

THE APPLICATION OF AN EARLY-WARNING BIOMONITORING SYSTEM (EWBS) IN A CANADIAN
CONTEXT

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by

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Master of Applied Science

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Abstract

The application of an early-warning biomonitoring system (EWBS) in a Canadian context

A nationwide jurisdictional analysis of drinking water frameworks was conducted to identify the political backdrop for the integration of the EWBS. Canada demonstrates no consistency in drinking water regulations and policies for EWBS application. While it is not possible for all specific contaminants to be monitored, the EWBS has the potential to effectively detect classes of contaminants applicable nationwide. A case study site was investigated for potential use of the EWBS. The general finding indicated that, despite having an advanced plant, unpredicted spills from upstream industries will continue to represent potential hazards for Walpole Island First Nation. Copper was identified as a contaminant of concern for the study site and was applied in behavioural bioassays using *Daphnia magna*. Three responses were examined upon exposure to varying concentrations of copper and results indicated change in swimming height as the most sensitive response for utility in an EWBS, followed by immobility.

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Contents

1.0 Introduction.....	1
1.1 Project Background.....	1
1.2 Early-Warning Biomonitoring System.....	4
1.3 Project Overview.....	5
1.4 Specific Project Role.....	7
1.5 Thesis Rationale and Objectives	7
2.0 Nationwide Jurisdictional Analysis	9
2.1 Introduction	9
2.1.1 Jurisdictional Roles.....	9
2.1.2 First Nations	10
2.2 Methodology	14
2.3 Results and Discussion.....	15
2.3.1 Drinking Water Advisories.....	15
2.3.2 Federal Government	20
2.3.3 Provincial and Territorial Drinking Water Frameworks	22
2.3.4 Nationwide Contaminant Comparison	38
2.4 Conclusion of Jurisdictional Analysis.....	40
3.0 Case Study Site	41
3.1 Introduction	42
3.1.1 Walpole Island.....	42
3.1.2 St. Clair River Area of Concern	45
3.1.3 “Chemical Valley”.....	46
3.1.4 Spills to the St. Clair River.....	49
3.1.5 Spill Monitoring in the St. Clair River	52
3.1.6 Operational Failures	54
3.1.7 Fate of Contaminants.....	55
3.1.8 St. Clair River Contaminants of Concern.....	56
3.1.9 Walpole Island Citizenry and Advocacy	59
3.1.10 Collaborative Research with First Nations Communities	61
3.2 Methodology	63
3.3 Results and Discussion.....	64
3.3.1 Communication with First Nations.....	64
3.3.2 Treatment Technologies and their Effectiveness.....	64

3.3.3 Study Site Contaminant Choice.....	73
3.4 Conclusion of Case Study	74
4.0 <i>Daphnia magna</i> Bioassay Using Copper.....	76
4.1 Introduction	76
4.1.1 Behavioural Bioassay	76
4.1.2 Bioassay Organism: <i>Daphnia magna</i>	77
4.1.3 Bioassay Contaminant	80
4.2 Methodology	87
4.2.1 <i>Daphnia magna</i> Culturing.....	87
4.2.2 Washing Procedures	88
4.2.3 Metal Solution	88
4.2.4 Behaviour Bioassay	88
4.3 Results and Discussion.....	90
4.3.1 Immobility	90
4.3.2 Swimming Height in the Water Column	92
4.3.3 Swimming Style	95
4.4 Summary and Conclusion of <i>Daphnia magna</i> Behavioural Bioassay	98
5.0 Research Summary and Future Applications.....	99
References.....	103
Appendices.....	117
Appendix A. Sierra Legal Defence Fund's 2006 national drinking water report card.....	117
Appendix B. Drinking water parameters tested in each province/territory as outlined in legislations and guidelines.....	118
Appendix C. St. Clair River priority point sources & contaminants as identified by the Remedial Action Plan.....	121
Appendix D. Ontario Ministry of Environment "Sarnia Sweep" compliance checklist	122
Appendix E. Arsenic as a bioassay contaminant.....	123
Appendix F. <i>Daphnia magna</i> swimming bioassay: immobility.....	125
Appendix G. <i>Daphnia magna</i> swimming bioassay: height in the water column.....	127
Appendix H. <i>Daphnia magna</i> swimming bioassay: swimming style	129

List of Abbreviations

AOC-Area of Concern
CCA-Chromated Copper Arsenate
DWA-Drinking Water Advisory
EC₅₀- the concentration of a contaminant which causes deleterious response depending on endpoint specified in 50% of organisms in a bioassay over a given period of time
Eh-Redox potential
EU-European Union
EWBS-Early-Warning Biomonitoring System
GAC- Granular Activated Carbon
GCDWQ- Guidelines for Canadian Drinking Water Quality
HCB-Hexachlorobenzene
ICESCR-United Nations International Covenant on Economic, Social, and Cultural Rights
INAC- Indian and Northern Affairs Canada
LC₅₀-the concentration of a contaminant which is lethal to 50% of organisms in a bioassay over a given period of time
LTSDWS-Long Term Safe Drinking Water Strategy
MAC-Maximum Allowable Concentration
MDL-Minimum Detection Limit
MTBE- Methyl *tertiary* Butyl Ether
NPRI-National Pollutant Release Inventory
OCMOH-Office of the Chief Medical Officer of Health
OMOE- Ontario Ministry of the Environment
PAH-Polycyclic Aromatic Hydrocarbon
PCB-Polychlorinated Biphenyl
PMRA-Pest Management Regulatory Agency
PPCP-Pharmaceuticals and personal care products
RAP-Remedial Action Plan
SLEA- Sarnia Lambton Environmental Association
THM-Trihalomethanes
USEPA-United States Environmental Protection Agency
UV-Ultraviolet
VOC-Volatile Organic Compounds
WHO-World Health Organization
WTP-Water Treatment Plant

1.0 Introduction

This thesis contributes to the overall project goal of developing holistic, real-time, multi-organism, early-warning biomonitoring technology for the detection of drinking water contamination. The research journey began with the idealistic goal of immediate transfer of early-warning biomonitoring system (EWBS) technology to areas of extreme water crisis, such as Africa and Latin America. However, challenges related to language barriers and fragmented information on drinking water frameworks in those countries resulted in a refocus to water issues in our own country, starting with the key question—where does Canada stand on drinking water protection? The assumption was that Canadian drinking water frameworks would compare to those of the United States. There, a consistent, legislated approach is applied so that drinking water is standardized across the country; all States must adhere to the Safe Drinking Water Act of 1974 and report to the federal government's Environmental Protection Agency (EPA). This knowledge led to an intensive Canadian legislative analysis of the current provincial and territorial drinking water frameworks in order to understand the political backdrop to which the EWBS would be applied. The legislative analysis indicated the level of protection already afforded to Canadian citizens. It also highlighted the baseline of contaminant testing carried out in each jurisdiction in order to form a clearer picture of the classes of contaminants that the EWBS would need to detect. The identification of a case study site provided insight into the value of EWBS technology, particularly for vulnerable water supplies, and identified marginalized populations within Canada who suffer from a reduction in safe drinking water. Additionally, through the use of aquatic invertebrate behavioural bioassays, the current thesis contributed to the ecotoxicological knowledge the system requires, and specifically examined organism responses upon exposure to the metal class of contaminants.

1.1 Project Background

Access to safe drinking water is a critical issue at a global, national, and regional level. It is a resource which is essential to human health and community development, and is therefore recognized as a basic human right (World Health Organization, 2008) and internationally, water has been recognized as a priority issue. The United Nations declared 2005 to 2015 the Water for Life decade which coincides with the Millennium Development Goal of reducing half the proportion of people without access to safe drinking water and sanitation by 2015. About 1.1 billion people, 18% of the world's population, lack access to safe drinking water and more than 2.2 million people, mostly in developing countries, die each year from diseases associated with poor water and sanitary conditions (United Nations, 2006). Microbial contaminants are the primary contributor to

waterborne disease in both the developed and developing world; however, chemicals also pose a significant health risk, particularly over time and levels of exposure (WHO, 2007).

Article 11 of the *United Nations International Covenant on Economic, Social, and Cultural Rights (ICESCR)* is a human rights treaty signed by 157 countries, including Canada. These member states “recognize the right of everyone to an adequate standard of living for himself and his family, including adequate food, clothing, and housing and to the continuous improvement of living conditions” (Office of the High Commissioner for Human Rights, 1976). Included in Article 11 is general comment No. 15 on the right to water, which focuses on the use of the word “including” in the Covenant. This indicates that the catalogue of rights was not intended to be exhaustive, and the right to water is clearly essential for securing an adequate standard of living. It is one of the most fundamental conditions for survival. General Comment 15 “is not legally binding per se, but it constitutes as an authoritative interpretation of the provisions of the *ICESCR* by the competent body” (United Nations Economic & Social Council, 2002). This provision has received wide acceptance by States parties, excluding Canada. Canada is internationally viewed as the primary state opposed to the right to water and sanitation (Khalfan & Kiefer, 2008). Reluctance to recognize the right to water is based on concern that this would force Canada to provide other countries access to Canadian water, the main concern being that the United States (U.S.) could demand Canadian water by claiming it under international obligations. However, this is unlikely because a claim on human rights grounds must meet very strict criteria. This lack of recognition of water as a human right is especially pertinent to marginalized people within our own country. For example, First Nations communities are suffering from a distinct reduction in water quality as compared to non-reserve communities.

Contamination of source waters occurs naturally or as a result of human-induced error and disregard. Gord Steeves, president of the Federation of Canadian Municipalities, stresses the common concern surrounding safe drinking water supplies, “We’re very concerned about the amounts of negative effluents going into water systems and finding their way into potable water systems as well” (Eggertson, 2008). The Federation of Canadian Municipalities, according to Steeves, is in favour of improving the quality of water, and meeting a nationally-implemented standard. A 1999 survey of 153 water providers in Canada and the U.S. found that most had experienced a significant source water contamination in the past five years (Gullick *et al.*, 2003). The threats most commonly cited by water providers with river water intakes included spills from transportation accidents, pipeline and storage tank releases, pesticides from agriculture, and pathogens from untreated sewage. This problem persists because adequate warning and a timely

test response are not always available and growing technologies are often costly and advanced, adding to the current cost of contaminant testing and water treatments. In addition, a lack of Federal legislative involvement in water quality results in a lack of uniformity across the country in terms of drinking water protection measures.

It is important to recognize that routine monitoring of contaminants has limitations; while it identifies components of the water's quality, it can only trigger a response to a problem after the threat has entered the water system. By this point, and certainly by the time a water advisory is issued, people have likely consumed the water. For example, microbiological tests require incubation times of up to 24 hours and if adverse test results are discovered, several more hours are needed for further investigation (Krewski *et al.*, 2002). This type of monitoring is an essential part of managing a water supply but it is not a preventative measure, and for this reason new approaches to water monitoring are necessary. A recent Canadian government workshop highlighted the need to deviate from current research practices demonstrating the effect of single compounds on aquatic organisms in laboratory settings and expressed the need for knowledge concentrating on the complexity of mixtures and influence of actual environmental conditions (Kleywegt *et al.*, 2007). Early-warning biomonitoring systems (EWBS) can provide timely information on water quality changes and ideally do so in a cost effective manner, with low maintenance and training requirements.

While it is important to consider global issues, one need not venture far to see the unequal distribution of necessary resources such as safe drinking water. There is huge variation in the management of drinking water across Canada. Currently there is no federal legislation¹, and provincial and territorial legislation is not always in place. The Sierra Legal Defence Fund has charged the federal government with a "top-down failure of responsibilities" (Christensen, 2006). National drinking water guidelines² are non-enforceable, and financial and administrative support is lacking; consequently, this places a greater burden on the provinces, which, without having to answer to the powers above, must weigh the protection of public health against high costs and enforcement responsibilities. The resulting situation leaves water systems and populations unprotected. This is most often seen in First Nations communities, where jurisdiction is a complicated web of shared responsibility at all levels of government.

¹ A proposed or enacted law or group of laws (The American Heritage Dictionary of the English Language, 4th ed., 2009)

² A statement or other indication of policy or procedure by which to determine a course of action (The American Heritage Dictionary of the English Language, 4th ed., 2009)

1.2 Early-Warning Biomonitoring System

Biomonitors are considered useful for measuring the changes in the behaviour of living organisms resulting from stress due to the presence of contaminants (Gullick *et al.*, 2003). Current examples of this process include dynamic fish, mussel, and *Daphnia* tests that measure changes in the organism's movement and physiological response as it is exposed to toxins. However, because different species react differently to different chemicals, it is suggested that a more holistic approach be used, incorporating organisms from different trophic levels (Gullick *et al.*, 2003).

The development of *in situ*, on-line biomonitoring of water quality and detection of toxins is supported by the United Nations Agenda 21 which calls for the protection of water as a restricted resource and sustainable management for future use (Gerhardt *et al.*, 2006). In order to understand the problems associated with degradation of water quality, it is useful to gain detailed information about the aquatic system and how it changes in time. The development of new methods to identify the presence of contaminants affecting water quality can better guarantee the provision of quality drinking water for human consumption. Automated biomonitors operate in real-time and use living organisms to detect toxins and provide continuous information as to the quality of the water (Kieu *et al.*, 2001; Allan *et al.*, 2006; Gerhardt *et al.*, 2006). The components that make up this type of system include: test organisms, an automated detection system, and an alarm—together all three provide an EWBS.

An EWBS provides environmentally relevant and scientifically rigorous monitoring that is lacking in traditional chemical monitoring. Living organisms have an integrated response to the surrounding environment, allowing the detection of subtle changes in water quality over time that can be missed by single, intermittent chemical analysis. Additionally, source waters contain a range of contaminants with potential synergistic or antagonistic biological effects that cannot be realized by standalone chemical monitoring (Winter, 2000). Utilization of an EWBS allows a timely response to contamination events and does not require the shipment of samples for chemical testing in laboratories. These factors indicate the critical role of an EWBS as a first response to contamination, which can then be followed by more detailed chemical analysis.

The basic ecology of organisms used in an EWBS must first be sufficiently researched through laboratory bioassays that include monitoring the behavioural responses of control organisms versus affected organisms at varying concentrations and exposure times. Behaviour provides a visual, measureable response at the whole organism level that can be used to complement routine chemical monitoring. These observations are generally made through direct researcher observation or through image analysis. Results can then be incorporated into a modelling component which can provide information about the specific type or concentration of the

contaminant present, and not simply that a threat is present. This important information reduces the amount of timely and expensive follow-up chemical testing that is normally required. A holistic system such as this is the eventual goal of the present research and will be a highly useful tool for water systems and the provision of safe drinking water.

1.3 Project Overview

Analogous to the “miner’s canary” once used to test air quality of mines, the EWBS that is currently being developed uses biological stress responses to warn the user of impact from stressors, and that an immediate response may be needed. It is a multi-organism-based strategy whereby ecotoxicity models are based on the characteristic responses of organisms from different trophic levels to specific classes of contaminants.

Team members are currently working to investigate a number of objectives including: 1) the identification of measurable responses in aquatic plants, invertebrates, and vertebrates to chemical stressors at environmentally-relevant concentrations in the laboratory; 2) the development of quantitative methods to detect the presence and abundance of pathogens in drinking water sources; 3) the construction and testing of a flow-through system at the intake point of a drinking water facility for stress-response determination in real-time; and 4) the development of models for a suite of stereotyped responses to chemical contaminants and pathogens (McCarthy *et al.*, 2008). A breakdown of researcher roles is provided in Table 1.

This system strives to be scientifically rigorous and environmentally relevant while being cost effective, limiting the use of chemical testing or complex equipment. It is useful for communities where expertise is limited and cost savings are critical.

Table 1: An overview of researcher roles in the development of an early-warning biomonitoring system (EWBS)

G. Marshall <ul style="list-style-type: none"> • Behavioural/physiological responses of three aquatic invertebrates to atrazine and tributyl tin 	C. Pearce <ul style="list-style-type: none"> • Physiological responses of four aquatic algae and plant species to atrazine and tributyl tin
A. Dort <ul style="list-style-type: none"> • Nationwide jurisdictional analysis: Investigation of Canada's drinking water frameworks • Investigation of case study site for applicability of EWBS in vulnerable populations • Assessment of <i>Daphnia magna</i> behavioural responses upon exposure to metal class of contaminants : copper 	I. Netto <ul style="list-style-type: none"> • Image analysis (Ecotox /Daphniatox) using <i>Euglena</i>, <i>Daphnia</i>, and <i>Hyalella</i> • Atrazine and Tributyl tin
A. Maradona <ul style="list-style-type: none"> • Modeling component • Multi-variable statistics to build a database of responses 	V. Fleet <ul style="list-style-type: none"> • Multi-species Freshwater Biomonitor (MFB): <i>Daphnia</i>, <i>Hyalella</i>, <i>Lumbriculus</i>, and <i>Chironomus</i>
M. Barrera <ul style="list-style-type: none"> • Pathogen/organic pollutants using UV /hydrogen peroxide 	S. Clarke <ul style="list-style-type: none"> • DNA- based system (real -time polymerase chain reaction) for rapid, real -time detection of waterborne pathogens
Z. Labbaf <ul style="list-style-type: none"> • agricultural /industrial land uses, and potential sources of contaminants surrounding the Welland Canal 	J. Solnik <ul style="list-style-type: none"> • ecological studies on behaviour of benthic invertebrates while under stress from toxins

1.4 Specific Project Role

The EWBS will eventually be applied for the protection of drinking water in Canada. In order to provide a context for the legal framework to which the EWBS will be integrated, a provincial and territorial breakdown of drinking water frameworks was examined, as well as a summary of contaminant testing. The successful application of a “miner’s canary” EWBS hinges on its location within a watershed and the impact it can have on water protection for at-risk populations. To highlight the range of water protection nationwide, and the possible application of EWBS, a case study is applied. Selection criteria are based on two characteristics: physical location and marginalized populations. Walpole Island is discussed in this report, and was selected because of its critical position downstream from the “Chemical Valley” of Sarnia, in the St. Clair River watershed. The island is a First Nation’s reserve which falls under the jurisdiction of the federal government, leaving it relatively unprotected from the land-use decisions made by the Province. Furthermore, through information gathered at the site, behavioural bioassays were used to assess the effect of a contaminant of concern on the biological organism, *Daphnia magna*.

1.5 Thesis Rationale and Objectives

As the supply of clean drinking water dwindles and demand continues to increase, it is becoming increasingly important to protect drinking water resources and take responsible steps to prevent further environmental damage. Canadians continue to experience resource inequality as a result of policy and management issues, coupled with exploitation of resources and social prejudice. The purpose of this study is to allow a contribution of knowledge to the development and application of the EWBS, and to provide the context for which the system is to be used; in particular, the study will provide a greater understanding of the potential use of the EWBS with vulnerable drinking water supplies. This will be accomplished through the following objectives:

1. The assessment of Federal/Provincial/Territorial drinking water frameworks, with a focus on First Nations reserves; this will allow a cross-Canada comparison of legislation, policies, and contaminant testing to highlight the political climate in which the EWBS will be integrated.
2. The investigation of a case study site for possible use of the EWBS, based on specific selection criteria; physical location and marginalized populations. This will highlight the need for the system, and determine sites for its use, as well as the provision of a site-specific contaminant of concern.
3. The use of the study site’s contaminant of concern in aquatic invertebrate behavioural bioassays which will contribute to the ecotoxicological knowledge that the EWBS requires. It will also satisfy the requirement for a metal contaminant, a class of contaminants not yet

modelled and which is necessary for the development of a comprehensive monitoring system, responsive to broad classes of contaminants.

2.0 Nationwide Jurisdictional Analysis

2.1 Introduction

The EWBS currently in development will eventually be applied at specific water treatment plants for the protection of drinking water in Canada. The successful application of the system requires a detailed understanding of the legal framework to which the EWBS will be integrated. A provincial and territorial breakdown of drinking water frameworks will be examined, in addition to a comparison of contaminants that are tested in each province and territory.

A comparison of provincial and territorial contaminant testing parameters and frequencies was not found in the literature; such details provide important public information as well as information on the setting in which the EWBS will eventually be integrated. A literature review was conducted to gain knowledge on the jurisdictional drinking water roles of all levels of government and on the unique position First Nations hold in the national drinking water setting. Policies pertaining to drinking water advisories were also considered, as they occur as a result of the main issues surrounding drinking water protection. These policies also provide the public with information on water safety and indicate potential public health issues.

Each province and territory has its own policies for supplying and monitoring drinking water; while often loosely based on Federal guidelines, this is not always the case. The jurisdictional analysis below highlights the underlying issues of Canada's drinking water protection, providing the setting for the remainder of this study and the integration of the EWBS.

2.1.1 Jurisdictional Roles

Responsibility for the environment was not specified in the *Constitution Act* of 1867. Significant overlap of responsibilities, and uncertainty regarding provincial/territorial and federal jurisdiction in Canada have existed since that time. Provinces and territories play an important and constitutionally specified role in creating water legislation and policies relevant to water supply. Provincial governments have constitutional power over natural resources. The main exceptions are federal lands, First Nations reserves, inland fisheries, and boundary and trans-boundary waters, all which fall within federal jurisdiction (Hill *et al.*, 2008).

The federal government plays a mainly advisory role in drinking water protection. Health Canada publishes the *Guidelines for Canadian Drinking Water Quality (GCDWQ)*, which are developed by the Federal-Provincial-Territorial Committee on Drinking Water. However, as noted in the Office of the Auditor General's *Report of the Commissioner of the Environment and Sustainable Development: Drinking Water in First Nations* (2005), there is a "significant backlog" of approximately 10 years in updating the guidelines. Many known contaminants are not even listed

because of the length of time it takes to update them. The Canadian guidelines list 165 chemicals that need to be eliminated or reduced. However, this number does not come close to the 23,000 toxic chemicals in commercial use, many of which have not been adequately tested. Similarly, over 7,000 pesticides containing 500 active ingredients are registered in Canada; 60 of these are banned in the U.S. and Europe (Christensen, 2006).

Provincial jurisdiction of drinking water occurs for a number of reasons, primarily its constitutional role as a natural resource owner. However, the provision of drinking water is often a responsibility passed onto municipalities. Decision-making is drawn to the level of the resource use and is localized to citizen and industry needs, as well as to local environmental concerns. Natural geography, populations, and local industry vary across the country, allowing region-specific governance which can consider all applicable factors. Lastly, economic capabilities and priorities vary enormously, and provincial jurisdiction allows provinces to work within their economic means. Provinces may delegate certain responsibilities to municipalities, which is often the case with the treatment and distribution of drinking water.

The state of drinking water protection in Canada has been documented by the Sierra Legal Defence Fund in the report, *Waterproof: Canada's Drinking Water Report Card*. The report was conducted in 2001 and again in 2006. It gave the federal government and each province a letter grade based on the following criteria: treatment standards, contaminant standards, system design, lab and operator certification, and public reporting (Appendix A). New Brunswick fared the worst, dropping to a D grade, with lab accreditation as its only plus. Ontario came out on top with an A-, mainly due to increased legislation as a result of the Walkerton tragedy of 2000 (Christensen, 2006). All other provinces and territories achieved some degree of improvement, increasing the letter grade assigned to them. The federal government received a failing grade, mainly due to a lack of federally-enforceable standards, failure to recognize the right to clean drinking water, and a lack of drinking water safety standards for First Nations (Christensen, 2006). Because of the tangled web of jurisdiction and bureaucracy, Canadians cannot assume that clean water flows from their taps. It appears that rural communities, and in particular First Nations, are most at risk of negligence by all levels of government.

2.1.2 First Nations

Indigenous awareness of the environment recognizes that all living things are connected. First Nations are intricately tied to the land, and to the water. Kincentric ecology “is awareness that life in any environment is viable only when humans view the life surrounding them as kin” (Bakker, 2007). A kincentric approach to water appreciates that water is sacred and connects all living

things and that all beings have an equal right to the Earth's water, necessary to sustain all life. Utilization of an EWBS affords a respect to the First Nation attitude towards the environment. Instead of chemical analysis, the system uses the behaviours of biological organisms to tell the user that there is a problem with the water.

