0.04278	0.269704	0	0

Table A2 – Source of Electricity Used for Electrolysis (GHGenius) <sup>48,49</sup>

Table A3 below is the total fuel cycle emissions from electricity generation provided by GHGenius. Units here are g CO<sub>2</sub>eq/kWh-delivered. This table is retrieved from the ‘Elec Emissions’ tab.

Coal	Fuel oil	NG/boiler	NG/turbine	Nuclear*	Wind	Other Carbon	Biomass	Hydro*	Other
1164.5	1104.5	596.0	531.7	31.9	5.3	743.0	30.9	46.0	5.3

Table A3 – Total Fuel Cycle Emissions from Electricity Generation (GHGenius) <sup>48,49</sup>

Table A4 below presents the calculated emissions from the grid. These values are obtained here by multiplying the values from Table A2 with the values from Table A3. The units are g CO<sub>2</sub>eq/kWh-delivered. Emission rate of 137g CO<sub>2</sub>eq/kWh-delivered was used to calculate the impact of using electricity from Ontario’s grid.

Coal	Fuel oil	NG/boiler	NG/turbine	Nuclear*	Wind	Other Carbon	Biomass	Hydro*	Other	Sum
0.839325	0.355271	107.1472	0	14.70792	0.238174	0	1.32291	12.4101	0	137.0209

Table A4 – Calculated Emissions from Grid

Table A5 is the calculation provided in GHGenius on the emissions by a heavy-duty vehicle in terms of g CO<sub>2</sub>eq /km. Emission rate of 1455.9g/km was used to calculate the impact of delivering chemicals by a tanker truck. This table was retrieved from the ‘Lifecycle Results’ tab.

Lifecycle Results – HEAVY-DUTY ICE VEHICLES, FOSSIL OR NUCLEAR FEEDSTOCKS  
(g/km and % changes):

Results for HDDV Trucks	
General fuel -->	<b>Petrol diesel</b>
Fuel specification -->	<b>0.0015% S</b>
Feedstock -->	<b>Crude oil</b>
Vehicle operation	1,076.7
C in end-use fuel from CO2 in air	0.0
Net Vehicle Operation	1,076.7
Fuel dispensing	1.9
Fuel storage and distribution	7.6
Fuel production	150.0
Feedstock transport	12.2
Feedstock recovery	76.1
Feedstock Upgrading	38.5
Land-use changes, cultivation	1.8
Fertilizer manufacture	0.0
Gas leaks and flares	55.3
CO2, H2S removed from NG	0.0
Emissions displaced by co-products	<b>-1.2</b>
Sub total (fuelcycle)	1,419.1
% changes (fuelcycle)	--
<i>Vehicle assembly and transport</i>	5.5
<i>Materials in vehicles</i>	31.2
Grand total	1,455.9

Table A5 – Emissions by a Heavy Duty Vehicle (GHGenius)<sup>48,49</sup>

## Appendix B. NRCAN Input Data

### B1. Salt Mining Data

Below is the table compiled from NRCAN and StatsCan on the average impact from salt mining between 2007-2014. After calculating the amount of salt required for NaOCl production (in tonnes), it was multiplied by the energy intensity to get the amount of energy required to mined the salt (in MJ). Multiplying the resultant energy with GHG Intensity calculates the environmental impact of salt mining in tonnes of CO<sub>2</sub>e.

	Value
<b>Total Salt Mines Energy Use (PJ)</b>	<b>2.4</b>
<b>Energy Intensity (MJ/tonne)</b>	<b>216.5</b>
<b>GHG Intensity (tonne/TJ)</b>	<b>62.8</b>

*Table B1 – Average Impact from Salt Mining (NRCAN)* <sup>65,66</sup>