Responsibility for First Nations drinking water in Canada is complex and poorly defined. Compounding this issue is the fact that jurisdictional responsibility for drinking water is dependent on a community's latitudinal position. There are approximately 800,000 people living in 606 First Nation communities (Indian & Northern Affairs Canada [INAC], 2008a). In First Nation communities located south of 60°N, the responsibilities for drinking water are shared between First Nation Band Councils, Health Canada, and Indian and Northern Affairs Canada (INAC). INAC provides funding for constructing or upgrading water facilities and also covers a portion of the operation and maintenance costs. Health Canada plays a mainly administrative role by ensuring that water quality monitoring programs and adequate training are in place. Band Councils are generally responsible for the maintenance and operation of water facilities in accordance with established federal or provincial standards (Health Canada, 2010). There is no federal legislation governing drinking water protection on First Nations lands, and responsibility is considered "shared." In First Nation communities located north of 60°N, responsibilities for drinking water generally fall under the territorial governments. While variation in provincial and federal involvement is appropriate, the fragmentation is problematic, which seems to be the case with First Nations drinking water governance.

A significant finding of the Auditor General's 2005 report, *Drinking Water in First Nations*, was that residents of First Nations communities do not benefit from the same level of drinking water protection as non-reserve communities. This imbalance stems from a lack of legislation and regulation for the provision of drinking water in First Nation communities (Office of the Auditor General of Canada, 2005). The funding, policies, and administrative guidelines currently in effect do not provide consistency or accountability. In addition to management weaknesses, the main problems identified include deficient infrastructure and system operations, along with a lack of expertise, and fragmented training and certification. Despite significant investments, government funding initiatives over the years have continued to fail when it comes to improvement. Between 1995 and 2003, the federal government spent approximately \$1.9 billion, to help improve drinking water and wastewater services on reserves. A 2001 INAC survey found that 75 percent of the water systems posed significant risk to the quality and safety of drinking water, an increase from 25 percent in 1995 (Office of the Auditor General of Canada, 2005).

The Health Canada operational standards for First Nations require water system operators to regularly test for just five of the 88 *GCDWQ* health parameters³ (INAC, 2006b; Health Canada, 2007). Total coliforms, *Escherichia coli*, turbidity, and free and total chlorine residuals are tested, but this neglects the many chemical, radiological and parasite parameters that are a risk to public health. Once a year, Health Canada tests for 35 of the 88 health parameters (Table 2); however, this is not frequent enough to ensure safe drinking water. Seasonal variations can introduce increased runoff, and unexpected contaminant discharges are not accounted for by the annual testing of just 35 parameters.

Table 2: List of parameters tested annually by Health Canada in First Nations communities (Source: Health Canada, 2007)

Alkalinity	Hardness
Aluminum	Iron
Ammonia as nitrogen	Lead
Arsenic	Magnesium
Barium	Manganese
Benzene	Mercury
Boron	Nitrate
Cadmium	pH
Calcium	Selenium
Chloride	Silver
Chromium	Sodium
Colour	Sulphate
Copper	Total dissolved solids
Corrosivity	Total solids
Cyanide	Turbidity
Dissolved Organic Carbon	Uranium
Fluoride	Vinyl chloride
	Zinc

Even with such limited standards, water providers are unable to meet the current guidelines, and reporting is limited. Water operators frequently indicated that they have not even heard of some of the standards they are required to uphold, and results from Health Canada's yearly testing are not always shared with the water treatment plants (Safe Drinking Water Foundation, 2008). In 2005, INAC statistics indicated that just 40% of the plant operators under its responsibility were certified. One region included in the statistics was found to include operators who had been trained and passed exams but had not been certified (Office of the Auditor General of Canada, 2005).

³ These 88 parameters are those assigned a maximum allowable concentration (MAC) value in the 2008 edition of the Guidelines for Canadian Drinking Water Guidelines and include microbiological, chemical, and radiological parameters.

In 2003, the government implemented the First Nations Water Management Strategy, which committed \$600 million over five years to drinking water improvements (Office of the Auditor General of Canada, 2005). A 2007 report measured the progress made in providing safe drinking water and treating wastewater effectively on-reserves over the life of the Strategy (INAC, 2007). The percentage of water systems that met the Health Canada requirements continues to be reduced. In the data provided for the most recent year (2005-2006), only 43 percent of First Nation water providers tested the water weekly for the required five parameters. Compliance with guidelines for annual chemical testing occurred in 77 percent of the water systems; however, environmental health officers were only asked if the samples had been collected and not about how often or what parameters were actually sampled. Sampling for THM occurred in 54 percent of water systems and it was not determined if the required quarterly sampling frequency was met. Overall, Health Canada controlled water quality properly in approximately 45 percent of First Nation communities (INAC, 2007).

In response to this report and the continued lack of substantial improvement, INAC, in April 2008, announced yet more funding for the drinking water cause, with a two-year \$330 million investment in the First Nations Water and Wastewater Action Plan (INAC, 2008b). The funding is intended: 1) to double the number of trainers in the Circuit Rider Training Program (this provides training to First Nation water operators); 2) to conduct yet another national assessment of water and wastewater systems in all First Nations communities; 3) to set clear standards to guide the planning, design and operation of water systems; and 4) to consult with community members regarding the creation of a federal legislative framework (INAC, 2008b). This last point is a critical component of change. Without legislative responsibility and therefore accountability, true provision of safe drinking water will not be realized. The weak administrative framework currently in place for drinking water in First Nations communities continues to be ineffective, despite continuous evaluations and funding. An INAC Expert Panel on Safe Drinking Water is currently in consultation to develop a regulatory system (INAC, 2008c). It must be pointed out that drinking water mismanagement has been clear for decades, and while the need for a regulatory regime has been fully recognized, necessary changes have not occurred.

The federal government's Plan of Action for Drinking Water was announced in 2006, with a budget of \$60 million (INAC 2008c). Its purpose was to address the drinking water concerns of all high risk systems in a total of 224 communities. In December, 2007, 116 communities with high-risk drinking water systems remained. The government attributes this improvement to the issuance of a clear protocol on water standards, increased operator training through the Circuit

Rider Training Program, the creation of an expert panel to provide options for a regulatory regime, and measures to address specific barriers in high risk communities such as source water, system design, system operation, operator training and the monitoring and reporting parameters (INAC, 2008c). Despite these successes, as of February 28, 2010, there were 114 First Nations communities across Canada under a drinking water advisory (Health Canada, 2010). The need for continued improvement is clear and the federal government continues to move forward with consultations on the development of a regulatory regime to oversee water quality on reserves. As part of a broader consultation process, engagement sessions were held in February-March 2009 with First Nations residents, regional First Nation organizations, and provincial/territorial government representatives, with a goal of working towards the development of a legislative framework for drinking water (INAC, 2009).

An overwhelming and confusing series of plans, reports, evaluations, and committees have been instituted for the management of First Nations drinking water, with a lack of definite improvement. All of the government's strategies seem to have the same objectives but it is clear that, despite funding and improvements to infrastructure and training, a distinct problem remains with drinking water in First Nations. This problem is consistently highlighted in comparisons with communities in non-federal jurisdictions, and the glaring difference seems to lie in the lack of enforceable standards.

2.2 Methodology

To accomplish the research objective of a cross-Canada comparison of drinking water frameworks, an in-depth review of each province and territory was examined for legislative reference and standards in relation to drinking water. The research process consisted of an extensive literature review which included both peer-reviewed and grey literature and in cases where there was a lack of published information or contradictions, personal communication with the responsible government department was necessary. The summary is not exhaustive due to a lack of information on some provinces.⁴ The following criteria were used in reviewing each province and territory 1) the responsible ministry, 2) the legislative references to water, 3) public reporting, 4) contaminant testing and frequency, and 5) source water protection measures. The nationwide analysis of baseline, commonly-tested parameters for each jurisdiction was surprisingly not found in the literature and is considered important information for both the public and researchers. Contaminant parameters tested in each province and territory were compiled into a

⁴ All information gathered regarding Quebec's position on drinking water protection was from the actual legislation, and any supporting government documents were provided in French only.

table. This nationwide contaminant table is useful to note specific differences relating to factors such as industry and geography, and ultimately indicates a set of contaminant parameters that can be used in the EWBS.

2.3 Results and Discussion

In light of the high degree of variability in water governance across Canada, and the increased spotlight on governments' failure to provide safe drinking water to all citizens, a systematic review of the provinces' and territories' legislation or policies governing drinking water was deemed necessary; in particular, those objectives pertaining to water monitoring, testing standards, and public reporting procedures. These processes are important aspects of drinking water protection that help instil confidence in the respective governing bodies.

There is little cohesiveness across the country when it comes to contaminant testing as a result of varied provincial and territorial regulatory frameworks. The number and type of contaminant parameters tested vary for each jurisdiction, and affect the suite of contaminants selected for monitoring by the EWBS. A number of provinces do not have legislation pertaining to drinking water and have only established guidelines. This perhaps follows the lead of the federal government's passive role in ensuring safe drinking water. Drinking water advisory (DWA) policies differ across the provinces and territories and consequently prevent an accurate assessment of the nation's drinking water.

The overall finding of the jurisdictional analysis was inconsistency. This gap certainly has implications for providing all Canadians with the same level of quality drinking water. A summary below of each province and territory highlights how safe drinking water is addressed, whether through legislation or in guidelines and includes a summary of contaminant testing parameters nationwide.

2.3.1 Drinking Water Advisories

There are approximately 90,000 drinking water related illnesses and 90 deaths reported by Health Canada each year (Christensen, 2006; Environment Canada, 2008). Despite the grave public health effects, there is currently no nationwide indicator representing access to safe drinking water in Canada. A number of Canadian agencies have attempted to assess the quality of freshwater but not as it is directly related to human consumption. Statistics Canada annually publishes an *Environmental Sustainability Indicator Report* which mainly presents freshwater quality as it relates to aquatic life. In recent years, further efforts have been made to develop indicators of drinking water quality for human consumption but as yet there are no published results (Statistics Canada, 2008). To achieve this, government will use information gathered by Statistics Canada's Survey of

Drinking Water Plants, which is also implemented by INAC in First Nation communities, to rank the quality of source and treated waters and determine how closely specific parameters of water quality conform to Canadian guidelines (Statistics Canada, 2008). The Federation of Canadian Municipalities, which holds the responsibility for the provision of clean drinking water for much of the public, collects data for key quality of life issues in select Canadian cities. The data capture water related concerns of wastewater treatment and water consumption, but not drinking water quality (Federation of Canadian Municipalities, no date [n.d.]). Based on the above information, DWAs continue to represent the best available indicator of safe drinking water in Canada. However, it is important to consider the limitations of this approach, particularly when making comparisons across jurisdictions, where many inconsistencies exist.

A recent study published in the *Canadian Medical Association Journal*, indicated that as of March 31, 2008 there were 1766 DWAs in effect in Canada, excluding First Nations communities (Table 3) (Eggertson, 2008). This number reflects the status of small, rural, and often isolated non-reserve communities, an important demographic that is often marginalized when it comes to the achievement of safe drinking water standards. The DWAs are issued for reasons ranging from adverse taste to high coliform count, or a breakdown in chlorination equipment. The totals indicate the number of advisories in effect on the day the research study occurred and can therefore vary day-to-day. Some had been in place for years; others just days. They include large and small water suppliers, such as trailer parks and business sites. The numbers provided are based on regulations⁵ and public notification procedures which are not federally mandated and vary greatly across the country.

⁵ A governmental order having the force of law (The American Heritage Dictionary of the English Language, 4th ed., 2009)

Table 3: Provincial breakdown of boil water advisories in effect on Mar. 31, 2008 (Source: Eggertson, 2008)

Province	Total Boil Water Advisories
Newfoundland and Labrador	228
Prince Edward Island	0
Nova Scotia	67
New Brunswick	2
Quebec	61
Ontario	679
Manitoba	59
Saskatchewan	126
Alberta	13
British Columbia	530
Northwest Territories	1
Yukon Territory	0
Nunavut	0

When considering the numbers associated with DWAs, it is first useful to consider the terminology. Inconsistent terminology can result in a loss of information regarding the severity of the event and can create challenges in making nationwide comparisons. The reasons surrounding an advisory, and the level of risk associated with it, can vary considerably and may be presented differently, depending on the jurisdiction. A *boil water advisory* or *precautionary advisory* is often used to indicate that precautions must be taken prior to use or consumption, such as bringing the water to a rolling boil. This type of advisory can be issued for a variety of reasons including the presence of unacceptable levels of disease-causing bacteria, turbidity, an interruption in treatment, or adverse aesthetics and taste. Should an advisory continue for an extended period of time, it may be classified as a permanent order, at which point it can no longer be considered as a preventative measure and may imply more severe issues. A *boil water order*, or *do not consume order*, is used when the outbreak of illness is linked to water consumption. *Do not use orders* indicate further severity when it is possibly harmful to come into contact with the water, such as the case in Kashechewan, where residents developed skin rashes (Isfeld, 2009).

Advisories are compiled from individual provincial, territorial, and sometimes regional health ministries. Surprisingly, Health Canada does not maintain a nationwide database, causing a potentially serious implication for travellers across the country. Not all provinces post their advisories to the public and each province has its own definition of an advisory, protocols and listing criteria—an inconsistency that appears to be widespread. The number of advisories issued in provincial and federal jurisdictions is likely influenced by the absence of nationally-enforced

standards and differences in quality standards, treatment requirements, and regulations. These factors can affect changes in the number of advisories over time. British Columbia's provincial health officer, Dr. Perry Kendall, explained the provinces' increased advisories in the past several years as a reflection of increased attention to monitoring and the application of new turbidity guidelines (quoted in Eggertson, 2008). Advisory numbers can also be affected by reporting differences within a province. This was recently evident in Alberta, where only five of the nine regional health authorities provided DWA information (Isfeld, 2009). Another example was British Columbia's Interior Health region which was found to have a three-month time lag in their advisory reporting (Eggertson, 2008; Isfeld, 2009).

There are a number of confounding factors that must be considered when analyzing the numbers associated with DWAs. Regional geology of natural occurring minerals and the geographical location of a community, be it in a valley or downhill from run-off, can influence its susceptibility to adverse drinking water. This is evident in Southern Manitoba, which lies in a floodplain and, as a result, experiences high incidences of drinking water contamination during spring flooding (Isfeld, 2009). Population density also influences the concentration of anthropogenic environmental impacts, therefore increasing risks to drinking water. Provinces also differ greatly in their level of drinking water standards, increasing or decreasing the point at which a boil water advisory is necessary. For example, the province of Ontario has stringent guidelines, a large population, and subsequently the highest number of advisories. However, Ontario Ministry of Environment spokesperson, Dave Jensen cautions that provincial public health units do not always report their advisories to the Ministry or report if, and when, the advisory is lifted (quoted in Eggertson, 2008). Often, the short-term procedural issue or problematic test result is presented in a DWA but the underlying cause, such as an upriver spill, is not provided with the announcement. The provision of these pertinent data would allow the public to make informed decisions regarding their health and other activities in the affected area. DWA frequency is also indicative of underlying economic factors. A common reason stated by Newfoundland water system operators for chlorination shutdown is a lack of funds for proper operation (Isfeld, 2009). In comparison to urban centers, small rural communities and First Nation reserves are often faced with the compounded challenges of isolated location and limited financial and technical resources.

Many jurisdictions fail to include information on the duration of water advisories or a history of past incidents. For example, Saskatchewan does not provide historical data on water advisories; after an advisory is lifted, the information is permanently removed from the database (Safe Drinking Water Foundation, n.d.(a)). This action prevents the use of information for

identification of possible trends in contamination events which could better equip communities for potential future events. In contrast, Newfoundland and Labrador includes a table of both current and historical advisories and is the only province to include the size of the population affected (Isfeld, 2009). The Northwest Territories and New Brunswick offer archival data for multiple years, while Manitoba, the Interior of British Columbia, and Nova Scotia include advisories lifted in the past calendar year. In Nova Scotia, only those advisories rescinded in the past week are included. All posted advisories are weighted equally, without consideration of the duration of an advisory; this is important information for identifying the impact of water advisories on communities and also highlights the need for improvement in this area.

Public reporting is not mandatory for all provinces and territories or even amongst regions, resulting in variations in the actual number of advisories announced. In 2006, the Sierra Legal Defence Fund's 2006 nationwide review of water policy found that many provinces lacked criteria such as specifying when an advisory should be listed, notification procedures, and requirements for public reporting. Since that time, improvements have been made. Eight provinces and territories (Manitoba, New Brunswick, Newfoundland and Labrador, Northwest Territories, Nova Scotia, Quebec, and Saskatchewan) maintain online advisories and three other provinces (Alberta, Prince Edward Island, and Ontario) provide online water data and reports. In the case of Alberta, the government's website clearly excludes emergency DWAs; the site's purpose is to provide monthly or annual reports and to post advisories for weather and physical water conditions (Government of Alberta, 2010). Nunavut and the Yukon continue to lack these improvements. Health Canada is responsible for drinking water quality in First Nation communities; it posts water advisories but provides only total numbers and does not specify the affected communities (Isfeld, 2009). In an attempt to improve public reporting, some jurisdictions have created a format for presenting data which is often confusing and challenging for the public; others may only provide a telephone number advising the public to contact suppliers or their regional health authorities if they have any questions (Isfeld, 2009). This process can be viewed as counter-productive and results in the responsibility being passed on to the citizen. As an example, Krewski *et al.* (2002) expressed frustration in repeated attempts to obtain DWA data from the Ontario Ministry of Health; the data were never provided, despite multiple requests. This inaccessibility of public information can lead to future mistrust of government's efforts to protect public health (Krewski *et al.*, 2002).

A clear lack of consistency exists in Canadian DWA data. This prevents a fair comparison from being made regarding the strength of drinking water protection across jurisdictions.

Provincial, territorial, and even regional differences to the approach of DWAs make it difficult to determine the national quality of drinking water.

2.3.2 Federal Government

Federal authority of freshwater encompasses water management on federal lands, First Nations reserves, boundary and trans-boundary waters, fish habitat, and navigation and shipping. INAC still possesses much of the responsibility of water resources in the territories; however, more of this responsibility is being transferred to the territorial governments.

The *Canada Water Act* was passed in 1970 in an effort to better manage Canada's water resource, and in recognition of the *Constitution Act*, the intent is that water management be accomplished in partnership with the provinces. The primary role of the federal government under the *Canada Water Act* is to work with the provinces to protect water resources, and to intervene when provinces fail to protect water resources of national concern. In partnership with the provinces, management plans are made for significant water sources (British Columbia Guide to Watershed Law and Planning, n.d.). The 1987 Federal Water Policy represents the federal government's philosophy and goals for Canada's freshwater, and the ways in which these goals can be reached. The Policy's view is that water is both a commodity and an important environmental component. It aims to protect and enhance the quality of water resources by preventing or minimizing contamination and by restoring those which have already been affected. The second policy goal is to promote the wise use of water and its efficient management. This can be done through scientific research, legislation, education, integrated planning, and promoting realistic pricing of water. The policy strives to have an open style of decision-making through committees and consultations, and is also aimed at Canadian citizens who share the responsibility for sustaining the country's water resources (Environment Canada, 2009).

Despite having the Federal Water Policy, the federal government departments are admitting that the initiatives outlined were not aggressively carried out, and that little was done to move things forward over the past 20 years. Since the Policy's inception, demands on water resources have only increased, along with the scientific complexity of effects on water as a resource, such as climate change and energy. The original policy, however, is outdated. Canada continues to be one of the few industrialized nations to lack enforceable national drinking water standards, is opposed to adopting water as a human right, and lacks laws against bulk water exports (The Council of Canadians, 2008).

The federal government, mainly Health Canada, plays an important guidance role in the provision of safe drinking water. The *GCDWQ* provide the direction for provincial and territorial

drinking water standards. The guidelines establish maximum allowable concentrations (MAC) for microbial, chemical, radiological, and operational and aesthetic objectives. The listed parameters and standards are not legally enforceable and act as guidelines for the provinces and municipalities to consider in the operation of public water supplies. The government's main responsibilities concerning drinking water are defined by Health Canada as: 1) the development of national drinking water guidelines with provincial and territorial drinking water authorities; 2) the provision of emergency advice when requested; and 3) the monitoring of drinking water quality on First Nations reserves (Health Canada, 2009). Nowhere in the government's list of responsibilities does it indicate a need for nationally-enforceable standards, which would help to ensure that other listed objectives are accomplished.

In comparison to Canada, other nations have federally legislated drinking water standards that require the compliance of all member states or countries. The U.S. *Safe Drinking Water Act* was passed in 1974 and gives the United States Environmental Protection Agency (USEPA) the responsibility to implement and enforce drinking water standards. The *National Primary Drinking Water Regulations* are legally-enforceable standards that apply to all public water systems and help to ensure that all drinking water in the country maintains the same level of safety. There are also non-enforceable secondary drinking water regulations that include aesthetic objectives. The monitoring of 90 contaminants, disinfection chemicals, and disinfection by-products is required, as well as mandatory reporting to the State or the USEPA. Furthermore, every five years, the USEPA develops a list of unregulated contaminants that may pose health concerns and these are subsequently added to the standards. Health Canada guidelines, in comparison, contain fewer contaminants in number and higher allowable limits, while some parameters are not even given a numerical value. As well, the removal of all viruses and protozoa is not recommended, as is the case with the USEPA 99.9% removal requirement (Safe Drinking Water Foundation, n.d.(b)).

The European Union (EU) directs drinking water regulation through the Drinking Water Directive. Under this directive, member countries are required to regularly test and monitor 48 microbiological and chemical parameters in drinking water. Monitoring is required at the tap, inside public and private premises, and reported every three years to the European Commission which then publishes a complete report, available to the public. The standards are derived from the World Health Organization (WHO). In comparison to Canada, the EU framework has considerably more accountability but is not as stringent as the USEPA regulatory framework (Safe Drinking Water Foundation, n.d.(b); USEPA, 2004; European Commission, 2009).

2.3.3 Provincial and Territorial Drinking Water Frameworks

This section provides an overview of the key components of provincial and territorial drinking water frameworks, proceeding from east to west across the country.

2.3.3.1 Newfoundland and Labrador

Newfoundland and Labrador (NL) is the only province that has taken responsibility for water quality monitoring; other provinces assign this duty to the municipalities and have them report to the Ministry. In NL, the Department of Environment and Conservation is responsible for the provision of safe drinking water. The *Water Resources Act* does not include specific standards in its legislation but refers to a set of policy guidelines to be implemented by public water suppliers with respect to water quality monitoring and reporting activities. The guidelines outline the parameters to be sampled, the frequency of sampling, and detailed reporting requirements for both the public water suppliers and the Province. Continuous disinfection, most often in the form of chlorine, is mandatory for all public water supplies. Bacteriological, chemical, and physical parameter guideline levels are based on those in the *GCDWQ*, but chemical and physical tests only identify parameters included in standard chemical analysis and metal scan packages (NL Department of Environment and Conservation, 2009). Sampling frequency for the inorganic parameters is, at a minimum, semi-annually and for disinfection by-products, at least four times a year. Bacteriological sampling occurs at a minimum once a month and this increases with the size of the population served (NL Department of Environment and Conservation, 2009). Water quality data are easily accessible to the public as the Department recently created a water resources portal that provides access to all community water resource reports, current DWAs, and a GIS mapping tool that visually represents water related data (NL Department of Environment and Conservation, n.d.).

The *Water Resources Act* is used to protect public drinking water supplies which upon initiation by municipal governments, are classified as protected areas. High-risk activities that could impair water quality are then restricted inside the protected area. Watershed Management Committees oversee land use management, development issues, and activities within the protected watershed and are comprised of interested stakeholders from government, industry, and the public (NL Department of Environment and Conservation, 2009).

2.3.3.2 Prince Edward Island

Prince Edward Island (PEI) is unique in that its entire population depends on groundwater as a drinking water source. Furthermore, 57% of the Island's population depends on private wells, the highest proportion in Canada (PEI Ministry of Environment, Energy, and Forestry, n.d.).

Disinfection of drinking water is not required by government regulations; however, it is practiced in all municipalities in order to ensure that the water is free from microbial contamination.

PEI's drinking water legislation originates from the Environmental Protection Act's *Drinking Water and Wastewater Facility Operating Regulations* and is administered by the Department of Environment, Energy and Forestry. This 2004 legislation deals with the registration, monitoring, reporting, and operator certification of public water systems. Regulations specify the minimum sampling requirements, based on the size of the water system and if chlorination is used. Water is sampled for the presence of total coliforms and *E. coli* and chemical analysis ranges from general testing for several metals and physical parameters to detailed chemical analysis, including numerous metals and inorganic constituents (*Drinking Water and Wastewater Facility Operating Regulations*, 2004). The monitoring frequency established in the *Regulations* differs depending on the water system type. Small public water systems, which serve fewer than 100 customers, are required to test for coliform bacteria and *E. coli* four times a year, a general chemical analysis once a year, and a detailed analysis at least once every five years. The monitoring frequencies are increased for chlorinated public water systems; a minimum of four bacteriological samples each month are required from the distribution system and one per month from the surface supply. A general chemical analysis is required once a year while a detailed analysis is required a minimum of every three years (*Drinking Water and Wastewater Facility Operating Regulations*, 2004). Public water suppliers are required to report a summary of water quality results to its customers at a minimum of once annually and are required to maintain all records of water quality analysis for at least five years.

For the protection of source water, the *Environmental Protection Act* stipulates that buffer zones must be set up between intensive livestock operations and water bodies or wetlands. Appropriate measures are necessary to prevent runoff contamination and agricultural crops are restricted from the buffer zone. Source water protection plans only exist in the form of wellhead protection plans which must be prepared by the owners of public drinking water systems, and be approved by the Department (Expert Panel on Safe Drinking Water for First Nations, 2006).

2.3.3.3 Nova Scotia

In 2000, Nova Scotia became one of the few regions in Canada to adopt the health-related GCDWQ as legally-binding standards, per the *Water and Wastewater Facilities and Public Drinking Water Supplies Regulations* of the *Environment Act*. Under this legislation, the Department of Environment and Labour is the designated lead agency for water management. The *Regulation* requires that a public drinking water system use disinfection water treatment and regularly test for

microbiological, general physical and chemical quality, disinfection residual, turbidity, fluoride concentrations, and any other substance deemed necessary by the Minister of the Environment and Labour, in a manner and at a frequency set out in the *GCDWQ (Water and Wastewater Facilities and Public Drinking Water Supplies Regulations 181/2009)*.

Chemical and physical parameter testing must be monitored at least once annually for surface water supplies, with the exception of operational parameters such as turbidity and chlorine residual, which is tested continuously or daily. Bacteriological parameters are sampled a minimum of four times a month, with this value increasing as the population served increases (Nova Scotia Environment and Labour, 2005). In the event that the *GCDWQ* allowable health related concentrations are not met, the owner must immediately notify the Department of Environment and begin to take corrective action. A guideline document for public drinking water supplies provides a table of contaminant parameters that outline minimum standards to be met by all water systems and enhancement to testing is used when needed (Nova Scotia Environment and Labour, 2005). While the public reporting of sampling data are not required, the province does provide updated online DWAs that indicate the length of the advisory and the community or water supply for which it applies. Nova Scotia does not provide historical data; however, the online advisories do indicate whether the advisory was present during the previous reporting period (Nova Scotia Environment and Labour, 2009). The Nova Scotia safe drinking water regulatory framework establishes a minimum standard to be met by all but also allows the enhancement of requirements when risks are suspected or known to be present (Personal Communication, Nova Scotia Environment and Labour, Apr. 3, 2009⁶).

Source water protection in Nova Scotia is under the authority of the Department of Environment and Labour. Restriction of activities affecting water quality, designation of watersheds as protected areas and the regulation of on-site sewage systems manage and protect water uses. The document, *A Drinking Water Strategy for Nova Scotia* outlines advances in source water protection but the province currently remains in the planning stages of official source water protection plans (Nova Scotia Environment and Labour, 2005).

2.3.3.4 New Brunswick

The responsibility for drinking water in New Brunswick is primarily under the Department of Health and specifically the Office of the Chief Medical Officer of Health (OCMOH). The Department of Environment also plays a role, although mainly in a source water protection

⁶ References to personal communication exclude the names of individuals and instead include their professional designation.

capacity. The department has the authority to issue certificates of approval to water systems using more than 50m³/day under the *Water Quality Regulation-Clean Environment Act*. This certificate of approval applies to the construction requirement of waterworks, discharge limits, and reporting requirements in the event of public health emergencies (*Water Quality Regulation 82-126*).

Municipally and provincially-owned and operated water systems are required to sample their water according to the *Clean Water Act*. This *Act* states that each system must submit sampling plans for the collection and testing of water, including the parameters tested, and the frequency and location of sampling (*Potable Water Regulation 93-203*). The water provider is required to have the water tested by an accredited laboratory, and the testing frequency is in accordance with Health Canada's recommendations. Public reporting procedures are not included in the *Act* or in its *Regulations*, and municipalities are not required to publicly report data, although some may choose to report some data parameters. Current DWAs are posted online, and historical data are maintained dating back to 2006. Within the legislation, the water system's required testing parameters are not clearly defined. One government source indicated that regulated water supplies must test for specific indicated physical, chemical, and microbiological parameters, but also stated that testing is in accordance with the *Clean Water Act*, which only mandates sampling plans. The Department of Health was contacted to clarify this discrepancy. The respondent stated that the Department of Environment and the Department of Health work closely in the regulation of drinking water (Personal Communication, Office of the Chief Medical Officer of Health, Oct. 13, 2009). The Minister of Health has the authority to issue sampling plans to systems that are owned and operated by municipalities or the Province, and concurrently, regulated water supplies must test for specific microbiological, organic, and inorganic chemical parameters and aesthetic objectives as indicated (Personal Communication, Office of the Chief Medical Officer of Health, Oct. 13, 2009). These guidelines are adopted from Health Canada's *GCDWQ*.

The *Watershed Protected Area Designation Order* is the main piece of legislation which protects source waters. The Order prohibits the undertaking of certain activities anywhere within a drinking water supply watershed. Other activities are permitted within the remainder of the drainage area, but not within the setback zone, 75 meters from the watercourse (Environment Canada, 2004).

2.3.3.5 Quebec

In 1984, Quebec originated as a forerunner in water protection by becoming the first province to develop its own legally-binding drinking water standards. These standards originally contained 42 parameters for testing and have since expanded to include some standards that go

beyond those of the federal guidelines (Hill *et al.*, 2008). The *Regulation Respecting the Quality of Drinking Water*, passed in 2005, strictly outlines treatment requirements for water distribution systems and is administered by the Ministry of Environment. Continuous disinfection is required, as well as filtration, unless the turbidity is less than or equal to a set level, and weekly samples are checked for fecal coliform bacteria and turbidity. Bacteriological samples are collected a minimum of twice monthly, and this frequency increases depending on the size of the population served. Inorganic substances must be sampled once in a period between July 1 and October 1. Nitrates and nitrites have a separate schedule and are required to be sampled quarterly. THMs are also sampled quarterly, and turbidity must be sampled once every month. Systems serving more than 5,000 people must sample organic parameters quarterly. A lengthy list of required substances is included in the *Regulation*, inclusive of metals, pesticides, and other organic substances (*Regulation Respecting the Quality of Drinking Water*, R.Q. c. Q-2, r.18.1.1). Public reporting of adverse test results is legally-mandated for the exceedance of microbiological parameters but adverse results for all other required parameters are only reported to the Minister and the Public Health Director. The DWAs, which are listed per region, include information on the type of advisory and the timeframe in which it has been in effect. The government does not however, provide annual drinking water reports, a process that would help the public better understand improvements or issues within their water system.

In 2002, the Quebec government implemented the Quebec Water Policy for the protection of source water. The Policy has committed to: 1) implementing integrated watershed management plans; 2) establishing watershed management agencies to protect and restore ecosystems; 3) encourage public participation; and 4) supporting volunteer organizations who are working to prevent environmental degradation (Papa and Edwards, 2004).

2.3.3.6 Ontario

The Walkerton, Ontario crisis in 2000 resulted in a sharp increase of awareness in drinking water safety in the province. With the crisis fall-out came a flurry of legislation that aimed to address previous legislative and enforcement gaps. The 2002 *Safe Drinking Water Act* resulted from the Walkerton Inquiry, in which Commissioner Dennis O'Connor recommended an act that would encompass all legislation and regulations relating to drinking water treatment and distribution. In 2006, Ontario enacted another important piece of legislation, the *Clean Water Act*, which focuses on source water protection and the formation of stakeholder committees. These committees are responsible for developing source protection plans in each watershed, in an attempt to identify potential water supply risks and to take actions to minimize these risks (Ontario Ministry of the

Environment [OMOE], 2009a). Also related to drinking water protection is the *Nutrient Management Act* of 2002, which was drafted prior to the Walkerton tragedy, and mandates that farmers develop nutrient management plans in order to manage nutrient-containing materials. Nutrients have important implications for drinking water, as fertilizers, manure, and biosolids eventually drain into waterways, thereby potentially impacting drinking water supplies. The mandated nutrient management plans are not directly linked to drinking water protection but aim to enhance environmental protection while providing sustainable options for future agricultural operation and rural development (*Nutrient Management Act*. S.O. 2002). The *Act* does not however, regulate pathogens, a serious concern associated with agricultural operations.

Ontario drinking water is the responsibility of the Ontario Ministry of the Environment's (OMOE) Drinking Water Management Division. Ontario's *Drinking Water Systems Regulation*, as outlined under the *Safe Drinking Water Act*, details the treatment and testing requirements for all regulated water systems. All municipal residential drinking water systems that obtain water from surface sources are mandated to utilize chemically-assisted filtration and primary disinfection. Microbiological parameters are sampled at least once a week, the frequency increasing with the size of the population served and the sampling point in the distribution system. Specific inorganic and organic parameters, including pesticides, are listed in the legislation. These require sampling at least annually for surface water supplies and every three years for groundwater supplies. THM, nitrites, and nitrates must be sampled every three months. The *Act* further protects the quality of water by stipulating that if a chemical parameter listed in the *Act* exceeds half of the standard set out in the *Ontario Drinking Water Quality Standards Regulation*, the frequency of sampling and testing for that parameter is increased to once every three months. Radiological parameters are included in the *Regulation* and drinking water systems are obligated to meet the prescribed standards (*Drinking Water Systems Regulation*, 170/03).

In the event of an adverse test result, the *Act* clearly outlines a different reporting procedure for each parameter type, and includes a requirement for appropriate corrective action. All exceedances result in verbal and written reports to the Ministry and the medical officer and in some cases, after all other actions have been carried out, public notices are given. However, there is no provincial level of notification. Advisories are not posted online but rather are posted by the municipal waterworks and local medical officer of health through local media and prominent locations within the affected area. Nevertheless, accountability to the public is present, as the owner of a drinking water system must complete an annual report providing information pertaining to the capability of the system in meeting existing and future uses, and detailing any

requirements under the *Act* and its regulations were not met (*Drinking Water Systems Regulation, 170/03*).

2.3.3.7 Manitoba

Manitoba is the first and only province to have a ministry devoted totally to water governance. The *Drinking Water Safety Act* is enforced and administered by Manitoba Water Stewardship, and requires both public and semi-public water suppliers to meet certain design, operational, and monitoring requirements. Under the *Drinking Water Safety Regulation*, all water in the distribution system must meet the bacteriological and chemical standards stated in the regulation, in addition to any parameters specified in the supplier's operating licence. The licence's issuing drinking water officer can alter testing parameters and frequency depending on characterizations of the water system. Disinfection residuals are required to be continuously monitored or minimally on a daily basis, and bacteriological sampling for *E. coli* and total coliforms must be done at a minimum of twice monthly. This increases with the population served. The minimum sampling frequency for the short list of inorganic and organic chemical parameters depends on the population served, and at a minimum, are sampled once every third year. The minimum frequency of sampling for THM is on a quarterly basis annually, and while the sampling frequency of physical parameters is not included in the *Regulation*, it is specified in the operating licence (*Drinking Water Safety Regulation 40/2007*). Acceptable concentrations for all parameters are detailed in the *Drinking Water Quality Standards Regulation*, along with appropriate corrective actions, which depend on the parameter that was exceeded and the water system type (*Drinking Water Quality Standards Regulation 41/2007*). Aspects of this regulation do not require immediate compliance. Microbial, chemical, radiological, and physical standards outlined in the regulation are not mandatory until five years after the day the *Regulation* came into force. This exception, however, does not apply to bacteriological standards. Additionally, a five-year transition period is also in effect for public water suppliers serving more than 5,000 people, at which point they must conduct continuous turbidity monitoring and periodically report the results to a drinking water officer. The public water supplier must develop a compliance plan within this transition period that details how they will comply with the new *Regulation's* standards (*Drinking Water Quality Standards Regulation 41/2007*).

Public reporting and accountability requirements are strengthened through the *Act* and its regulations. The issuance of boil water advisories is mandated in the *Act* and requires that the medical officer, drinking water officer or water supplier give notice to the users through appropriate means such as publishing advisories in the local media. If a health risk is imminent and

there is no time for the director or the drinking water officer to obtain approval from a medical officer, these individuals have the authority to issue a boil water advisory (*Drinking Water Safety Act*, 2002). Following the end of the government's fiscal year, the director of the Office of Drinking Water must submit a report of the office's activities during that year. Effective in 2008, water utilities that serve 1,000 people or more were required to produce an annual report about the operation of their water system during the previous year and were to ensure accessibility to all public users by providing free copies of the report and an online copy (*Manitoba Regulation 40/2007*).

The Manitoba government has developed the Water Stewardship Fund that provides financial assistance to projects that maintain and improve water sources. The fund, along with the *Water Protection Act*, encourages the development of water management plans through the identification of watersheds and the formation of watershed planning authorities (Manitoba Water Stewardship, n.d.)

2.3.3.8 Saskatchewan

In Saskatchewan, the management of drinking water is accomplished through the coordinated efforts of various government entities. The Ministry of Agriculture is responsible for water resources in relation to agricultural activities, such as irrigation, and the protection of surface and groundwater supplies affected by intensive livestock operations. The Ministry of the Environment is the primary regulator of municipal water systems and publicly accessible private systems with a flow rate greater than 18,000 litres per day. The Ministry of Health regulates semi-private water systems with flow rates less than 18,000 litres per day as well as private waterworks, which are not regulated. The regional health authorities will interpret test results and provide water advice. The Saskatchewan Watershed Authority is responsible for watershed management and source water protection. It has the responsibility to balance competing land and water issues which may have an impact on water quality (SaskH20, 2009b).

The Water Regulations is included under the *Environmental Management and Protection Act* and was passed in 2002, following the North Battleford *Cryptosporidium* outbreak in drinking water. Six to seven thousand people were infected by this parasite and fortunately, there were no fatalities. An inquiry into the incident found that treatment practices were not optimized in the years leading up to the incident, coupled with operator certification issues and lack of inspection (The North Battleford Water Inquiry, 2002). The Long Term Safe Drinking Water Strategy (LTSDWS) responds to the commission's recommendations, and works toward future changes in

drinking water management. The LTSDWS has been a key driver for Saskatchewan's changes in legislation, regulations, and administrative departments (SaskH2O, 2009b).

While all parameter standards included in *The Water Regulations* are not all immediately effective, there was immediate testing for fecal coliform and total coliform. Turbidity standards that are monitored daily or continuously were immediately effective for newly-constructed systems and for existing waterworks, and were set to be in place by December 2008 for those serving less than 5,000 people and by December 2006 for systems serving populations greater than 5,000. The allowable turbidity levels are dependent on the type of filtration in place and continuous disinfection by chlorination is mandatory. The chemical parameter testing standards include inorganic and organic contaminants, with a separate category of pesticides selected as commonly used in Saskatchewan. All parameters are monitored at a frequency specified by the system's operation permit. Furthermore, the standards include two radiological parameters, gross alpha and beta activity. Compliance with chemical, pesticide, and radiological parameters was immediate for newly-constructed waterworks and was phased-in by existing waterworks by December 2008 for those serving more than 5,000 people and by December 2010 for remaining systems. The *Regulation* also includes a list of objectives which are parameter standards that are not mandatory but include physical and chemical properties that if found in excessive concentrations would not be acceptable for consumers and are therefore strongly suggested for monitoring (Saskatchewan Ministry of Environment, 2006).

The Ministry of the Environment is the key administrator of the *Environmental Management and Protection Act* but does so in consultation with other ministries, the Saskatchewan Watershed Authority, and the public. Each year, the ministry is responsible for preparing a State of the Drinking Water Quality Report which is submitted to the Minister and the Legislative Assembly. The *Act* gives the Minister the authority to issue both precautionary and emergency DWAs if the water is deemed to have, or potentially have, an adverse effect on human health. Each year the water suppliers are required to supply consumers with notices of the quality of water supplied compared to levels specified in regulations (*Environmental Management and Protection Act* C. E-10.21. 2002)

The Ministry of Environment has created an online information system regarding drinking water in the province. It includes both precautionary DWAs as well as emergency boil water orders currently in effect, their location, and the reason for the warning. In addition, consumers can select their designated waterworks and view current and historical sampling requirements, the frequency, allowable limits, and test results. This allows the public to stay informed at their

convenience and not just annually, when the year-end reports are made available (SaskH2O, 2009a).

2.3.3.9 Alberta

Alberta was the first province to adopt a strong regulatory framework, shaped from the USEPA stringent reporting and enforcement regime (Bakker, 2007). In 1972, the province fully adopted the health based parameters of the *GCDWQ*, and made it legally binding in the 1978 *Municipal Plant Regulation* (Bakker, 2007). In the case of turbidity, Alberta actually exceeds the *GCDWQ* guideline for turbidity, but for fluoride, the province allows a higher limit. It was also the first Canadian province to adopt the enhanced surface water treatment rule, based on the U.S. *Safe Drinking Water Act*, which makes filtration a mandatory treatment process. The majority of Albertans receive their drinking water through public systems managed by Alberta Environment; however, for approximately 500,000 people living on farms, First Nation reserves, and receiving water from communal systems, drinking water is managed by Alberta Health and Wellness and in the case of First Nations, by the Federal government (Alberta Environment, n.d.). Alberta Health and Wellness also utilizes the *GCDWQ*, through the *Public Health Act*.

The *Alberta Water Act* came into being in 1999 and centers on water management planning, use, and enforcement. It emphasizes the wide use of the province's water while also protecting the sources. The *Act* allows for water diversions for a number of uses but also requires approvals from Alberta Environment, with some exemptions. The *Act* strives to streamline administrative processes to recognize the need for both economic growth and water resource protection (Alberta Environment, 2004). This *Act* does not apply to drinking water quality, which is primarily covered by the *Environmental Protection and Enhancement Act* and the *Potable Water Regulation*. Under this legislation, water systems are required to meet facility requirements such as design, performance, and operation standards. Facilities must maintain at a minimum, the physical, chemical, radiological, and microbiological guideline levels in the *GCDWQ* and Alberta Environment's *Standards and Guidelines for Municipal waterworks, Wastewater and Storm Drainage Systems* (*Potable Water Regulation* 277/2003). Treated water turbidity must be monitored continuously while raw water turbidity must be monitored daily. Microbiological parameters such as *E. coli* and total coliforms are monitored at a frequency recommended by the *GCDWQ* or as directed by the Ministry. *GCDWQ* recommends that public water systems test for the presence of these parameters minimally four times a month, the frequency increasing with an increase in the population served (Health Canada, 2008). Physical, inorganic, and organic chemical and pesticide parameters are classified as primary and secondary categories. Primary substances are those with a MAC in the

GCDWQ, while secondary substances are those with aesthetic objectives, or those without identified guidelines in the *GCDWQ*. The frequency of monitoring for both classes of substances is twice per year for surface water supplies; once in the summer and the winter, and at two points in the system—after treatment and prior to distribution (Alberta Environment, 2006).

Source water protection aims to minimize the potential for contaminants to enter source waters. Alberta identifies watershed management planning as the first barrier in a multi-barrier approach to drinking water protection. The province has a source-to-tap program which works to address water system facility operation and certification, reporting, and adverse test notification procedures, but does not instruct how or when these watershed management plans will be implemented. Source water protection is briefly addressed through: 1) approvals and limits on municipal, industrial, and pesticide discharges; 2) public health sanitation regulations; 3) regulations for taking of water; and 4) implementation of setbacks from water bodies when undergoing potentially damaging activities and structures (Alberta Environment, n.d.).

In Alberta, water suppliers are required to follow their respective facility approval conditions, which outline the frequency of monitoring and reporting processes. The public is provided online access to these approvals. Public reporting of sampling data can be viewed on line but is restricted to data which the government views as most important—turbidity, microbiological, and disinfectant residual. However, not all water facilities are required to participate in online reporting and instead may make the information available through the regional Alberta Environment office. The issuance of DWAs is the responsibility of the Regional Health Authorities, who must notify the public and recommend appropriate procedures to follow. These advisories are not posted online and are announced via media sources (Alberta Environment, n.d.).

2.3.3.10 British Columbia

British Columbia's (BC) *Drinking Water Protection Act* and associated regulations legally establish requirements for the provision of safe drinking water in the Province. Drinking water falls under the jurisdiction of the Ministry of Healthy Living and Sport, which is divided into regional Health Authorities who employ drinking water officers, public health engineers, and medical health officers. These authorities administer and enforce the *Act*, ensuring compliance from water system operators. Highlights of the *Act*, pertaining to water testing and public reporting, include: 1) the requirement of minimum water treatment standards, monitoring, and water quality standards; 2) the analysis of microbiological samples by provincially-approved laboratories; and 3) the public notification of adverse water quality conditions (BC Ministry of Healthy Living and Sport, n.d.). The

BC regional health authorities participate in public accountability by regularly updating and posting boil water advisories clearly on their website. The Water Stewardship Division is responsible for ground and surface water protection. An important aspect of the department's new strategic plan is the development of partnerships with other agencies and stakeholders in the creation of Drinking Water Teams to identify and act on potential risks to watersheds (BC Ministry of Environment, 2008).

The majority of BC's source drinking water originates from surface supplies. Drinking water suppliers are only required to disinfect this water, and filtration is not mandated under the *Act (Drinking Water Protection Regulation, 2003)*. In the 2002 Drinking Water Review Panel final report, the reviewers found that many communities have a critical need, but lack the funding for, adequate water treatment and particularly filtration (BC Ministry of Healthy Living and Sport, 2002). Filtration plays an important role in safeguarding against microorganisms and also helps decrease the high number of DWAs, which are often due to levels of unreasonable turbidity. Under the *Drinking Water Protection Regulation*, suppliers must monitor for total coliform and *E. coli* four times per month, depending on the size of the population served. There are no set requirements for chemical parameter testing. The *Regulation* states that testing requirements for chemical parameters are determined on a case-by-case basis by the drinking water officer, in consultation with the water supplier (*Drinking Water Protection Regulation, 2003*). The drinking water officers' guide suggests the consideration of the *GCDWQ* and factors such as the water source, system type, and system location, to help form the basis for the decision to monitor or treat chemical parameters (British Columbia Ministry of Healthy Living and Sport, 2007). The Vancouver Island Health Authority was contacted to get a better understanding of the process. The regional coordinator advised that there is, in fact, no provision for the frequency of testing and required chemical parameters. The Health Authority adheres to the list of parameters issued in their *Guidelines for the Approval of Water Supply Systems* (Vancouver Island Health Authority, n.d.). These parameters include a number of metals, physical, and microbiological parameters at a frequency of sampling that is discretionary depending on previous test results, parameters of concern, specificity to a particular area, and the size of the water system. An example was provided for clarification;

"a small municipal system might test two out of their eight wells annually and rotate the wells until all have been done, essentially a four-year cycle, while a large municipal system might test all four of their wells annually. Some of the Gulf Islands have issues with arsenic so that may be monitored regularly, with a more comprehensive analysis less frequently. Surface

water supplies may test for THM quarterly and those subject to cyanobacterial growth may sample for toxins" (Personal Communication, Vancouver Island Health Authority, Nov. 24, 2009).

2.3.3.11 Northwest Territories

The Department of Health and Social Services is the main government entity that regulates drinking water in the Northwest Territories (NWT) through administration of water licenses, infrastructure funding, technical support, and regulation of releases into the environment. The Territory's strategy in managing drinking water quality is based on a multiple-barrier framework which is to ensure and maintain NWT drinking water safety. In the NWT, the federal government has responsibility over water resource management; however, it is working to transfer this responsibility to the Territory. NWT currently does not have a specific source water protection strategy. Source water protection is approached through various means such as licensing the amount of water that can be taken from a source and outlining mitigation measures within the licence to prevent contamination.

Requirements under the *Water Supply System Regulations* became fully enforceable on April 1, 2010 and apply to all water systems in the NWT. Requirements include: 1) approval by the Chief Public Health Officer for all existing systems; 2) mandatory operator certification; and 3) system compliance with the legislated water quality standards, including the *GCDWQ*, the NWT drinking water sampling testing requirements, and standard operating procedures. If any of the standards are not met or there is a risk of serious illness due to drinking water, the Environmental Health Office and Chief Medical Health Officer must be notified (NWT Regional Health Office, n.d.). The drinking water sampling and testing requirements as referred in the *Act* and its regulations. Chlorine disinfection is required for all water systems; however, most water systems use both chlorination and filtration to ensure safe drinking water. Bacteriological sampling requirements for treated water are a minimum of four samples a month for piped water distribution, increasing with the size of the population; a minimum of one sample a month from each water truck is required in trucked water distribution. Turbidity requirements include continuous monitoring where practical, downstream from the treatment process; where continuous monitoring is not feasible, one grab sample must be taken daily, followed by an additional sample every four hours of plant operation. THM must be sampled a minimum of four times per year. Twenty-eight chemical and physical parameters are listed in the standards and are required for sampling once a year (NWT Health & Social Services, 2007).

The issuance of a DWA is the responsibility of the Chief Public Health Officer, who notifies the public when it is deemed necessary (*Public Health Act, S.N.W.T. 2007*). The Department of Municipal and Community Affairs maintains a drinking water quality database on its website which allows users to select a community and see the most recent chemical and bacteriological test results, sampling locations, and any current or historical boil water advisories. A separate database lists all community water systems, including information on the type of treatment used and the community's water source. Information is also provided regarding which parameters water operators must test and the frequency of testing. While water suppliers are not legally required to report to the public, a user-friendly format of information-sharing has been made available (NWT Municipal and Community Affairs, n.d.).

2.3.3.12 Yukon Territory

The *Drinking Water Regulation* is included under the Yukon Territory's *Public Health and Safety Act* and is administered by the Department of Health and Social Services. The water system owner must submit an annual report that summarizes inspections, test results, any corrective actions taken, a description of system modifications, and an update of operator certification and training. The *Regulation* dictates that in addition to disinfection, filtration is also mandatory within five years of the regulation being passed. Boil water orders are issued by the health officer or the system owner by methods deemed appropriate by the officer. The water supplier is responsible for making all assessments, annual reports, and test results available to the public, but to obtain them, the onus is on the public to visit the plant during normal business hours (*Drinking Water Regulation, 2007*).

Large public drinking water systems are defined as systems which have 15 or more service connections to a piped distribution system or five or more delivery sites on a trucked distribution system. Facilities that service over 3000 users are required to sample *E. coli* and total coliforms once a week, both from a raw water source and at a point where treated water enters the distribution system. Two samples from the piped distribution system and another 12 representative samples throughout the distribution system per month are also required. For systems serving 501 to 3000 users, samples are also taken once a week from a raw and treated source and a total of six additional samples are taken from representative points in the distribution system and piped distribution system. Water systems serving less than 500 people are required to sample bacteriological parameters twice a month from a raw and treated source as well as a total of four samples from representative points in the distribution system. Turbidity is to be monitored continuously for water systems serving over 3000 users, and twice a day for all other systems. For

all water systems, THM are to be tested four times a year. Chemical and physical parameters are required for testing once a year or as required by a health officer; chemical parameters include total dissolved anions, nutrients and total metals (*Drinking Water Regulation*, 2007).

The Yukon does not currently have a source water protection regime. The protection of source water is implied through water licensing and permits and the control of contaminants entering the environment. The *Yukon Waters Act* and *Waters Regulation* is administered by Environment Yukon, which guides the deposit of waste and the maintenance of water body quality and water use through enforcement and compliance of water licences (Environment Yukon, 2010). Municipally, the city of Whitehorse has a watershed management plan that strives to maintain the city's drinking water supply by abiding by appropriate guidelines, by encouraging the recognition of the riparian zone of water quality protection, by protecting groundwater in recharge areas, and by re-evaluating storm water management in community planning (City of Whitehorse, n.d.).

2.3.3.13 Nunavut

The Health and Social Service's Office of the Chief Medical Officer of Health guides the regions of Nunavut in the monitoring of drinking water supplies. This is administered through the *Public Health Act* and *Consolidation of Public Water Supply Regulations*. Under the *Nunavut Waters and Nunavut Surface Rights Tribunal Act*, the Nunavut Water Board had the authority to issue, renew, amend, and cancel a water licence but does not have compliance and enforcement powers; this falls under the jurisdiction of INAC. The Nunavut Water Board has responsibilities over the use, management, and regulation of inland water uses. Its objective is to provide for the utilization and conservation of waters, while providing optimal benefits for Nunavut residents, but also recognizing First Nations land claim agreements (Nunavut Water Board, n.d.). The federal government has responsibility for the management of water resources in the NWT and Nunavut. Water use and disposal of substances in or near water is regulated by the federal government under the *Department of Indian Affairs and Northern Development Act* of 1985, and must be licensed or authorized under appropriate federal legislations (INAC, 2008d).

Sampling frequencies for contaminant parameters are determined by the Chief Medical Health Officer but the *Regulation* indicates suggested sampling protocols. Drinking water must be disinfected through chlorination or receive other appropriate bactericidal treatment. Bacteriological characteristics of drinking water are monitored minimally once a month for suppliers serving less than 500 people, and sampling is increased as the population served increases. Physical characteristics should be monitored daily and should not contain offensive taste, sight, or smell. The frequency of sampling for chemical characteristics is once every two years and

substances are listed which should not be present under normal circumstances in the water supply, above the allowable concentrations. These substances mainly include metals. Radioactive substances are mentioned in the legislation but the frequency of sampling is strictly at the determination of the Chief Medical Health Officer, after the presence of significant amounts is determined. Public reporting is not covered in the legislation and is not identified on the government website (*Consolidation of Public Water Supply Regulations* R.R.N.W.T. 1990).

Source water protection planning for Nunavut is not reported. However, the legislation does indicate that nothing may be done within the watershed to adversely affect the raw water quality supply for public water systems, unless given approval by the Chief Medical Health Officer (*Consolidation of Public Water Supply Regulations* R.R.N.W.T. 1990).

Table 4 highlights a key point from each jurisdiction that distinguishes it from other provinces and territories.

Table 4: Key Points Identified in Provincial and Territorial Drinking Water Frameworks

Province	Key Point Identified in Drinking Water Framework
Newfoundland and Labrador	No sampling parameters indicated in legislation, instead included in a set of guidelines
Prince Edward Island	Entire population dependent on groundwater as drinking water source
Nova Scotia	GCDWQ health related parameters adopted in legislation, although government also specifies minimum standards to be met by all systems
New Brunswick	Sampling parameters and frequency not specified in legislation but are set out in sampling plans on a case-by-case basis
Quebec	First province to develop its own legally-binding drinking water standards, some of which exceed federal guidelines
Ontario	Enacted the <i>Clean Water Act</i> , aimed to focus on source water protection and the formation of stakeholder committees
Manitoba	The first and only province which has a ministry solely devoted to water governance
Saskatchewan	Recently adopted stricter testing requirements for turbidity, protozoa, viruses, and chemical parameters
Alberta	First province to adopt a strong regulatory framework by making the GCDWQ legally binding in its 1970 regulation
British Columbia	No set requirements for chemical parameter testing, determined on a case-by-case basis. Only microbiological parameters included in regulations
Northwest Territories	Increased parameter sampling and operational requirements were recently initiated through regulations
Yukon Territory	New regulation recently passed that strengthens operating requirements and dictates mandatory filtration
Nunavut	Sampling of chemical parameters is only required every two years

2.3.4 Nationwide Contaminant Comparison

A nationwide comparison of commonly tested parameters provided an estimate of potential common contaminants to be included for monitoring by the EWBS. The similarities of nationwide tested contaminants were quite limited in relation to the number of contaminants recommended for testing in the GCDWQ. All Canadian provinces and territories were included in the comparison of inorganic, organic, and microbiological parameters and the top drinking water parameters tested

for by the majority of provinces and territories are detailed in Table 5. Many jurisdictions maintain a baseline of testing with further testing occurring at the discretion of the ministries on a case-by-case basis. As an example, data included for British Columbia only cover microbiological testing, as that is all that is specified in its legislation. A table, detailing the baseline parameter testing for each province and territory, and observed similarities of the top physical, chemical, and microbiological parameters across the nation is provided in Appendix B.

Table 5: Top 21 drinking water parameters tested by the majority of provinces and territories

	NL	NS	PEI	NB	QC	ON	MB	SK	AB	BC	YK	NWT	NU
Inorganic Parameters													
Arsenic	X	X	X	X	X	X	X	X	X		X	X	X
Fluoride	X	X	X	X	X	X	X	X	X		X	X	X
Lead	X	X	X	X	X	X	X	X	X		X	X	X
Nitrate	X	X	X	X	X	X	X	X	X		X	X	X
Barium	X	X	X	X	X	X		X	X		X	X	X
Cadmium	X	X	X	X	X	X		X	X		X	X	X
Chromium	X	X	X	X	X	X		X	X		X	X	X
Selenium	X	X	X	X	X	X		X	X		X	X	X
Uranium	X	X	X	X	X	X	X	X	X		X	X	
Organic Parameters													
Trihalomethanes	X			X	X	X	X	X	X		X	X	
Benzene			X	X	X	X	X	X	X				
Tetrachloroethylene			X	X	X	X	X	X	X				
Benzo(a)pyrene			X	X	X	X		X	X				
Carbon tetrachloride			X	X	X	X		X	X				
1,2 dichlorobenzene			X	X	X	X		X	X				
1,4 dichlorobenzene			X	X	X	X		X	X				
Dichloromethane			X	X	X	X		X	X				
Pentachlorophenol			X	X	X	X		X	X				
Trichloroethylene			X	X	X	X	X		X				
Micro Parameters													
Total coliforms	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Escherichia coli</i>	X	X	X	X	X	X	X		X	X	X	X	

Inorganic contaminant testing is similar in all provinces for arsenic, fluoride, lead, and nitrate. Testing for barium, cadmium, chromium, selenium, and uranium is done in most provinces, except Manitoba. The nationwide similarities are further reduced with organic parameters. For the most part, similarities exist between PEI, New Brunswick, Quebec, Ontario, Manitoba, Saskatchewan, and Alberta. Benzene and tetrachloroethylene are tested in all seven provinces. Benzo (a) pyrene, carbon tetrachloride, 1, 2/1, 4 dichlorobenzene, dichloromethane, and

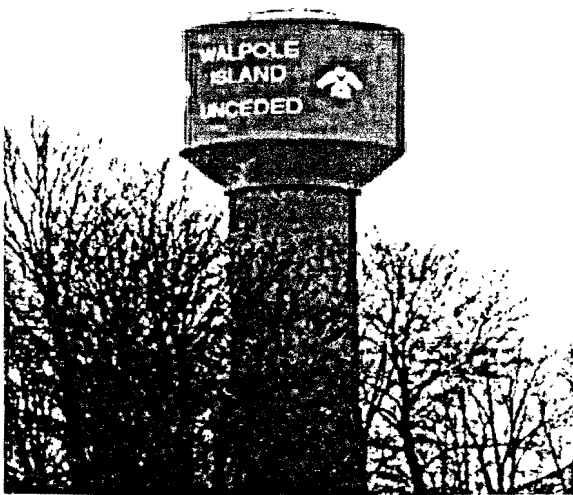
pentachlorophenol testing occurs in six of the above provinces, excluding Manitoba. Trichloroethylene testing occurs in Manitoba but not Saskatchewan. THM are tested for in all provinces, excluding Nova Scotia, PEI, and Nunavut. However, it is very likely that this is included in most cases, based on the discretionary nature of respective regulatory frameworks. Very few provinces test for pesticides, which are used in some form in all regions for aesthetic purposes on golf courses or, at the greatest impact, in agriculture.

2.4 Conclusion of Jurisdictional Analysis

Across the provinces and territories, Canada demonstrates inconsistency when it comes to drinking water standards and frameworks. Significant variations in provincial and territorial testing requirements result from a lack of federally-legislated guidelines and as a result, provinces and territories test according to local geology, industry, and available financial resources. The nationwide contaminant comparison indicates a truly inconsistent framework for the setting in which the EWBS can be applied. While it is not possible for all individual contaminants to be monitored, the EWBS has the potential to effectively detect classes of contaminants applicable in all provinces and territories. Jurisdictional differences in contaminant testing are important to consider early in the EWBS development. The identification of these differences will aid in the selection of contaminant classes, and their representative contaminants, and will enhance early understanding of the system's integration into the legal frameworks to which eventual users must adhere.

3.0 Case Study Site

A case study site was investigated for possible *in situ* use of the EWBS. The case study also aims to highlight the need for the system in areas of vulnerable water supply and to provide a site-specific contaminant of concern for bioassay research. The case study focuses on the fact that many drinking water problems exist between urban and rural areas within a province/territory, as well as between First Nation's reserves and non-reserve communities. Selection criteria include: 1) the physical location of the site, such that its water intake is affected by upstream contamination; and 2) the increased susceptibility of marginalized populations, such as First Nations and rural communities. These populations generally receive a disproportionate reduction in drinking water quality, when compared to urban and non-reserve communities, and are therefore primary candidates for EWBS technology, which would be user-friendly and of a biological rather than chemical premise.



(Sources: Sustainable Development Institute, n.d.; Visser, 2005)



3.1 Introduction

3.1.1 Walpole Island

In the southern portion of the St. Clair River, six islands are separated by a series of channels to form the Walpole Island Indian Reserve, the southernmost reserve in Canada (Figure 1). Bkejawong (Walpole Island) means “where the waters divide” in Ojibwe. Walpole Island is 740 square kilometres in size; two-thirds are dry land and one-third is comprised of marshes, sloughs, and interior lakes (Environment Canada, 1996; Vanwynsberghe, 2000). Approximately 2,300 Ojibwa, Potawatomi, and Ottawa people reside in the area and form the Three Fires Confederacy (VanWynsberghe, 2000). Walpole Island is on the boundary of Canada and the U.S., connected to the Canadian mainland by a swing bridge, and to the U.S. by ferry. The physical location of Walpole Island on the St. Clair River places it in a mix of jurisdictions. Both Canadian and U.S. federal governments govern transboundary waters; Ontario provincial and Michigan State governments have jurisdiction over industry and the pollutants they emit; the Canadian federal government and the Band Council have responsibility for infrastructure and the provision of drinking water on First Nations reserves, while Ontario has responsibility for drinking water in the province as a whole.



Figure 1: Location map of the St. Clair River watershed and the case study site, Walpole Island (NASA, 2006)

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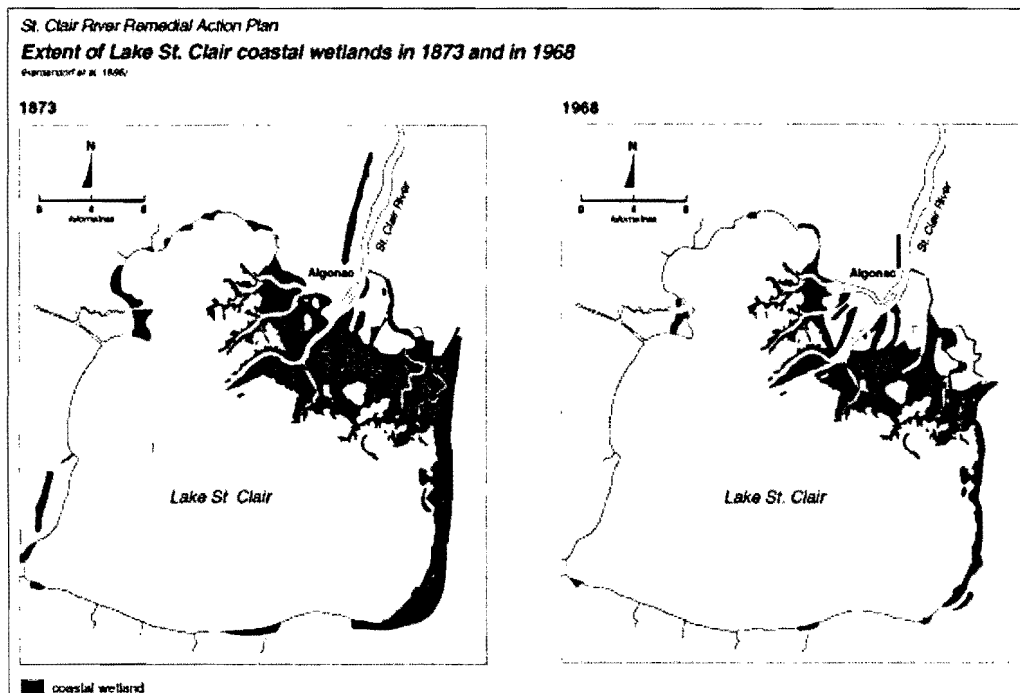


Figure 1: Location map of the St. Clair River watershed and the case study site, Walpole Island (NASA, 2006)

Walpole Island's resource-based activities are seasonal and mainly include hunting, fishing, and trapping. This seasonal variability leads to high unemployment rates during parts of the year. Agriculture is the second largest industry after tourism, with over 4,850 hectares in use and the primary crops grown are corn and soybean. Most of this land is leased to off-reserve farmers, but, as leases expire, they are being purchased by an Aboriginal-run cooperative called Tahgahoning Enterprises and this group now farms 1,950 hectares (Environment Canada, 1996). The commercial fishery on Lake St. Clair was closed in 1970 because of high mercury levels in fish, and remains closed, except for one licence which is issued to a family on Walpole Island (Environment Canada, 1996). Fish consumption advisories are still in effect, a situation that greatly affects the diets of people on the reserve, as fish is a major food source.

Walpole Island is biologically-diverse and contains the most significant tall-grass prairie and oak savannah habitat in Canada. It also contains Carolinian forests, and one of the largest wetland systems in the Great Lakes basin. Oak savannah and tall-grass prairie are two of the most threatened vegetation types in North America; in Canada, the oak savannah is only indigenous to Southern Ontario (Environment Canada, 1996). Ecosystem loss has occurred due to high suitability for agriculture, followed by residential and industrial development, and invasive species. The loss of ecosystem has also resulted in a loss of habitat for many plant and animal species. The Walpole Island delta is a key staging area for migration, spawning and nursery behaviours, and the Island's diverse habitats are home to many rare plants and animals. Walpole Island makes up only 0.002 % of Canada's landmass, yet contains 12 % of Canada's species at risk (Natural Resources Canada, 2004). More than 800 species of vascular plants, 96 of which are provincially rare, and 44 rare animal species occur on the island. This is the largest number for any single natural area in the province (Natural Resources Canada, 2004).

Substantial land use changes since the late 19th century haven altered the wetland ecosystem of the lower St. Clair River delta and Walpole Island (Figure 2). For example, between 1963 and 1978, 4.5% of the wetlands were dyked and converted to agricultural use (Environment Canada, 1996). From 1965 to 1984, the southern wetlands dwindled from 3,574 hectares to 2,510 hectares (Figure 3). Drainage for agriculture accounted for 92 percent of the losses, and marina and cottage development consumed the remaining eight percent (RAP, 1991). This caused a crucial loss of habitat for breeding, spawning, feeding, and protection. The RAP included remediation efforts for this critical habitat. Approximately 106 hectares of wetlands have been created, acquired, and rehabilitated around the Chenal Ecarte, a major tributary of the St. Clair River (RAP, 2005).



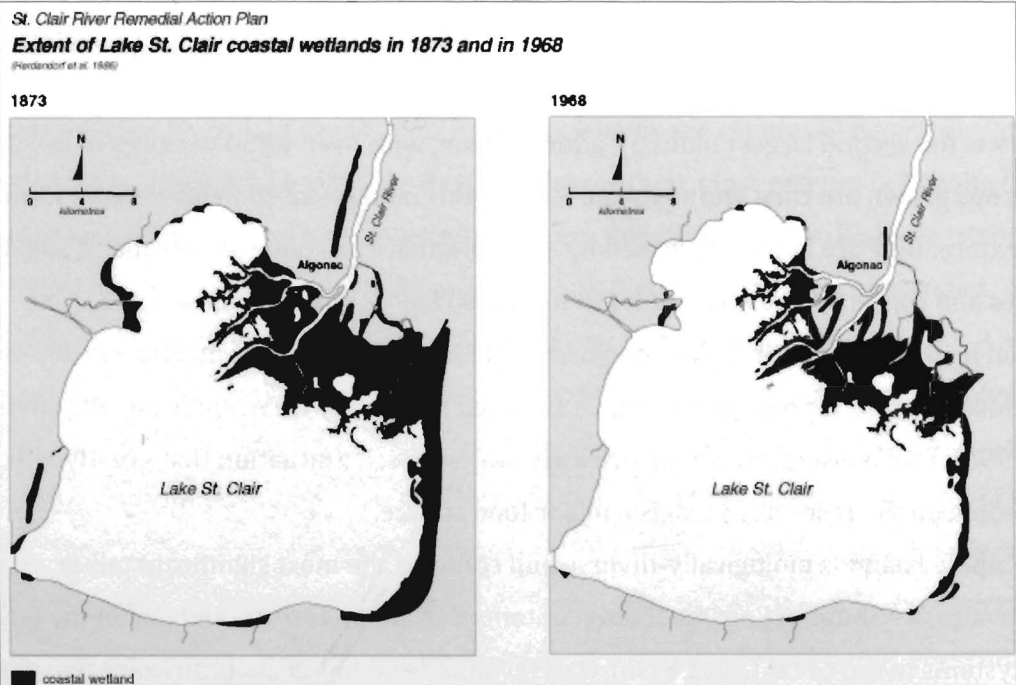


Figure 2: Maps indicating the extent of the Lake St. Clair wetlands in 1873 and 1968 (Source: RAP, 1995)

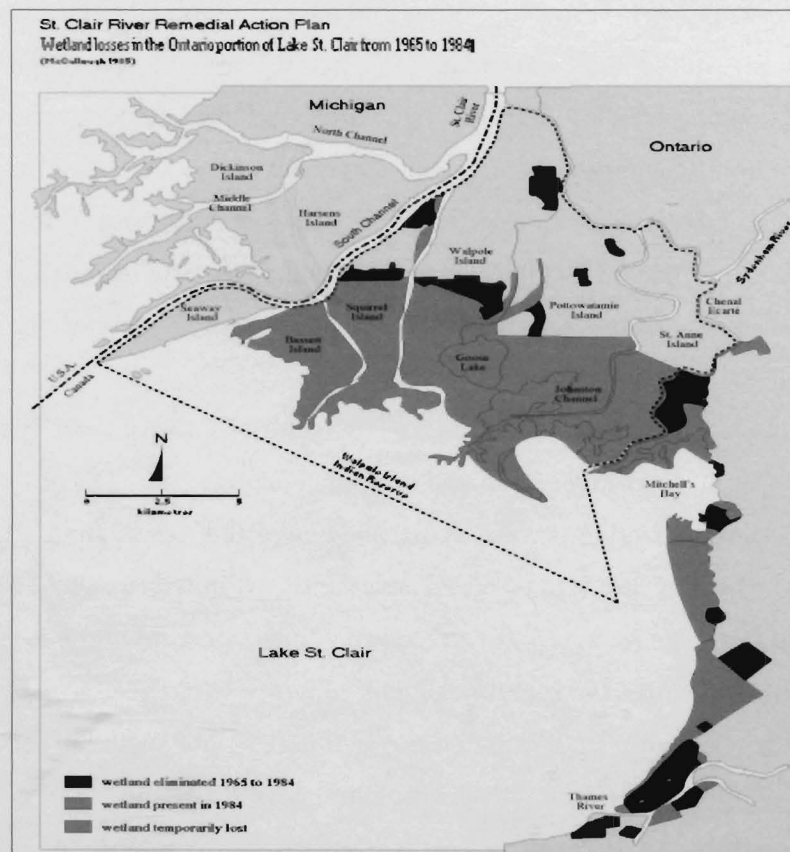


Figure 3: Map indicating the extent of wetland loss in the Lake St. Clair delta from 1968-1984 (Source: RAP, 1995)

3.1.2 St. Clair River Area of Concern

The St. Clair River flows southward from Lake Huron, running a distance of approximately 64 km, as it connects to Lake St. Clair (Figure 4). The average annual flow from 1900–1986 was reported as 5200 m³/s, with monthly mean discharges ranging from 3000 to 6700 m³/s (Szalinska *et al.*, 2007). Over 170,000 people live on or near the shores of the river which acts as a partial border between Ontario and Michigan (Remedial Action Plan, 1995).

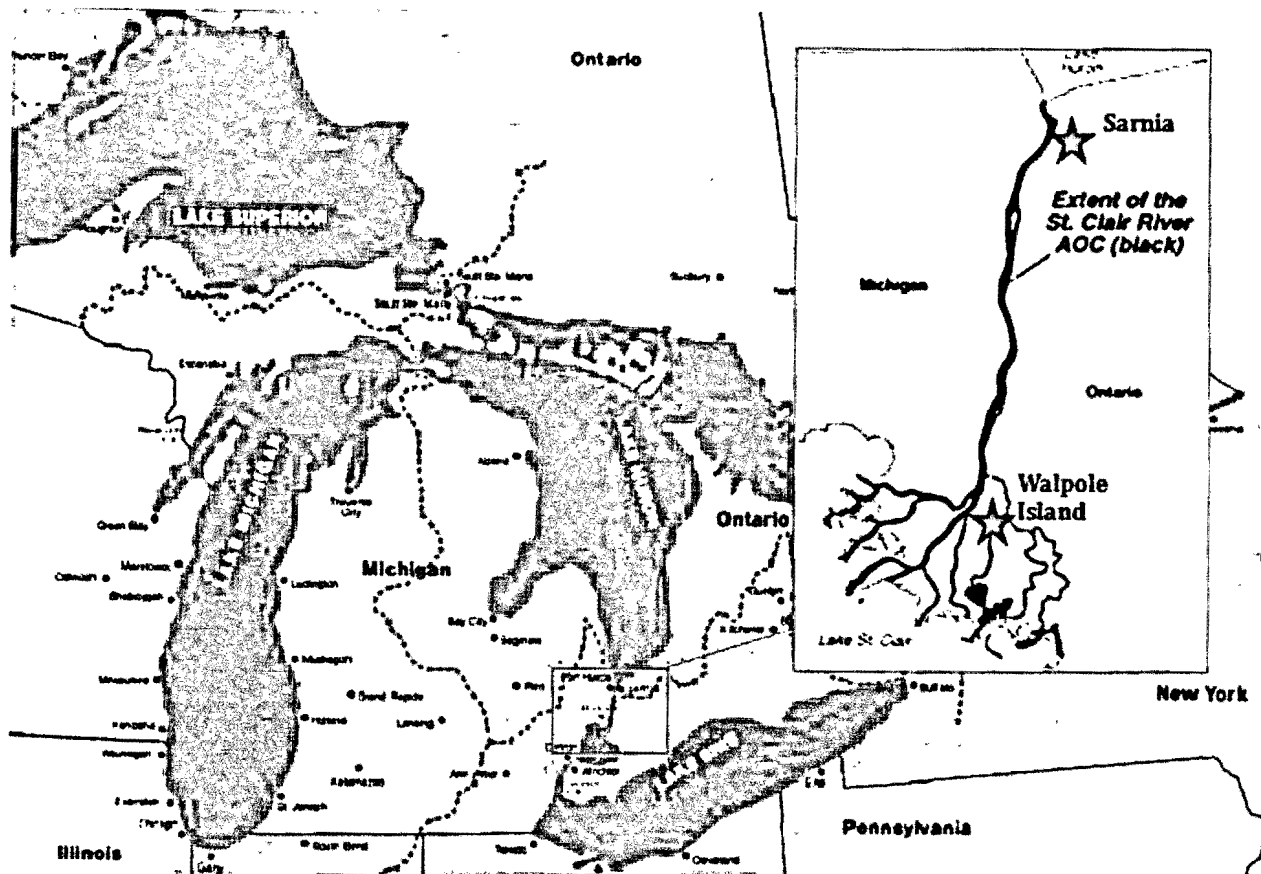


Figure 4: Location map of the St. Clair River Area of Concern within the Great Lakes (Adapted from: RAP, 1995; Michigan Sea Grant, 2009)

The primary biological zones are hardwood forest in the upland portion and wetlands in the southern delta. The area supports 91 fish species, 20 species of amphibians, 25 species of reptiles, 250 species of birds, and 60 mammal species (RAP, 1995). Unfortunately, these areas have been cleared and drained for development purposes with the predominant land-use being agriculture and intensive industrial development has occurred in and near the cities of Sarnia and Port Huron. The Canadian side of the river is dominated by industries and the American side mainly consists of residential development. The greatest environmental impacts occur as a result of extensive municipal and industrial uses of the river as a water supply and effluent receiver, with additional

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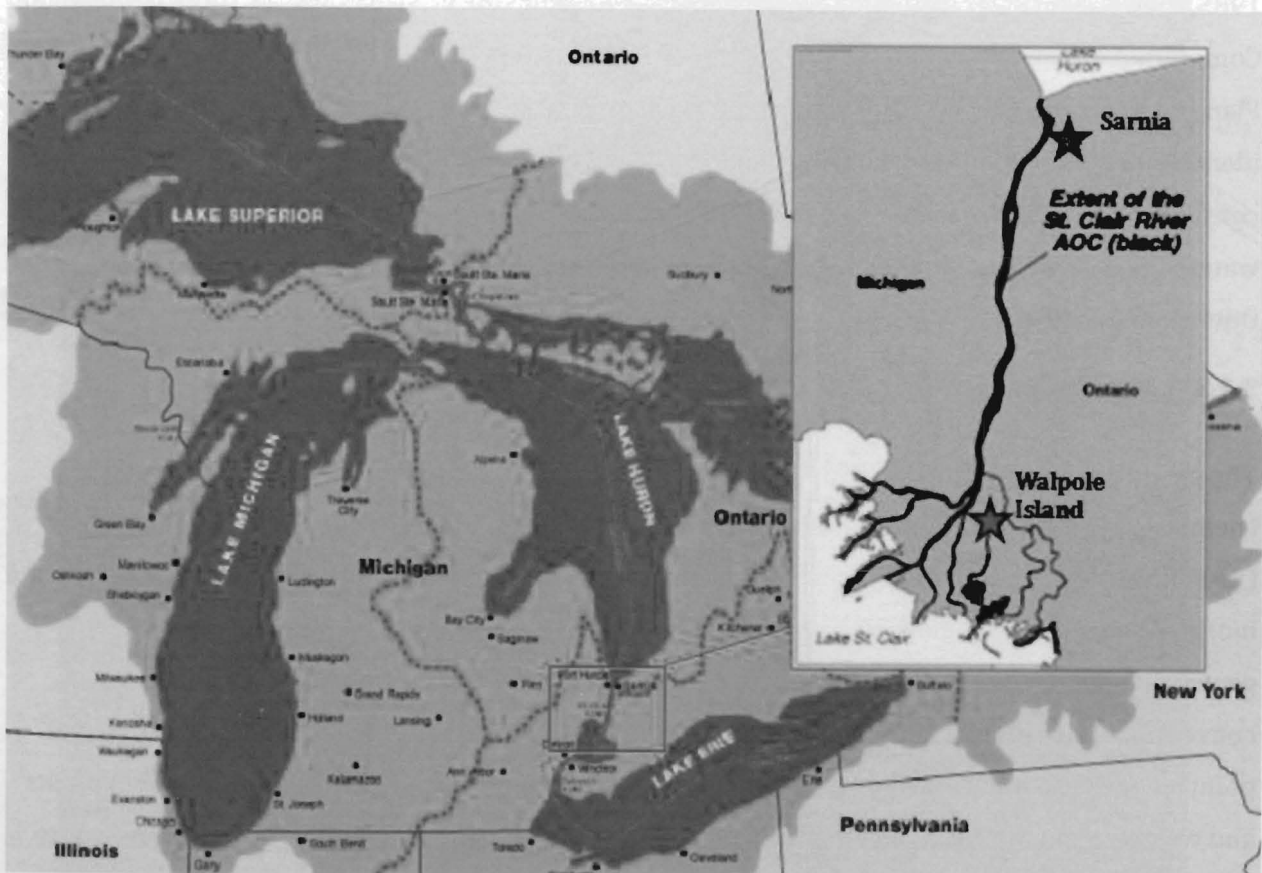


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impacts occurring from recreational boating and the shipping of commodities as part of the Great Lakes Seaway. Navigation often requires dredging which can re-suspend contaminants adsorbed to the sediments, further exposing biota (RAP, 1991). Most of the Michigan communities receive their water directly from the River, and in the province of Ontario, Walpole Island is the first community to receive its water from the St. Clair River (International Joint Commission, 2006).

Pollution sources are international in nature and are considered a shared responsibility. In 1985, the St. Clair River watershed was listed as an Area of Concern (AOC) by the International Joint Commission (Lake St. Clair Canadian Watershed Coordination Council, 2005). A Remedial Action Plan (RAP) was established through the Great Lakes Water Quality Agreement and this plan identified 14 use impairments of the river. Of particular interest is the restriction of drinking water consumption, including taste and odour impairment. The main environmental impact on the watershed and the surrounding ecosystem is “Chemical Valley”, an industrial area outside of Sarnia, Ontario (RAP, 1991).

3.1.3 “Chemical Valley”

“Chemical Valley” is a result of the industry boom to support the war effort in the 1940s. The geographic area of the St. Clair River satisfied two criteria for production of chlorinated chemicals: water supply from the River, and natural underground deposits of sodium chloride (RAP, 1991). The main industries which occur along the River are petroleum refineries, organic and inorganic chemical manufacturers, paper companies, salt producers, and thermal electric generation plants. Industrial point sources have been identified as significant contributors of conventional and metal contaminants, and the primary contributors of most organics. Municipal point sources are also contributors of contaminants with municipal water pollution control plants and wastewater stabilization lagoons (RAP, 1995). A total of 56 point sources are discharged into the river and its tributaries from both Ontario and Michigan (Figure 5). The total discharges from these point sources is approximately 11,800,000 m³/day and make up approximately 3% of the river’s average daily flow (SLEA, 2005). The RAP Stage 2 Report in 1995 identified the highest priority point sources for the St. Clair River. A Point Source Task Team developed a ranking system for contaminants and sources using a formula: *Parameter impact score = # of beneficial uses impaired x [100/ (parameter yardstick/ mercury yardstick)] x total loading*. The parameter “yardstick” value is the numerical environmental objective which is converted to a relative scale, in which mercury is assigned a value of 100. Parameter impact scores for each media (water, soil, and biota) are summed to obtain the total quality ranking for each parameter by source. The highest priority sources were identified as Cole Drain, Dow Chemical, ESSO Petroleum, Novacor Petroleum,

Polysar, Suncor, Marysville WWTP, Port Huron WWTP, and Sarnia WPCP (Appendix C) (RAP, 1995). These industrial and municipal sources mainly contribute heavy metals, organic chlorine, and volatile organic contaminants to the river.



Figure 5: Map indicating the locations of St. Clair River municipal (circles) and industrial (triangles) point sources (Adapted from: RAP, 1995; NASA, 2006; SLEA, 2009)

Contaminant data from industrial sources for the St. Clair River can be accessed from Environment Canada's National Pollutant Release Inventory (NPRI). Copper is the contaminant with the greatest concentration of annual water releases to the St. Clair River (Table 6). However, consideration must also be given to contaminant emissions to the air and to waste disposed of on

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and off-site. The 2007 reported copper releases to air totalled 0.593 tonnes, and on-site releases totalled 99 tonnes (Environment Canada, 2007).

Table 6: Top 10 contaminants released to the St. Clair River based on 2007 annual water releases from top industrial emitters in the Sarnia region. Source data: NPRI database

Ranking	Contaminant	Annual release (Kg)
1	Copper	3400
2	Zinc	1503
3	<i>tert</i> -Butyl alcohol	940
4	Methanol	345
5	Toluene	198
6	Lead	97.7
7	Cyclohexane	95
8	Xylene	83
9	Benzene	67
10	Arsenic	62

Data reporting to the NPRI is the responsibility of companies under the *Canadian Environmental Protection Act, 1999*. While reported quantities may appear low, it is important to consider unpredicted spill events which may occur at any time. Both constant effluent loadings and unforeseen contaminant spills contribute to the importance of EWBS research and application.

The NPRI reporting requirements indicate that facilities meeting certain thresholds and criteria must report their best estimate of the amount of pollutants they release into the air, water, and land, and transfer off-site each year. Annual reporting thresholds include facilities which have manufactured, processed, or used an applicable contaminant in concentrations greater than or equal to 10 tonnes, or the total number of hours worked by all employees was greater than 20,000 hours (Environment Canada, 2009). There are numerous limitations to the NPRI data. The data do not cover all potential harmful pollutants. With 23,000 substances currently in use according to Environment Canada's Domestic Substances List, only 300 pollutants are included on the 2006 NPRI list. The database does not cover the following pollutants which can still have potential negative effects: pollutants that have pesticide applications only, greenhouse gases, or contaminant releases less than 10 tonnes. Releases from mobile sources such as cars, trucks, and construction equipment are not included, nor are harmful toxins from sources such as dry-cleaners and gas stations. Reporting is not required from facilities such as schools, research facilities, forestry, fishing, agriculture, or mining; however, the processing of mined materials is included in NPRI.

Non-point sources were not a focus of the RAP for this particular AOC. Agriculture is more of a focus in the Thames River watershed; however, both are connected via tributaries which deposit into Lake St. Clair and thereby affect the lower St. Clair River delta. A significant non-point source of polychlorinated biphenyls (PCB) and mercury is from atmospheric deposition into Lake Huron. Non-point sources and Lake Huron contribute at least ten percent of the total loadings to the River for copper, iron, lead, mercury, nickel, cadmium, cobalt, polycyclic aromatic hydrocarbons (PAH), and PCB (RAP, 1995). However, the Lake is not part of the St. Clair River AOC and is situated below the drinking water intake for Walpole Island. The six non-point sources focused on were urban and rural storm runoff, waste sites without leachate and runoff collection, malfunctioning septic systems, domestic sources not connected to municipal treatment facilities, and generation of household hazardous waste (RAP, 2005). Non-point source control projects are considered alongside habitat restoration programs and include: 1) the conversion of leaking septic systems to bio-filter systems; 2) proper manure storage; 3) the fencing of streams to prohibit livestock use; 4) conservation tillage; 5) soil testing; 6) benthic monitoring; and 7) the conversion of road and drain sides to natural corridors using native species. Cooperation with municipalities on factors such as enforcement of regulations regarding lawn fertilizers and domestic pesticides, advanced landfill design criteria, as well as strict enforcement under Ontario's *Nutrient Management Act* are central to the success of these projects (RAP, 2005).

3.1.4 Spills to the St. Clair River

Over the past two decades, a number of notable spills have occurred, some of which resulted in the closure of downstream water intakes or legal action (Table 7). A major contributor of pollution and specific spills is Dow Chemical. In 1985, the chemical manufacturer was responsible for a large spill of tetrachloroethylene (perchloroethylene). Approximately 30,000 L of the toxic dry cleaning solvent was spilled, 11,000 L of which reached the St. Clair River. Divers from the University of Windsor's Great Lakes Institute also discovered that the bottom sediment was polluted with mercury, chlorine-based compounds, and other chemicals, all of which was dubbed the "blob." Clean-up began immediately, and thousands of cubic yards of sand and gravel were brought to the surface, tested, treated, and then buried in Dow's landfill (RAP, 2005). In 1989, ICI Nitrogen experienced a spill of Selexol, a solvent that dissolves acid gases from the feed-gas produced by gasification of coal, coke, and hydrocarbon oils (RAP, 1991). This spill resulted in the closure of downstream water treatment plant (WTP) intakes. Levels were found entering the treatment plants at concentrations far above the guideline of 60µg/L. Two other spills occurred in 1990 and 1991 at Dow Chemical. 3,600 kg of ethylbenzene from the 1990 spill resulted in the

closure of WTP intakes at Walpole Island and Wallaceburg. Maximum concentrations recorded at the Walpole Island and Wallaceburg water treatment plants were 40.2 mg/L and 44.4 mg/L respectively. The Canadian Drinking Water Quality Guideline at the time was 2.4 mg/L. The second spill of ethylbenzene also resulted in the closure of the Walpole Island water treatment plant (RAP, 1991).

Table 7: Timeline of critical spills to the St. Clair River indicating the company responsible and the contaminant spilled

Year	Company Responsible & Contaminant Spilled
1985	Dow Chemical: tetrachloroethylene "blob"
1989	ICI Nitrogen: selexol
1990 & 1991	Dow Chemical: ethylbenzene
2000 & 2001	Nova Chemical: benzene
2003	Royal Polymers: vinyl chloride
2004	Imperial Oil: methyl ethyl ketone, methyl iso-butyl ketone

Five large spills occurred between 2000 and 2004. In 2000, approximately 4,600 to 4,700 barrels of product containing 30 to 35% benzene was released from Nova Chemicals. The spill entered the storm water pond which discharges to a creek, subsequently leading to the St. Clair River. Again in 2001, Nova Chemicals experienced a spill of about 300 to 400 barrels of product. The spill occurred in an open field from a broken pipe but no chemical escaped to the River (RAP, 2005). None of these incidents resulted in WTP intake closures.

In 2003, during a massive power outage, the OMOE responded to two vinyl chloride spills into the St. Clair River from Royal Polymers. Precautionary measures were taken and down-river water treatment plants and local health agencies were notified; however, vinyl chloride was not detected in the treated drinking water supplies. Royal Polymers was charged under the *Ontario Water Resources Act* for the discharge of a material that may impair the quality of the water and received a fine. They were also charged for failing to immediately notify the OMOE of the discharge and for operating a sewage works not in accordance with the Certificate of Approval (RAP, 2005). Also at this time, sewage treatment plants reported overflows of untreated or partially-treated sewage. There were some reports of people downstream feeling ill but this was never directly linked to the sewage or chemical spills (IJC, 2006). In 2004, the OMOE responded to a spill of methyl ethyl ketone and methyl iso-butyl ketone into the St. Clair River from Imperial Oil Ltd. Downstream water users were notified and the water intakes were subsequently shut down at Walpole Island

and Wallaceburg. Once again, charges were laid, but this time under the *Fisheries Act* for permitting the deposit of a deleterious substance into a water body frequented by fish (RAP, 2005).

The number of contaminant spills into the St. Clair River has declined since the mid-1990s. However, the high profile spills of 2003 and 2004, along with a number of other spills, have contributed to public alarm and unrest regarding the safety of the River's water (IJC, 2006). In 2006, the International Joint Commission produced a report on spills in the Great Lakes basin, which focussed on the St. Clair-Detroit River corridor. The occurrence of spills and the effectiveness of intergovernmental plans were assessed. However, the report did not cover the impact of spills or address permitted discharges by industries and municipal facilities, despite these being large contributors of pollutants into the connecting channels. The main findings of the review centered on the inconsistency in data management between the U.S. and Canada, as well as monitoring and spill prevention procedures (IJC, 2006). There was a lack of shared data despite the fact that discharges potentially affect all citizens on either side of the River. In general, the Commission found a need for enhanced monitoring programs, accurate spill detection, and simplified notification procedures—all which would lead to increased protection of human health. All recommendations put forth by the Commission were intended for shared implementation between both countries, in an effort to provide consistency and safety for the respective citizens (IJC, 2006).

Data maintained by Canada and the U.S. are not directly comparable as a result of differing government mandates, approaches, and distinction of what defines a spill. Spill data for more recent years were found to be incomplete and data were not presented consistently, with varying formats from year to year (IJC, 2006). Canadian and Ontario spill data are maintained by Environment Canada and are difficult to access publicly. Canadian spill data are not published or posted online, and the last summary reports provided by both Ontario and Environment Canada were published in 1995 (IJC, 2006). In Ontario and Michigan, discharges are regulated under varying systems of certificate approval. Permitted discharges are not considered in spill data, while any exceedances of limits are supposed to be included. However, in Canada, it is unclear whether all exceedances are reflected in the databases, and overflows from sewage treatment plants and sewers are often not considered, despite containing a complex mix of substances. A further discrepancy in Canadian spill data is the exclusion of vessel-related spills from the database, which is instead reported to the Canadian Coast Guard's pollution prevention officer. Any information on significant vessel spills is passed onto the province (IJC, 2006). A clear need for a shared binational database between all levels of responsible governments is needed. Such a database would allow for precise determination of spill trends, some of which have already been observed through current

data. Within the St. Clair-Detroit River corridor, more Canadian spills occur in the St. Clair River, while there are more American spills in the Detroit River. The majority of American spill types are of oil and hydrocarbons from the petrochemical industry, while Canadian spills are mainly of a chemical nature from the chemical manufacturing industry (IJC, 2006). While spill numbers have declined, their numbers and locations are related to areas of high population and higher industrialization, and cannot be guaranteed to remain low.

The spill notification procedures currently in place for the St. Clair River are reported as functioning well, but entail numerous steps that can complicate communication (IJC, 2006). Initially following a spill, details on the nature of the spill are only partially shared between the governments, contributing to uncertainty and an inability to make informed decisions surrounding community protection measures, such as the closure of water intakes. It is critical to efficiently communicate, not only binationally but also to plant operators and the affected communities. Integrated communication, for all interested parties, needs improvement, and ideally a shared notification protocol is necessary (IJC, 2006).

3.1.5 Spill Monitoring in the St. Clair River

The most critical step identified in spill prevention and the overall protection of drinking water supplies is the use of effective monitoring. Monitoring must immediately detect a spill, and once this occurs, modelling and continuous monitoring at water intakes is necessary to determine the speed and trajectory of the plume. In-stream, real-time monitoring is recommended to accomplish the early detection of contaminant spills, or to verify an already reported spill, and can accurately indicate the travel projection of the contaminant. A big challenge, when designing a monitoring system, lies in deciding what contaminant parameters should be monitored, based on necessity, system capabilities, and costs. The *IJC Report on Spills* details biomonitoring in its recommendations for increased protection of water sources (IJC, 2006). Biomonitoring technology, as a complement to chemical monitoring, has multiple benefits. Beneficial uses include monitoring of source water quality, enhancing the detection and response to, as well as protection from, deliberate spills or terrorist attack. The Commission suggests the implementation of real-time monitoring and biomonitoring that can monitor for a broad suite of biological and chemical contaminants, be incorporated with back-up power, and be integrated with advanced river flow models (IJC, 2006). The EWBS, currently in development, has similar monitoring roles, and would be an important addition to the limited monitoring presently in place in the St. Clair River.

The only real-time monitor in operation on the St. Clair River is the Sarnia Lambton Environmental Association's (SLEA) monitoring station, located near the town of Courtright,

approximately halfway downstream from the petrochemical industries and upstream from four municipal drinking water intakes (IJC, 2006). The station continually monitors for 20 organic compounds associated with the oil refining and petrochemical production industries that make up the SLEA (Figure 6). Contaminant plumes, passing the monitor, reach the drinking water intakes several hours later, with real-time analysis of the plumes allowing decisions to be made regarding the closure of downstream intakes, or the storage of water in anticipation of a closure. However, because only a limited number of specific parameters are monitored, neither of the spills of vinyl chloride or methyl ethyl ketone in 2003 and 2004 was detected by the monitoring station, despite both companies being members of the SLEA (IJC, 2006).

benzene	hexane
carbon tetrachloride	methyl-tertiary-butyl-ether
chloroform	perchloroethylene
cyclohexane	styrene
1,3-dichlorobenzene	tetraethyl lead
1,2-dichloroethane	toluene
1,2-dichloropropane	trichloroethylene
1,2-diethylbenzene	meta xylene
1,3-diethylbenzene	ortho xylene
ethylbenzene	para xylene

Figure 6: Twenty target volatile organic compounds monitored by the SLEA (Source: IJC, 2006)

The analysis system consists of a purge-and-trap sample concentrator, an automatic stream sampler, and a gas chromatograph with two detectors. The detectors are a flame ionization detector and an electron capture detector, coupled with a computing integrator (Grayman *et al.*, 2001). The purge-and-trap concentrator is programmed to have the automatic stream sampler take a five millimetre sample every hour. For backup purposes, the automatic sampling device archives the three most recent hours of samples. The River sample, along with an internal standard, is transferred to the concentrator where VOCs are purged with helium and adsorbed onto a carbopack adsorbent trap. The compounds are thermally desorbed and, following separation, are detected concurrently by flame ionization and electron capture. Output voltage signals are sent to the computing integrator that identifies the target compounds based on the time it takes for them to emerge from the chromatograph column (Grayman *et al.*, 2001). On-site data collection is protected by an uninterruptible power supply, capable of supplying 75 minutes of backup power. However, sampling is halted during extensive power failures. Data are transferred by phone lines once per hour and logged into a database which is only accessible by password to SLEA members

and contracted technology company, ORTECH. Calibration and blank analyses are carried out weekly, as well as the hourly internal standard in which bromodichloromethane is injected into each sample, with software-based control limits. This identifies fluctuation in operating conditions and alerts technologists via pager. A one ppb threshold limit was established as an arbitrary value, well below the provincial guidelines and above the minimum detection limits (MDLs) for the monitored compounds. This value can also be applied year to year regardless of changes to method detection limits. As an example, 1997 results were indicated as typical. 8,642 samples were analyzed, leading to 172,840 reported results with approximately one percent of those being greater than the MDLs. Contaminants which most frequently exceeded the MDLs were toluene, cyclohexane, and benzene (Grayman *et al.*, 2001).

There is an inherent inability for industry to definitively predict what contaminants will be spilled and at what quantity. The contaminants associated with spills to the St. Clair River and the current monitoring procedures in place are varied. This variation has implications for the selection of contaminant parameters to be monitored by the proposed EWBS. Despite the current presence of VOC monitoring, the inclusion of an EWBS provides an opportunity for supplementary monitoring of VOCs by the EWBS, in a location further downstream from the SLEA monitoring site. Additionally, an EWBS has the capability to respond to mixtures of contaminants that perhaps may occur in association with VOCs.

3.1.6 Operational Failures

In February 2004, the Ontario Ministry of Environment's Sector Compliance Branch conducted an inspectional sweep of industrial facilities in the Sarnia area (OMOE, 2005). A number of facilities in Sarnia's industrial sector had allowed potentially harmful chemicals to spill into the St. Clair River, two of which resulted in the precautionary closures of downstream drinking water intakes. The downstream communities of Walpole Island First Nation, Wallaceburg, and Stag Island were frustrated and concerned regarding the safety of their drinking water supply. Environmental officers conducted an 11-month inspection of 35 petrochemical and related facilities to ensure that all were brought into compliance with environmental legislation. Results of the sweep indicated zero non-compliance issues leading to immediate impacts on human health or the environment, but a number of common troubling deficiencies were identified. Of the 35 facilities inspected, 34 were found to be in non-compliance with one or more legislative and regulatory requirements (Appendix D). A summary of the main issues included: 1) no spill contingency and/or spill prevention plans; 2) waste-water collection and treatment works not approved, or altered contrary to approval; 3) equipment maintenance, calibration, and record-keeping inadequate or lacking; 4) improper

chemical handling, storage, and identification; 5) waste manifesting and generator registration practices not in compliance with regulations; 6) air emission control equipment not approved, or altered contrary to Certificate of Approval; 7) lack of internal standards for staff training of equipment operation and maintenance; 8) treated effluent streams being monitored separately, but not after being combined before final discharge to receiver as a single stream; 9) no temperature monitors on stack flares; and 10) no monitoring of internal process waste during operations or monitoring of process cooling water at the source intake (OMOE, 2005).

The above operational failures are potential causative factors for future chemical accidents. Perrow (2007) cites three categories of failures associated with chemical industry disasters and dangerous operational failures. Organizational failures occur when workers or management fail to properly do their job, or the job makes demands beyond available resources. Executive failures occur at the top echelon of business as executives make deliberate, knowing choices that have potential to harm the organization and/or its customers and the environment. Regulatory failures stem from a lack of regulation and standards, which if in place, have great potential for avoiding disasters or reducing their consequences. The chemical industry, as with many industry sectors, has a preponderance of groups that do not try hard to prevent the chances of occasional disaster. For these companies, prevention costs money in the short-term and short-term advantages often pay off in competitive capitalism, even if not in the long run (Perrow, 2007). Perrow concludes that organizations will always be imperfect and even the best are unable to provide complete security or avoid the inevitable mistakes that lead to accidents.

3.1.7 Fate of Contaminants

The OMOE has a contaminant transport flow model which predicts the time of travel for a contaminant plume to reach downstream intakes along the St. Clair River. The model assumes that the contaminant travels as a single mass, and cannot account for water characteristics (IJC, 2006). This was the case with the 2004 methyl ethyl ketone spill, and the model could not predict the flows due to ice cover on the river. The U.S. Geological Service has recognized this shortfall, and recently developed a hydrodynamic flow model that accounts for water dynamics such as wind direction and ice cover (IJC, 2006).

The hydraulic action of the St. Clair River is important in understanding the fate of contaminants within it. The River has two deep navigational channels separated by a more shallow section. These formations affect the water's flow characteristics and affect how substances are moved, re-suspended, and deposited in the River (IJC, 2006). The flow and discharge rate of the St. Clair River sufficiently transports sediments in traction. Sedimentation occurs in a few sites along

the River which then broadens out in the southern reach to form one of the largest freshwater deltas in the world, as a result of sediment deposition (Szalinska *et al.*, 2007).

The distribution of heavy metals in aquatic environments is often determined by both anthropogenic inputs and gradual sorting and settling of particles. Szalinska *et al.* (2007) studied the spatial patterns of sediment contamination in the Huron-Erie Corridor to assess the role of anthropogenic versus natural processes in regulating metal concentration and distribution. The study showed that anthropogenic factors were the primary regulating force of metal distribution and mobilization within the Corridor, with the spatial pattern of metal distribution in the St. Clair and Detroit Rivers reflecting local industrial sources. The average concentration of mercury in the St. Clair River was found to be 10-fold higher than the Lake Huron values, and it was concluded that anthropogenic sources are dominant in the river. The sediment transport rate in the River is high and because elevated concentrations of mercury were still found in the sediments, it was determined that current sources of contamination continue to be an issue. Elevated concentrations of other trace metals were also identified for cadmium, copper and nickel—although in lower concentrations. Furthermore, a lack of correlation between concentrations of cadmium, copper, and nickel with aluminum indicate anthropogenic sources of contamination. Aluminum was selected as the normalizing element to estimate the anthropogenic input of each metal, as it represents the main group of minerals found in fine sediment and has negligible anthropogenic input (Szalinska *et al.*, 2006).

3.1.8 St. Clair River Contaminants of Concern

Information regarding current contaminants of concern for the St. Clair River has not been updated by the RAP team for some time. Data regarding water quality are therefore retrieved through sediment and water column studies from separate U.S. and Canadian research groups.

Environment Canada has been collecting data on St. Clair River sediment and water quality since 1986. The Temporal Trend Data for the St. Clair River (Head and Mouth Survey) monitor two sites, at the head of the river in Port Edward, and at the mouth in Port Lambton (Figure 7).

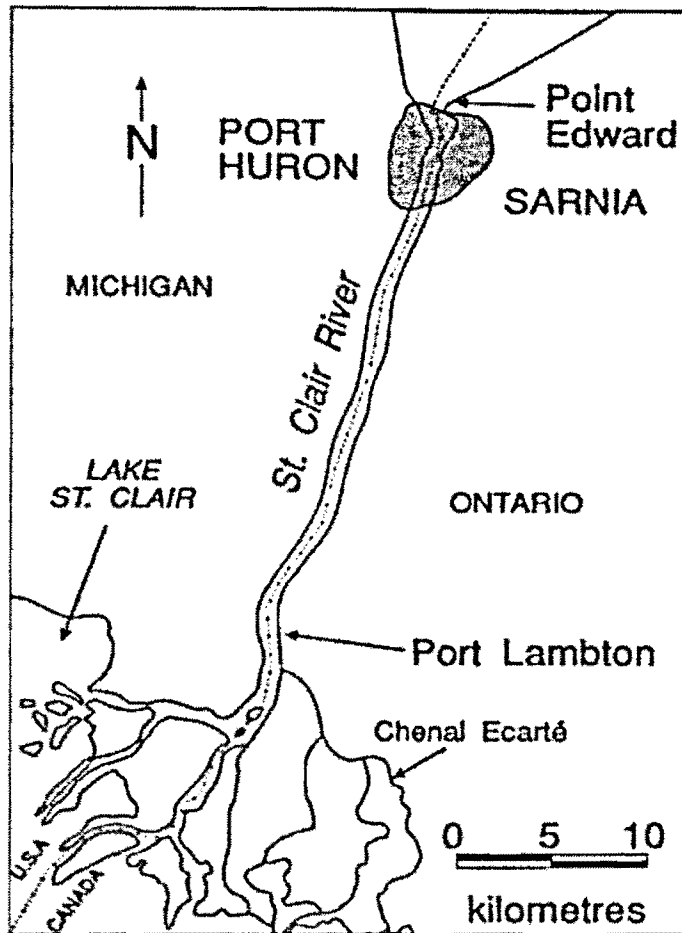


Figure 7: Location of head and mouth survey monitoring sites on the St. Clair River: Point Edward and Port Lambton. (Source: Chan, 1993)

Samples are collected up to 20 times per year and analyzed in the laboratory. Water samples are analyzed for nutrients, phosphorus and nitrogen, major ions, metals, and persistent organic contaminants. Suspended sediments are only analyzed for organic contaminants including organochlorine pesticides, chlorobenzenes, total polychlorinated biphenyls, polynuclear aromatic hydrocarbons, hexachlorobenzene (HCB), hexachlorobutadiene, and octachlorostyrene (Chan, 1993; RAP, 2005). Temporal trend data were compiled from 1986 until 2000, at which point the analytical methodology of the study changed (RAP, 2005). An overview of results indicates a number of important trends (Table 8).

Table 8: Overview of selected temporal trend data for the St. Clair River Head and Mouth Survey

Contaminant	Data Overview
Copper	Concentrations showed greater variability at Point Edward, occasionally exceeding 5 µg/L yardstick at Port Lambton
Cadmium	Concentrations at Port Lambton exceeded the detection limit occasionally but remained above the 0.5 µg/L yardstick
Hexachlorobenzene	Concentrations higher at Port Lambton than Point Edward, but with decrease over time
Octachlorostyrene	Concentrations only detected at Port Lambton, showing a decrease over time but above detection limit

Copper concentrations show greater variability at Point Edward than at Port Lambton, with concentrations at Port Lambton occasionally exceeding the 5 µg/L “yardstick”, or numerical environmental objectives. Only five values for cadmium were above the detection limit at the downstream station in the early 1990s; however, concentrations were below the 0.5 µg/L yardstick value. Lead concentrations in the St. Clair River water showed little difference between sampling stations but concentrations frequently have been above the 2.9 µg/L yardstick value. Dissolved phase HCB concentrations tended to be higher at Port Lambton relative to Point Edward, indicating input sources along the River. Concentrations of HCB overall have decreased with time, with larger decreases observed at Port Lambton. The most recent sampling results indicated that concentrations were near the 0.04 ng/L method detection limit. Octachlorostyrene concentrations were presented from suspended sediment data and were only detected at Port Lambton, indicating continued inputs. Concentrations have decreased over time but remain above the 2.7 ng/g detection limit (RAP, 2005).

As part of Michigan’s Water Chemistry Monitoring Project, Great Lakes’ Connecting Channels are chosen for monitoring (RAP, 2005). Two water quality stations monitor the headwaters and mouth waters of the St. Clair River monthly each year during the open-water season. The parameters included in the study include phosphorus (total phosphorus and orthophosphorus), nitrogen (total Kjeldahl nitrogen, nitrate, and nitrite), total chloride, total suspended solids, total dissolved solids, water temperature, conductivity, dissolved oxygen, pH, turbidity, alkalinity, total organic carbon, sulphate, hardness, calcium, magnesium, potassium and sodium. The metals data include cadmium, copper, chromium, lead, mercury, nickel, and zinc. Chlorinated organic compounds are not included in this study. Results showed that total phosphorus concentrations declined from the 1980s. Total phosphorus, orthophosphate, ammonia, and nitrite concentrations were higher at the downstream station, with seasonal fluctuations apparent in most of the nutrient parameters. A definite increase was observed for most metal

concentrations analyzed in the latter part of 1999, followed by a general decrease in 2000, and then variable levels between 2001 and 2003. The elevated metals concentrations measured throughout the study appeared to be related to elevated concentrations of suspended solids. Several of the metals, including chromium, copper, lead, nickel, and zinc, showed a statistically significant increase in concentration downstream compared to the concentrations measured upstream, an indication of upstream input of contaminants (RAP, 2005). The 2004 upstream concentrations of copper ranged from 0.348-0.586 µg/L, while the downstream range was 0.517-0.783 µg/L (Great Lakes Environmental Center, 2005).

Data collected from previous St. Clair River research, reflect the low presence of contaminants during periodic sampling. However, this can change suddenly with pollution pulses resulting from significant upstream sediment contamination, coupled with ice cover changes, large vessel navigation, and spills.

The Ontario Ministry of Natural Resources and the OMOE *Guide to Eating Ontario Sport Fish* (2009-2010) publishes advisories on the consumption of several fish species in the upper, middle, and lower St. Clair River (Ontario Ministry of Natural Resources, 2009). This is a result of elevated concentrations of mercury, PCBs, dioxins and furans, chlorinated benzenes, and pesticides. Species include walleye, northern pike, rock bass, carp, white sucker, and red horse sucker throughout the River as well as lake trout, chinook, freshwater drum, yellow perch, and gizzard shad in some locations. Studies show great variability in the mercury levels found in St. Clair River walleye. There was a reduction in tissue concentrations of Upper River fish from 1985 to 1999, with a slight increase found in 2003. There was no visible trend for walleye from the middle and lower portion of the river, and temporal data suggest that overall mercury concentrations in walleye have not decreased significantly (RAP, 2005).

3.1.9 Walpole Island Citizenry and Advocacy

From 1986 to 1992, industrial and municipal sources lining the St. Clair River produced 550 chemical spills, seventeen of which were severe enough to force Walpole Island's WTP to shut down (Vanwynsberghe, 2000). These incidents cultivated further mistrust by the community's residents of financially-driven companies, but also of the government, and its failure to protect them and their traditional environment. The level of mistrust and the community's opposition is eloquently expressed in the poem below, written by a local resident:

Island residents, please beware
toxic chemicals are in the St. Clair
Poisoned water is a threat to your health

But water is a very precious resource
And it's very vital to sustain our life-force
So is the situation totally under control?
I guess it is, or at least that's what we've been told.

Is there a set of facts and figures to back this claim
Does the Ministry of Environment fully explain
Or are we being told just what we want to hear
So that we believe there's really nothing to fear

I just believe there's room for debate
And a cause for concern from which we can't escape
Those yet unborn will have to live on this land
And that's one problem facing the Walpole Island Band
Will our children have to deal with it, too
That just depends on me and you
For our conscience' sake, let's deal with it now
And make sure this type of tragedy isn't allowed

Jibkenyan, 22 May 1987 (VanWynsberghe, 2000)

The Heritage Center, or Nin.Da.Waab.Jig (which means "those who seek to find"), is a community-based research entity that is part of the governing tribal council. It has gained the community's support by also representing the community's cultural values. One of the Center's main goals is to transfer local knowledge of the surrounding water, considered the Island's lifeline to the world (VanWynsberghe, 2002). Early criticisms of the Center were centered around the focus on scientific research, such as water and air sampling, but community advocacy and activism was also necessary. The toxic "blob" of 1985 became a turning point for the Heritage Center to expand its research practices to include advocating for the environment and as a result, for First Nations. Advocacy was necessary because the exact contents of the blob were unknown and water now had to be trucked-in. Additionally, the corporations responsible had hidden their activities. In response to the many spills, the community wanted the Center to take a firm stand against the corporations whom they felt did not respect the community's approach to the environment, a stark contrast to that of larger "White" society (VanWynsberghe, 2002). The Heritage Center began to mobilize community members in taking a stand against various actions which posed threats to their land. In 1989, the Center fought the dumping of dredged materials from the St. Clair River into Lake St. Clair. Walpole Island lost this case, but was financially compensated, and learned from this outcome that it would be important to substantiate their claims in the future. In 1992, the Center intervened

to prevent the digging of a large railway tunnel under the St. Clair River, which would potentially impact the environment and existing land claims. This outcome was successful. That same year, anti-spill marches were organized and a group of 500 people marched the length of the River to Sarnia, the theme of their march being “War on Chemical Valley”. This environmental justice movement on Walpole led to increased scrutiny of the St. Clair River’s toxic contamination, and strengthened the stand that First Nations were taking against oppressive social practices (VanWynsberghe, 2002). Also in 1992, Walpole Island turned down the federal government’s proposal of a \$60 million water pipeline project. The pipeline would bring water to Walpole directly from Lake Huron but was not accepted because its construction would have compromised the community’s stance on zero discharge into the River, and likely would have halted cleanup of the river. Despite providing clean drinking water, implementation of a pipeline encroached on Walpole Island’s beliefs that the River was a spiritual force and a traditional source of food and recreation. Instead, in 1995, a water tower was built which could hold three days of water in the event of a water plant closure. This water tower was financed by INAC, the Ontario government, and the community (VanWynsberghe, 2000).

3.1.10 Collaborative Research with First Nations Communities

It has been reported that many minority communities do not trust scientific research due to a series of past bad experiences. Often, knowledge provided by communities has been used inappropriately or skewed for financial and professional benefit, a benefit that does not involve the communities. The public reporting of research conducted in these communities can cause destructive notoriety and stigmatisation for the research subjects (Herbert, 2009). An aboriginal physician of Kahnawake First Nation emphasizes this sentiment, “Outside research teams swooped down from the skies, swarmed all over town, asked nosey questions that were none of their business and then disappeared never to be heard from again” (quoted in Herbert, 2009). Walpole Island has also felt this trepidation towards science and visitors to their land. Dean Jacobs of the Walpole Island Heritage Center relates this back to the 17th century when the French “discovered” them. He indicates that, in many cases, these visitors immediately tried to place the First Nations within their ideal framework of knowledge, not recognizing culture, and denying traditional knowledge. He acknowledges that over time things have changed. The Walpole Island First Nation hope to greet visitors on terms of equality, and develop partnerships with individuals and organizations that take the time to visit and share knowledge on the First Nations’ terms (cited in VanWynsberghe, 2002).

The use of participatory research initiatives are suggested as a way in which those who are affected by the issue being studied are involved as collaborators. This form of research follows a series of principles: 1) all partners are viewed as experts; 2) power differentials pertaining to politics, age, gender, and culture are sensitively addressed; 3) communities are informed of both potential harm and benefit that can come from the research; 4) the research is an ongoing collaborative venture; 5) the research design and questions are formulated by researchers and the community; 6) all results are shared with all participants and capacity building is an important focus for all involved (Herbert, 2009). This method was employed in Walpole Island by the University of Western Ontario. Both groups had a shared interest in potential damage to human and ecosystem health from exposure to environmental pollutants. The first project collaboration looked at mercury exposure in residents through fish consumption. Community members volunteered for baseline monitoring of mercury in blood and hair and the presence of persistent organic pollutants in blood lipids. Initial results indicated that 11 of the 91 Walpole Island residents who participated had higher levels of mercury than the WHO allowable mercury intake value of 1.6 µg/ kg body weight per week. Mercury concentrations exceeded guidelines in 18 percent of fish sampled and in 30 percent of predatory fish (bass, pickerel, and bowfin) (Herbert, 2009). Oral histories were included in the research in order to link traditional knowledge with health and the environment and to learn community perception of these concerns. Results indicated that water pollution is perceived as a major problem and residents also exhibited signs of psychosocial stress associated with fear of contaminant exposure (Herbert, 2009).

Collaborative research has also been done with another First Nation community located within the St. Clair River AOC called the Aamjiwnaang First Nation. This community reported a reduction in male births in recent years. As part of a community based participatory research project between the University of Ottawa, the Aamjiwnaang Environment Committee, and Occupational Health Clinics for Ontario Workers, the sex ratios of births were assessed. The proportion of male births showed a significant decline over the most recent ten year period of 1994-2003, with the most pronounced decline occurring from 1999-2003 (Mackenzie *et al.*, 2005). The community is in close proximity to Sarnia and its petrochemical, polymer, and chemical industrial plants, which are suspected to be a potential cause of the male birth decline. There is mounting evidence that environmental and occupational exposures to chemicals such as dioxin, dibromochloropropane, hexachlorobenzene and methylmercury can affect the sex ratio. However, before concluding that the causative factors have been identified, there are a number of variables that must be considered. These variables surround parental exposure to contaminants, the age of

exposure, the parent's sex, the route of exposure, and the contaminant concentration. A community health survey is currently being administered to obtain more information on the health of the community (Mackenzie *et al.*, 2005).

These types of collaborative research help in capacity building for those involved, documents traditional knowledge, and allow data to be incorporated into a database to be used by the community's health and heritage centers for the identification of potential health trends and the provision of information for preventative care (Herbert, 2009). Collaboration with First Nations, and in particular the people of Walpole Island, can provide insight into local drinking water and environmental concerns. Collaborative working relationships and respectful communication will allow both the community and researchers to benefit from the cultural and scientific knowledge gained.

3.2 Methodology

The use of a case study was the chosen research method for this thesis and the EWBS study as it provided a mechanism for visualizing where the application of the EWBS would be most beneficial within a Canadian context. The case study selection criteria centered on two factors—the physical location of a community in relation to increased risk of drinking water contamination, and the available marginalized population base, such as a First Nations and rural communities. These populations often suffer from a reduction in drinking water quality when compared to urban and non-reserve communities. Walpole Island First Nation was selected because of its critical location downstream from Sarnia's "Chemical Valley", within the St. Clair River AOC. The area has a history of chemical spills and subsequent closures of drinking water intakes. Furthermore, the community is located in Southern Ontario and was therefore relatively accessible for a site visit. An extensive introduction to the St. Clair River AOC, and of "Chemical Valley" and Walpole Island, which lie within it, provided a complete setting of complex interactions between the economy, the environment, and social interests of its residents. The site visit provided an opportunity to develop a trusting relationship with members of the community, which in turn allowed information to be gathered regarding treatment technologies and testing protocols in place at the WTP. Once this information was obtained, it was possible to assess the WTP's capabilities in terms of the potential contaminants being inputted into the drinking water source. Information gathered from a literature review of the "Chemical Valley" also provided a contaminant of concern for use in laboratory bioassays. This, at the same time, satisfied the requirement for a metal contaminant, necessary for the development of an EWBS responsive to classes of contaminants.

3.3 Results and Discussion

3.3.1 Communication with First Nations

Communication with Walpole Island First Nation began in March, 2009, at which point the tribal council departments affiliated with drinking water were contacted via phone and email. The treatment plant, the public works manager, and the heritage center were contacted with questions related to drinking water testing and treatment. No one contacted was able or willing to provide these answers, and transferred the duty on to someone else. Any answers that were given were vague and contradictory to other information sources and a real sense of discomfort was noticed. Also at this time, INAC was contacted with the intent of obtaining a copy of the environmental assessment conducted for the building of the new plant. The INAC contact became interested as to why this information was needed and in a telephone discussion provided advice on appropriate and cautious communication processes with the First Nation community, as they would unlikely be forthcoming to an outsider. It was recommended that the first step in gaining information was to write a formal letter to the Chief, expressing interest in visiting the Walpole Island First Nation. Visiting the community unannounced would cause suspicion and would not effectively open the lines of communication. A letter was written by Dr. Ron Pushchak, in consultation with a previous First Nation graduate student, who helped introduce the research team and open the lines of communication with the Heritage Center Director. The Director referred the research team to the public works manager and consent was given for a site visit.

3.3.2 Treatment Technologies and their Effectiveness

In 2005, INAC announced funding for a \$10 million WTP on Walpole Island (INAC, 2005). The plant was completed in 2008 as part of INAC's First Nations Water Management Strategy to update water treatment technologies. Water intake is directly from the St. Clair River, a somewhat precarious location downstream from "Chemical Valley". A site visit was made in November, 2009 following dialogue with Mr. Tony Tino of INAC; Mr. Burke Fisher, Plant Operator; and Ms. Judy Jacobs, Public Works Manager.

Because Walpole Island First Nation is a reserve, the provision of safe drinking water is therefore a federal responsibility. However, the WTP adheres to the more stringent Ontario standards for the testing of drinking water. Physical parameters such as pH, chlorine levels, and temperature are sampled numerous times a day on both raw and treated water. Bacteriological parameters and chlorine levels are tested at each sampling point in the plant and distribution systems once a week and, in addition, one sample per week is sent to an outside laboratory for detailed analysis. Ontario drinking water standards specify that inorganic and organic parameters are to be sampled at least once per year for surface water supplies. The WTP is also included in

the Ontario Drinking Water Surveillance Program (DWSP) which monitors for over 250 inorganic, organic, and radiological water quality parameters 4 times per year. Samples are sent to outside labs for testing, with an approximate turn-around time of two weeks for results. The DWSP is a science based monitoring program that is separate from routine, legislated monitoring of drinking water (OMOE, 2009b). The DWSP monitors contaminants of potential concern to Walpole Island drinking water including 1) pesticides such as glyphosphate, metolachlor, and atrazine, 2) volatile organic compounds such as toluene and benzene derivatives, and 3) metals such as cadmium, copper, and arsenic.

Approximately 1000m³ of raw water enters the Walpole Island WTP per day, and the intake pipe is on the floor of the St. Clair River, directly in front of the treatment WTP (Figure 8). Michigan is very close on the opposite river bank, which is lined with homes, and a ferry runs just upriver. The water tower holds a three-to-four day reservoir, and is topped up daily before the plant's operations are shut down at the end of each day. There is also an on-site reservoir which holds the treated water prior to distribution. Raw water which enters the WTP undergoes numerous treatment steps and includes recent, specialized technologies of membrane filtration, granular activated carbon, and ultraviolet (UV) disinfection.

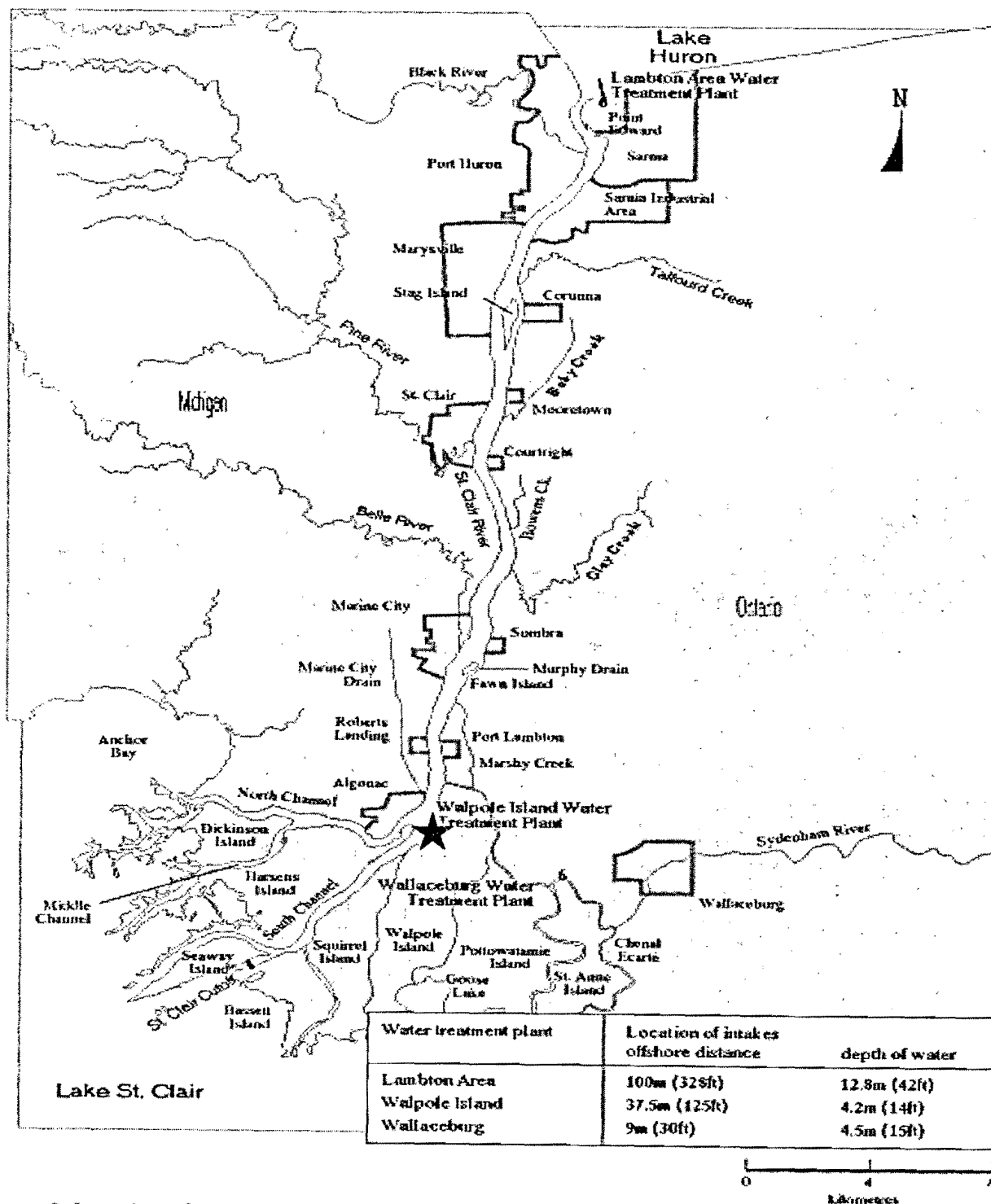


Figure 8: Location of water intake for the Walpole Island Water Treatment Plant (Source: RAP, 1995)

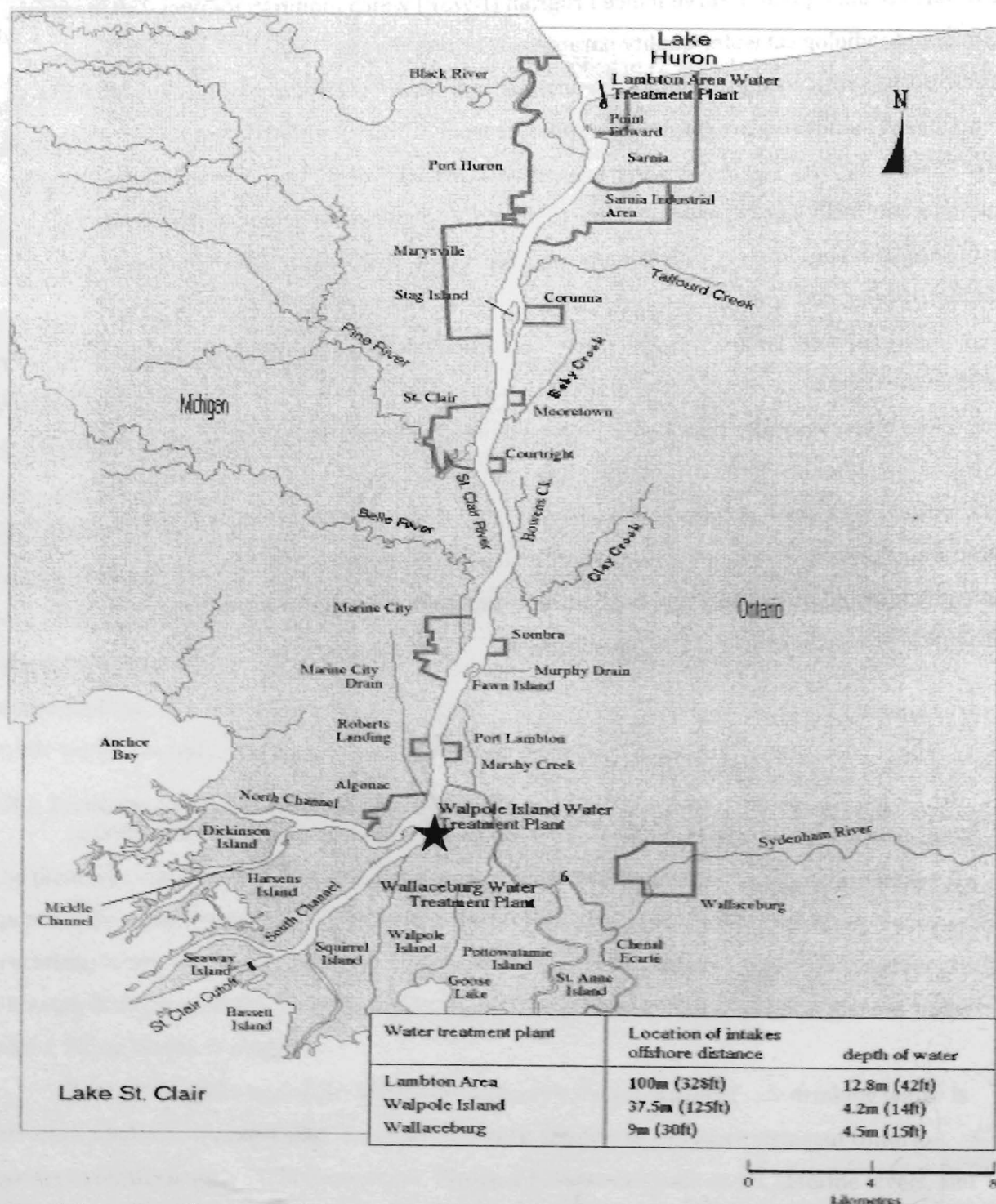


Figure 8: Location of water intake for the Walpole Island Water Treatment Plant (Source: RAP, 1995)

The main contaminant concerns for Walpole Island are a result of its critical position downstream from highly industrialized Sarnia, ON. This location puts the community at increased risk of exposure to discharges and sudden spills of heavy metals and organic compounds. INAC's *Design Guidelines for First Nations Water Works* stress the expectation of water systems' owners to make every effort possible to first obtain naturally safe source water, and to not only rely on water treatment. Safe source water is the first step in long term public health protection, and strict reliance on a water treatment device cannot assure the output of safe drinking water (INAC, 2006a).

A number of advanced treatment technologies are employed at the Walpole Island WTP. Prior to chemical treatment, raw water is guided through treatment by membrane filtration, granular activated carbon, and ultraviolet (Figure 9). Chemical treatment of the water occurs with the addition of chlorine in the form of sodium hypochlorite for disinfection, sodium bisulfite to remove excess chlorine, and caustic and acid feed to adjust the pH and neutralize the water. Wastes from this step are sent to the neutralization tank before they are released to the river. The plant also has space allocated for potential future use of ozone treatment; this would aid in disinfection of microorganisms and oxidation of organic and inorganic contaminants.

A vulnerability assessment of Walpole Island's drinking water system was conducted to examine the capabilities of currently utilized treatment methods in response to contaminant spills and chronic contamination, in particular in response to copper, the selected contaminant of concern.

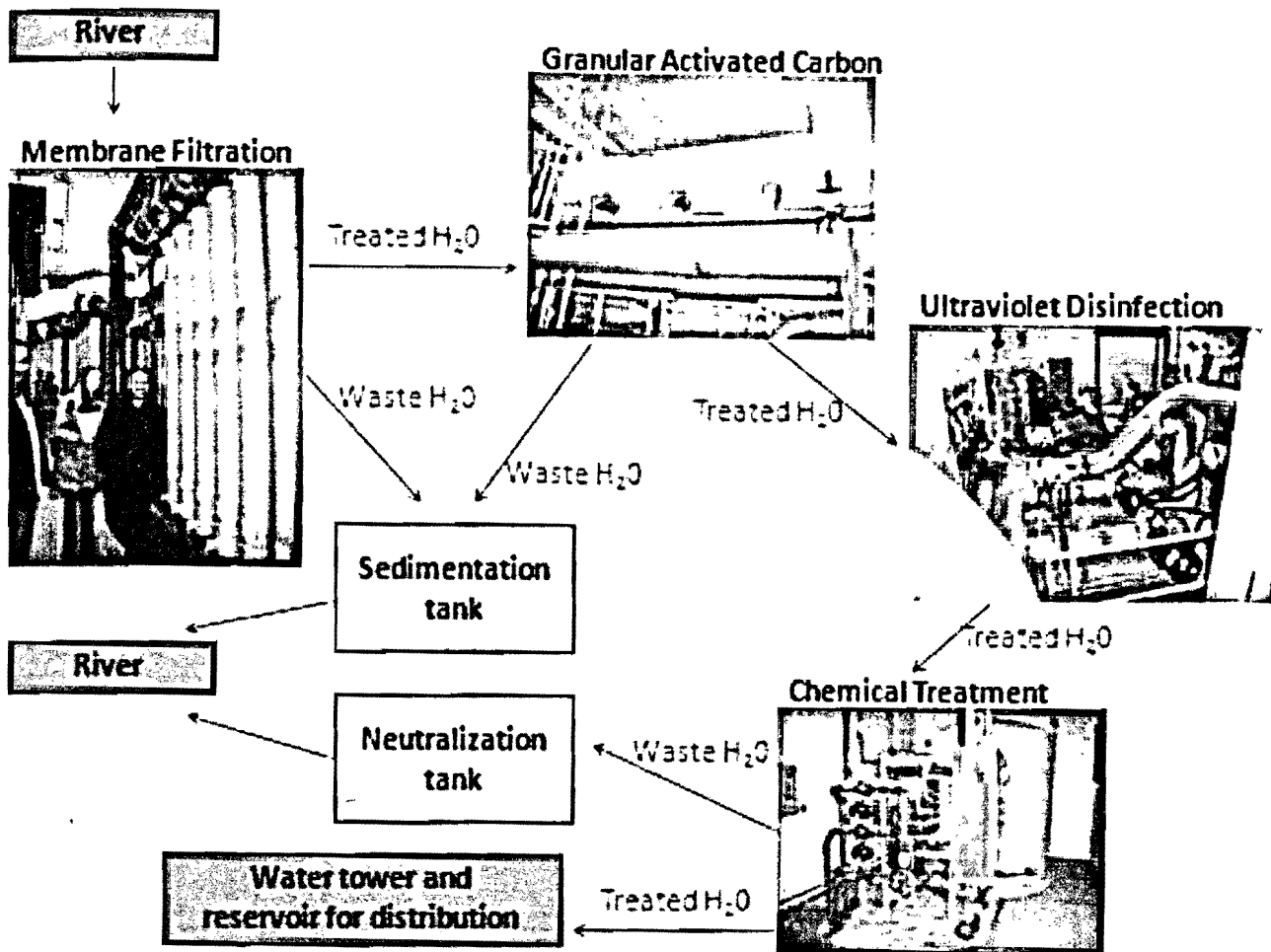


Figure 9: Treatment steps utilized by the Walpole Island Water Treatment Plant

3.3.2.1 Membrane Filtration

Following the site visit and in subsequent communication with an engineer from the First Nations Engineering Limited, it was determined that the Walpole Island WTP utilizes microfiltration and specifically, the use of a Pall membrane microfiltration system (Personal communication, First Nations Engineering Ltd, Nov. 30, 2009). The Pall membrane systems are successful as a stand-alone filtration treatment as well as in combination with pre-treatment processes. Minimum pre-treatment consists of a 400µm strainer to remove large particles and to prevent fouling. The system operates as two parallel rows of modules. Individual modules can be accessed or removed independently, and the system can therefore operate without all modules functioning. To reduce fouling and maintain optimum operating pressure, the system is air-scrubbed and reverse-filtered every 15 to 30 minutes (American Water Works Association, 2005).

The use of membrane filtration is effective as a replacement to traditional granular media filtration processes. Both microfiltration and ultrafiltration are effective in the removal of particulate and colloidal material bigger than the membrane pore size, such as bacteria, *Giardia*,

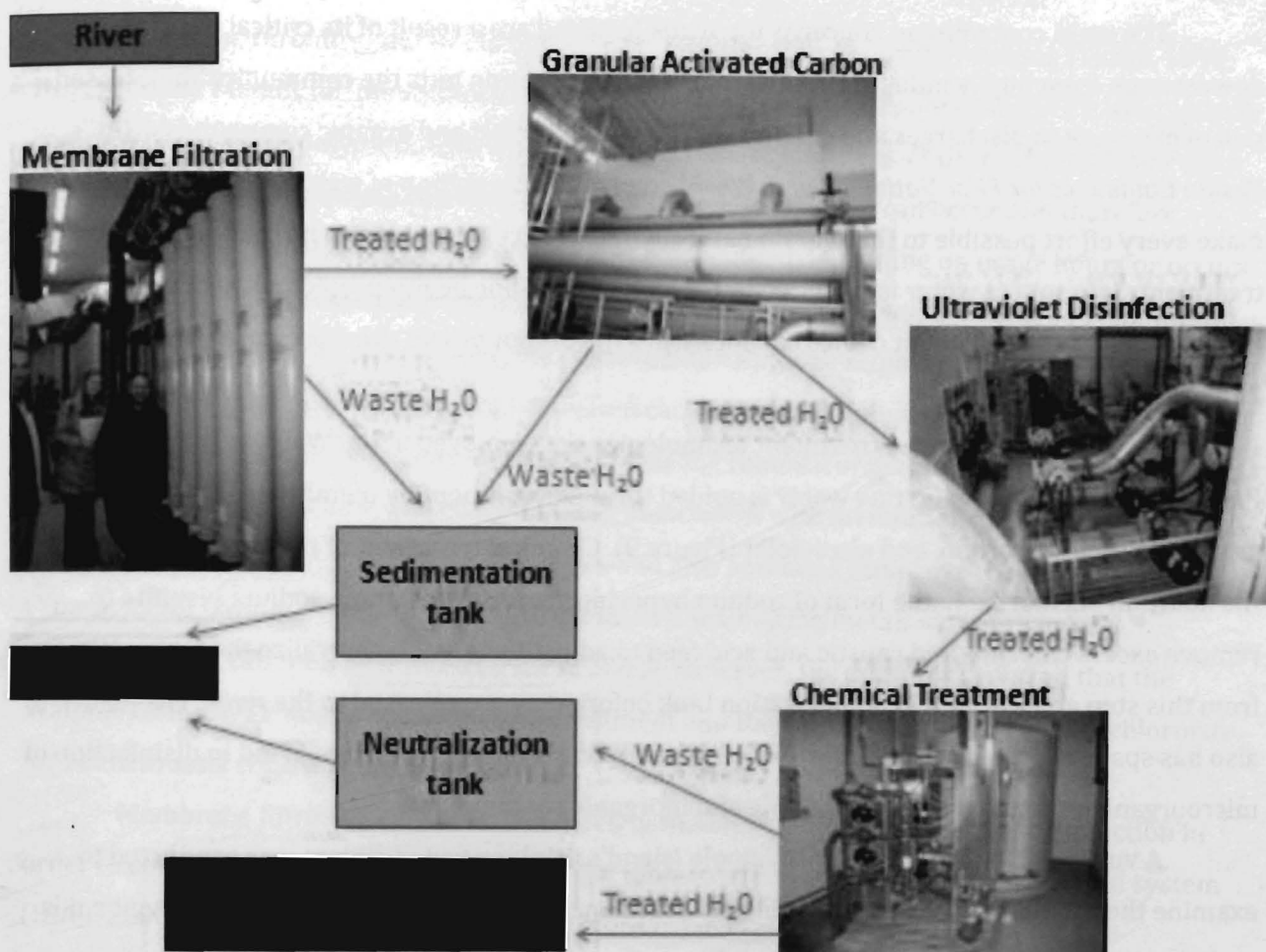


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Cryptosporidium, turbidity, and in the case of ultrafiltration, the removal of viruses (Yuasa, 1998; INAC, 2006a). Membrane microfilters, such as those in use at the Walpole Island WTP, are typically composed of organic polymers with a pore size of 0.1-0.2 μm . As a result of small membrane pore size, fouling of the membrane due to organic and inorganic build-up can occur and therefore requires periodic backflushing and cleaning that is scheduled depending on usage hours or occurs when the required operational pressure is reduced. Due to the microporous nature of membrane filtration, dissolved inorganic and organic constituents cannot be removed without the aid of pre-treatment processes such as powdered activated carbon, coagulation, and/or oxidation. The use of powdered activated carbon adsorption can increase the removal of dissolved organic matter; lime is added to soften the water, and coagulation in association with membrane filtration can increase the removal of high molecular-weight organics and also potentially improve the filtration rate (Yuasa, 1998; USEPA, 2005). Oxidants are useful in precipitating metals such as iron and manganese that can then be filtered (USEPA, 2005). However, the operator reported that the Walpole Island WTP does not use any pre-treatment and that while the system can pre-chlorinate for zebra mussel control, it does not.

Membrane filtration cannot be practiced without the added protection of disinfection in order to control the growth of pathogens on the filters and protect the entire distribution system (INAC, 2006a). A study compared the effectiveness of microfiltration combined with pre-coagulation and the sole ultrafiltration process for the removal of various parameters. Turbidity was completely removed by both processes; background organics (KMnO_4 demand and THM) were more successfully removed by the coagulation-microfiltration process and metals (iron, manganese, and aluminum) were better removed by the sole ultrafiltration process. However, when ultrafiltration was combined with granular activated carbon (GAC) adsorption, the removal of background organics was increased as well as micropollutants, such as pesticides (Yuasa, 1998).

Membrane filtration has become increasingly used for treating inorganic effluent, and is not only considered useful for the removal of suspended solid and organic compounds, but also inorganic compounds such as heavy metals (Kurniawan *et al.*, 2006). Kurniawan *et al.*, (2006) assessed various treatment methods for the removal of metals from industrial effluent. The use of chemical precipitation can increase the effectiveness of inorganic contaminant removal. Adjustment to a basic pH and the addition of a precipitating agent such as lime converts dissolved metal ions to an insoluble solid phase, preventing them from passing through the micro pores. Coagulation uses: adjustment to a basic pH; a coagulant such as ferric/alum salts, which destabilizes colloidal particles by overcoming the repulsive forces between the particles; and flocculation, which

transforms the unstable particles into bulky flocs. A study was conducted investigating the removal of the heavy metal ions copper and zinc from synthetic wastewater using ultrafiltration and the addition of water soluble chitosan (Juang & Shiau, 2000). At a neutral pH, copper removal was more efficient than other metals, and at a pH < 6, metal rejection by the membrane decreased slightly and increased by raising the pH. With the addition of chitosan, the rejection of copper ions, in a solution with pH < 6, was 6 to 10 times greater than without it and achieved approximately a 100% rejection rate at pH 8.5-9.5 for copper (Juang *et al.*, 2000). Depending on the membrane used, ultrafiltration can effectively remove 90% of metals with a concentration between 10 and 112mg/L at a pH range of 5-9.5 (Kurniawan *et al.*, 2006).

The Walpole Island WTP operator has indicated that chemical pre-treatment is not administered prior to microfiltration and the use of other possible pre-treatment methods was not specified. The water treatment plant's lack of pre-treatment methods potentially decreases the system's ability to effectively remove metal contaminants.

3.3.2.2 Granular Activated Carbon

Adsorption occurs when a substance is transferred from the liquid phase to the surface of a solid through physical and/or chemical interactions. Adsorption using activated carbon can effectively remove metals, including copper, from inorganic effluent (Kurniawan *et al.*, 2006). GAC adsorption cannot be used as a single filtration method in INAC water works unless deemed sufficient through pilot testing or the approval of the reviewing authority. Provisions must be made for the frequent replacement or regeneration of the media and treatment for the control of bacteria growth (INAC, 2006a). The Walpole Island WTP utilizes GAC following microfiltration. The plant has four tanks of GAC operating simultaneously. The adsorbent is required to be back-flushed every 500 hours; however, the plant does so every 240 hours. Back-flush waste is diverted to a sedimentation tank which is then deposited back into the River without further treatment.

In a similar setting as Walpole Island, the Cincinnati (Ohio) Water Works receives its source water from the highly industrialized Ohio River and most spills into the River are organic chemicals. In 1992, the facility was the first to install GAC post-filtration adsorbers as an added protective shield against potential organic chemical contamination within the watershed. The Cincinnati water works pioneered the use of GAC treatment and has one of the largest GAC facilities in the US. In order to maximize the adsorption function of GAC, the facility includes onsite regeneration and maintains an efficient operational flow through system (Logsdon *et al.*, 2006). After settling and filtration, water at the facility is filtered through beds of GAC which adsorb organic substances, removing them from the water. One cup of GAC has the surface area of about 25 football fields

(1,300,000 square feet). The Cincinnati Water Works latest upgrade includes the installation of UV disinfection in 2009/2010. The department hopes to be better guarded against known incidents of municipal and industrial wastewater system raw sewage discharge or treatment malfunctions which, along with contaminants of concern, can contain *Cryptosporidium*, an organism not effectively destroyed by chlorine disinfection (City of Cincinnati, n.d.)

Activated carbon, such as that used in the Walpole Island WTP, has a large surface area, a micropore structure, and a high degree of surface reactivity—attributes which make it a good adsorbent for the adsorption of organics and inorganics from water. Through the proper selection of activated carbon and operational conditions such as pH and surface loading, a high degree of heavy metal removal by activated carbon adsorption is possible (Corapcioglu and Huang, 1987). Goyal *et al.* (2001) studied the removal of copper from water by adsorption on activated carbons. Previous researchers found slow uptake of copper (II) ions at a pH below 2 but when increased to a pH of 4, maximum uptake of the ions occurred. When the pH was increased to 6 the adsorption study was not possible due to the precipitation of $\text{Cu}(\text{OH})_2$. The change in the solution's pH results in the formation of different ionic species. There is excessive protonation of the carbon surface at a pH less than 3 which results in decreased adsorption of the copper ions. At a pH greater than 4, increased hydroxide ions resulted in a competition with the carbon surface for the copper (II) ions, thereby decreasing copper adsorption to the carbon (Goyal *et al.*, 2001). In the case of Walpole Island's WTP, without the addition of chemicals prior to treatment by GAC, it is uncertain whether the carbon surface is effective in the removal of inorganic contaminants such as heavy metals.

The use of GAC, the carbon surface utilized by Walpole Island's WTP, has been identified as one of the best methods for treating a maximum number of synthetic organic contaminants, including many taste and odour-causing organics. Adsorption is affected however, by the water's pH and the presence of other materials. Shih *et al.* (2003) studied the removal efficiency of GAC on levels of methyl *tertiary*-butyl ether (MTBE) in groundwater and surface water, with or without the presence of *tertiary*-butyl alcohol, benzene, toluene, and p-xylene (BTX). A significant reduction in GAC adsorption of MTBE was observed due to competitive adsorption from the soluble fuel components, BTX. Additionally, the increased presence of natural organic matter in surface water resulted in increased competitive adsorption with MTBE and therefore a decreased rate of adsorption of MTBE by the GAC (Shih *et al.*, 2003).

3.3.2.3 Ultraviolet Disinfection

INAC's *Design Guidelines for First Nations Water Works* mandates drinking water disinfection, ideally in two stages (INAC, 2006a). The primary disinfection method recommended is

the use of ultraviolet (UV) radiation to inactivate or kill bacteria, protozoa, and some viruses and then follow-up with chlorine to completely destroy pathogens and provide disinfection residual throughout the distribution system (INAC, 2006a). The Walpole Island WTP has two alternating UV treatment tubes which operate following GAC treatment. They do not use hydrogen peroxide (H_2O_2) with the UV disinfection.

A UV system uses electromagnetic energy from a mercury arc lamp to damage the genetic material of an organism. The radiation penetrates the cell wall and destroys the cell's ability to reproduce. The effectiveness of UV is dependent on the exposure time of organisms to the radiation, the intensity of the UV, and the concentration of colloidal and particulate matter in the water (USEPA, 1999). The optimum wavelength to effectively inactivate microorganisms ranges between 250-270 nm and the intensity of the lamp's radiation decreases as the distance from the lamp increases. UV disinfection is advantageous as it is an effective treatment for a range of microorganisms including bacteria, protozoans, cysts, viruses, and spores. This form of disinfection, utilized by the Walpole Island WTP, is a physical process and therefore reduces the risks associated with chemical use and unlike chlorine disinfection, runs no risk of residual effects. UV disinfection is more efficient, needing less contact time with the water and requires less space within the WTP. This method has its disadvantages; if the dose of UV contact is low, it will not fully inactivate the microorganisms, and it is possible that some organisms can repair the destructive effects of UV through photo reactivation, once again posing a health risk. A number of physiochemical factors present in the water can affect the performance of the UV system. Turbidity and total suspended solids adsorb UV radiation and shield organisms embedded within them, pH and hardness affect solubility of metals that can then absorb UV light and can lead to the precipitation of carbonates on the tubes; and the presence of humic material and iron decrease energy absorbed by microorganisms due to their high absorbency of UV light (USEPA, 1999).

The UV treatment process is effective in numerous configurations. Treatment of UV irradiation on its own, or in combination with ozone and/or hydrogen peroxide, generate highly reactive hydroxyl radicals which react with many organic chemical compounds and subsequently destroy them (Trach, 1996). Beltran, Ovejero and Acedo (1993) looked at the effect of UV radiation on the organic pesticide, atrazine. Results showed that the oxidation of atrazine with direct UV radiation at 254 nm on its own, and with the presence of H_2O_2 , combined with the same source of radiation, resulted in a high elimination rate of atrazine but a higher rate of oxidation with the UV/ H_2O_2 system. However, factors such as the presence of bicarbonate ions, strong hydroxyl radical scavengers, reduce the action of hydroxyl radicals on the organics. Similarly, humic matter has a

negative effect due to the scavenging of hydroxyl radicals and the absorption of radiation by the humic matter (Beltran *et al.*, 1993).

The use of UV in association with H_2O_2 oxidizes various organic substances in water through the formation of the hydroxyl radical, which is an extremely reactive and nonselective oxidant. Therefore when the radical is produced in sufficient quantities it can lead to the complete oxidation of organic compounds into carbon dioxide, water, and inorganic ions (Liao and Gurol, 1995). The researchers investigated the oxidation of a model organic compound, n-chlorobutane (BuCl), and the photolytic decomposition of H_2O_2 under various types of water quality and operational conditions. Results indicated that the higher the rate of H_2O_2 photolysis, the higher the oxidation of the organic compound. The oxidation efficiency of BuCl was hindered with increasing pH, the total inorganic carbon concentration, and the concentration of humic material in water (Liao *et al.*, 1995).

A wide variety of organic contaminants are susceptible to elimination by UV-oxidation treatment, including petroleum hydrocarbons, halogenated solvents, phenol, pentachlorophenol, pesticides, dioxins, glycols, polychlorinated biphenyls, vinyl chloride, benzene, toluene, ethylbenzene, xylenes, methyl tertiary butyl ether, cyanide, mixed organic/radioactive waste, and other organic compounds. The removal of organic contaminants such as benzene through UV treatment can be successful to a point of non-detectable levels while other contaminants, such as 1,1-dichloroethane, have a decreased reduction of 96 percent (Trach, 1996). Unfortunately many Canadian water systems, including Walpole Island's WTP, do not utilize UV-oxidation treatment, decreasing the effective removal of potentially hazardous organic contaminants.

3.3.3 Study Site Contaminant Choice

Development of the EWBS requires laboratory testing of a number of chemical contaminants. Numerous researchers have begun to explore this work, and the research continues as current researchers study organism responses to a variety of contaminants including atrazine, tributyl tin, and microbial pathogens. For the current thesis, copper was selected for use in laboratory bioassays.

Copper was identified as a contaminant of concern from the St. Clair River AOC. Through the previously discussed literature review, research studies, and government reports pertinent to the St. Clair River watershed and "Chemical Valley", copper was chosen for study in laboratory behavioural bioassays. The choice of copper also satisfied the requirement for a metal contaminant, a class of contaminants not yet used in the development of the EWBS and which is necessary for a system responsive to classes of contaminant. Metals are an important class of contaminants which

can affect the quality of aquatic ecosystems and the safety of drinking water. Many organic chemical compounds and metals are deposited by the petrochemical processing, chemical manufacturing, and energy generation industries, along with municipal waste water discharges. These effluents collectively input contaminants on a daily basis which can alter the quality of the river's water. Additionally, unforeseen spills are a constant threat and can lead to a pulse of contaminant input which, when added to daily permitted discharges, puts increased pressure on drinking water facilities, and threatens the safety of drinking water for human consumption.

3.4 Conclusion of Case Study

Walpole Island has made significant improvements in its water supply system and monitoring processes. The Walpole Island WTP has numerous treatment methods that are comparable to plants sharing a similar position downstream from industry (Cincinnati WTP). Walpole employs the same GAC technology as the Cincinnati WTP but has the additional advances of microfiltration and UV disinfection. The main contaminant concerns stemming from Walpole Island's location, in relation to highly industrialized Sarnia, is an increased risk of exposure to heavy metal contamination and organic compounds from chemical manufacturing, petrochemical processing, energy generation, and municipal wastewater. While it appears the WTP sufficiently manages the treatment of contaminants through advanced technologies, the unpredictable nature of spills will always remain a threat. Furthermore, treatment methods currently in use have limitations which require pre-treatment and additional technologies to effectively remove contaminants of particular concern to Walpole Island. The plant is part of a response chain following a contaminant spill and is notified by the Ministry of Environment's Spills Action Center. The operators are notified about most spills, including those that are small and negligible, although suspicions that not all spills are reported remain a concern.

Despite improvements in Walpole Island's water supply system, some health-related and environmental concerns remain. While it is possible that government's funding of the technically advanced WTP has aided in dissipating some of the community's fears, stories of tumours on fish and a concern over mercury poisoning remain. The Island's ecosystem is diverse and boasts plenty of species, but stories such as these have left the local health center advising residents to reduce consumption. The Heritage Center, which is the environmental and research branch of the Walpole Island council, is interested in ongoing research and is currently working with another university on an epidemiological study that involves sampling the hair of residents and comparing bioaccumulation of contaminants with the amount of wild foods eaten. During the site visit, the

Center also identified a great need for improvements regarding the sewage system and the upkeep of septic tanks, both of which are major potential health concerns.

Unfortunately, Walpole Island remains vulnerable because of its location downstream from the highly industrialized Sarnia region. This vulnerability also makes the community a potential suitable location for testing of the EWBS because of an increased likelihood of contaminant presence in source water, and the convenient logistics of its WTP location in relation to the St. Clair River. Furthermore, Walpole Island has expressed interest in collaboration on beneficial research as the biological nature of the EWBS is more philosophically congruent with the First Nation community's bond to nature than is a chemical monitoring system.

After the November 2009 site visit, a second meeting took place in June 2010, between the researchers and the Walpole Island members, to provide a more descriptive overview of the EWBS project and research intentions. As previous connections had been made, the second meeting was much easier to establish, and communication between the researchers and Walpole Island WTP operators was increasingly open and informative. During this meeting, operators and community environmental members indicated some of their concerns which included carcinogens in the air and water, the discovery of feminization in leopard frogs, and mistrust of spill reporting from prominent companies upstream. Operators were increasingly supportive of the implementation of an EWBS and truly saw its benefit for their water system. The research team will continue to respect the sensitive history of Walpole Island, and use this research process as an opportunity to work with the community in a mutually beneficial way.

4.0 *Daphnia magna* Bioassay Using Copper

The overall goal of the current research study is not only to develop an EWBS, but to develop a system that is holistic in nature. The system will be multi-organism based, and respond to classes of contaminants, thereby securely protecting the quality of drinking water. An important component of the system's development is the identification of appropriate organisms, and their behaviours, for use in laboratory bioassays. The utility of *Daphnia magna* behavioural responses for the detection of environmentally-relevant concentrations of copper is examined and discussed.

4.1 Introduction

4.1.1 Behavioural Bioassay

The degree of water and soil contamination can be determined through the use of chemical analysis; while alternatively, bioassays determine the biological impact of the contamination. Chemical analysis offers a more exact reading; however, due to the wealth of environmental contamination and the high cost of analysis, it is difficult to decide which chemicals to test. As well, there is no information provided as to the toxic effect on the ecosystem and its inhabitants. Bioassays offer the advantage of demonstrating the total impact that a contaminant, a group of contaminants, or the current pollution level of a system will have at the organism level (Michels *et al.*, 2000; Fjallborg *et al.*, 2006).

If carefully standardized, behavioural criteria can be used as a more sensitive and efficient indicator of stress when compared to morphological or life history traits that have been traditionally utilized. Behavioural responses are stated as taking one-tenth as long to measure when compared to life history responses and are therefore sensitive bioassay indicators for the detection of toxic substances (Dodson *et al.*, 1995). Using *Daphnia* as the test organism, previous studies have determined important parameters of *Daphnia* swimming behaviour including velocity; vertical and horizontal orientation; and variances such as hops, spins, and escape reactions (Dodson *et al.*, 1995, Baillieul *et al.*, 1999; Untersteiner *et al.*, 2003). A number of studies show statistically significant changes in *Daphnia* at sublethal concentrations of contaminants (Michels *et al.*, 2000; Kieu *et al.*, 2001; Martins *et al.*, 2007). Changes in phototactic behaviour were found to be useful for detecting copper contamination up to 32 times lower than the reported EC₅₀ and LC₅₀ values (Martins *et al.*, 2007). Martins *et al.* (2007) used phototactic response as an indicator for 11 chemicals and the values detected were in all cases much lower than the reported EC₅₀ and LC₅₀ values. Furthermore, most chemicals were detected at exposure times between 0.24 and 3.5 hours. Michels *et al.* (1999) and Kieu *et al.* (2001) both determined the copper concentration that

significantly influenced *Daphnia* phototactic behaviour to be as low as 37% of the LC₅₀ (48h) value of 0.054 mg/L.

An organism's behaviour is the endpoint in a series of neurophysiological events that include the activation of sensory and motor neurons, muscle contractions, and the release of chemical messages (Untersteiner *et al.*, 2003). The evaluation of behaviour can therefore be an accurate measure of the toxicological effects of contaminants in the environment. The presence of toxins or the appearance of predators induces a stress situation and disrupts the normal functions of organisms such as *Daphnia* (Dodson *et al.*, 1995; Untersteiner *et al.*, 2003). To compensate for the imbalance of the stress response, *Daphnia* are forced to use part of their metabolic energy for escape, adaptation, or protection reactions, all which alter the swimming behaviour of the organism (Wolf *et al.*, 1998; Untersteiner *et al.*, 2003). The energy allocation theory postulates that the inhibition of growth and reproduction can be explained due to reduced production of energy and/or increased use of energy. Toxic stress increases metabolic costs and inhibits food assimilation, resulting in a reduction of growth and reproduction. An increase in metabolic activity may be required for normally unnecessary functions such as, the restoration of bio-molecules damaged by accumulation of copper-induced redox cycling, detoxification processes such as metallothionein production, and for copper storage in granules (De Schamphelaere *et al.*, 2007).

Changes in the swimming velocity, swimming participation, and the distribution of *Daphnia* in the water column are important indicators of acute sublethal stress. Important activities such as food collection and predator avoidance depend on swimming activity which in turn depends on muscle activity, particularly the beating of secondary antennae (Baillieul *et al.*, 1999). In particular, a change in the organism's velocity results in changes to swimming style and height in the water column, as the reduction in muscle activity reduces secondary antennae use and the ability to resist the force of water (Wolf *et al.*, 1998).

4.1.2 Bioassay Organism: *Daphnia magna*

Daphnia magna, small (0.5-5.0mm) freshwater crustaceans, are referred to as a "keystone" species in ecotoxicological food webs and their behaviours can serve as an indicator of toxic conditions (Figure 10) (Poynton *et al.*, 2007). *Daphnia* have a broad distribution in North America and worldwide in the northern hemisphere and hold an integral place in the herbivore level of lake ecosystems (Dodson *et al.*, 1995; Adamowicz *et al.*, 2002).

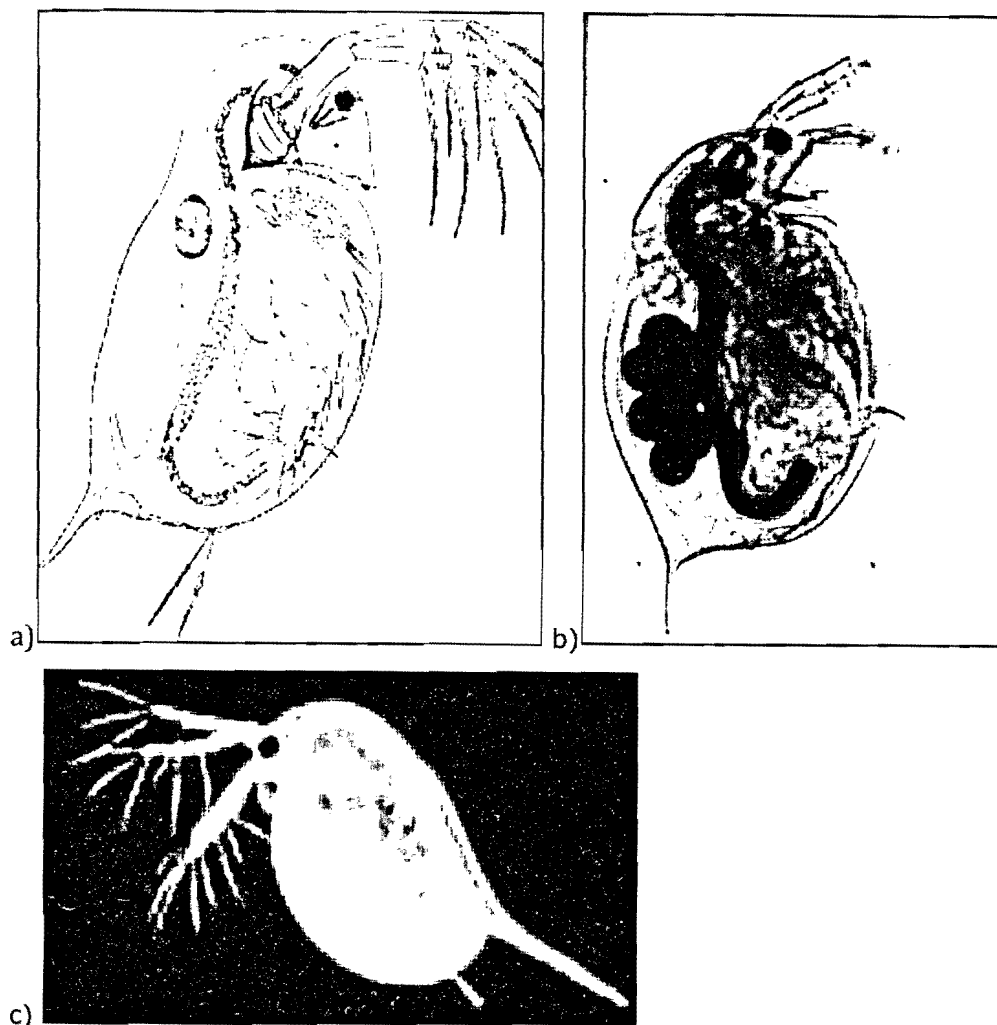


Figure 10: a) Diagram of *Daphnia magna* (Source: University of Iowa, 2001) b) *D. magna*. Adult female with clutch of eggs in brood chamber (Source: Ebert, 2005) c) *D. magna* neonate (< 24hr old) (Source: Ebert, 2005)

As an important dietary component for larger aquatic species and a consumer of phytoplankton, *Daphnia* play an important role in transferring energy through the food web and are a suitable representation of the possible detrimental effects on the aquatic community. Subtle changes in *Daphnia* biology can possibly affect other trophic levels (Dodson *et al.*, 1995). *D. magna* are widely used in aquatic exotoxicity research as their physiology and behaviours are extensively catalogued and they are easily cultured and maintained in the laboratory; they also have a high frequency of reproduction thereby enabling constant replenishment of test organisms. This species is often used in laboratory bioassays to assess the acute toxicity of effluents, or the chronic impact of contaminants from rivers or sediments (Dodson and Hanazato, 1995; Terra and Feiden, 2003). The German field report, *Recommendation on the Deployment of Continuous Biomonitoring for the*

Monitoring of Surface Waters, rated the use of *Daphnia* as the first priority in the development of a complete, holistic biomonitoring system (cited in Gullick *et al.*, 2003).

Swimming behaviour has great energy metabolism implications for permanently swimming organisms such as *Daphnia*, as it is energetically costly but also contributory to predator avoidance and foraging success (Dodson and Hanazato, 1995; Bailleul *et al.*, 1999; Untersteiner, 2003).

Daphnia swimming behaviour has been well-documented in both nontoxic and toxic conditions. Changes in swimming behaviour can result from avoidance of substances in the water or from toxic impairment of metabolic reactions (Green *et al.*, 2003). *Daphnia* react to stress situations, induced by chemical compounds and changes in the natural environment, by exhibiting escape, adaptation, or protection reactions (Wolf *et al.*, 1998). *Daphnia* possess a variety of life history, behavioural, and morphological traits that are influenced by the environment. These traits can be triggered by changes in temperature, light, or food levels but also by chemical signals from predators. While the traits initially present themselves in response to natural triggers, they can also be cued by anthropogenic chemicals. Locomotion in daphnids has been found to decrease upon exposure to heavy metals and organic contaminants (Wolf *et al.*, 1998; Bailleul *et al.*, 1999; Riddell, Culp and Baird, 2005).

As filter feeders, *Daphnia* must continuously expend energy for food location and consumption and to power their secondary antennae. This constant movement is contingent on the heavy use of muscular activity, which is highly energy demanding; therefore, a decrease in swimming activity is necessary when energy input is lower during toxic environmental conditions (Schmidt *et al.*, 2005). Inhibition of movement can result in a destruction of population behaviours such as diel vertical migration, possibly leading to increased predation or confinement to unsuitable conditions, away from optimal food patches (Schmidt *et al.*, 2005). Diel vertical migration is most likely the result of a compromise between predator avoidance and foraging opportunities. During the day, light penetrates the upper reaches of the water column and increases both photosynthesizing algae and visibility to predators. Migration to deeper waters during the day decreases predation but is also costly because it reduces the population growth rate through a reduction in feeding time, a diversion of energy to swimming, and exposure to cooler deeper water which slows growth and reproduction (Dodson, 1990). Therefore, the presence of even low concentrations of toxins can lead to a disruption in the migratory balance of *Daphnia* and contribute to a decrease in the population (Schmidt *et al.*, 2005).

4.1.3 Bioassay Contaminant

A contaminant of concern selected from the case study site was used in aquatic invertebrate behavioural bioassays, to contribute to the ecotoxicological knowledge that the EWBS requires. This also satisfied the system's requirement for a metal contaminant, a class of contaminants not yet modelled, and which is necessary for the development of a comprehensive monitoring system. The initial contaminant choice was arsenic (Appendix E); however, following difficulties of its use in the laboratory, it was replaced by copper, another site-specific metal of concern.

4.1.3.1 Copper

Background

Copper is a transition metal that is stable in its metal state and often occurs in the environment in the oxidation states of copper (I) or cuprous ion and copper (II) or cupric ion. Metallic copper has an atomic weight of 63.546, a melting point of 1356 K and a boiling point of 2868K (Copper Development Association, n.d.). A common salt of copper, copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) has a water solubility of 316 g/L (WHO, 2004). Copper and its compounds are well distributed in the environment and are found frequently in surface and ground waters (Health Canada, 2002). Health Canada's GCDWQ recommend an objective guideline value of ≤ 1.0 mg/L.

Metallic copper has a number of properties such as malleability, durability, ductility, electrical and thermal conductivity, and alloying ability that make it suitable for widespread use in society (Mansilla-Rivera *et al.*, 1999). Copper is naturally abundant as a trace metal in rocks and minerals; however, greater uses of copper have increased its production and emissions into the environment. It is estimated that in almost a century, between 1900 and the 1980s, copper emissions increased 500-fold (Mansilla-Rivera *et al.* 1999). In 1981, Canada ranked fourth in worldwide copper production from mines with 8.33 percent of 8.3 million tonnes and sixth in the production of refined copper with 0.477 million tonnes. 36.6 percent of Canada's mining production occurred in Ontario (Health Canada, 1992). Copper is used for plumbing, for the production of electrical wire, for the manufacturing of alloys such as bronze and brass, for electroplating and for roofing. It is used in chemical manufacturing as a catalyst and for the removal of mercaptans in oil refining (Health Canada, 1992).

The amount of copper accessible in the environment varies greatly by geography and by the input of anthropogenic sources. Copper enters the soil, air, and water due to many anthropogenic activities. Copper integrated in sediments acts as a sink for the metal, and levels vary widely. In

1985, the Great Lakes Water Quality Board reported metal-contaminated sediments as a major concern for the Great Lakes, particularly in sites near industrial activity (Flemming and Trevors, 1989).

Ironically, copper is also an essential micronutrient to all life forms and is necessary in a range of metabolic processes in both prokaryotes and eukaryotes. While considered an essential element, copper does become toxic at increased concentrations (Flemming and Trevors, 1989; Mansilla-Rivera *et al.*, 1999). Therefore it is important to consider copper levels in the natural environment and its degree of bioavailability. The bioavailability of copper depends on the form taken by the metal. It must occur in its soluble form which is dependent on physiochemical factors such as pH, redox potential (E_h), soil or sediment type, water hardness and organic content. As these factors vary considerably in the environment, the toxicity of copper also varies (Flemming and Trevors, 1989; Health Canada, 1992). Dissolved metals include not only free metal ions but also ions that have formed complexes with organic and inorganic ligands (Welbourn, 2003). These complexes affect the mobility, bioavailability, and subsequent toxicity of the metal. The main dissolved inorganic complexes are chloro-, carbonato-, sulfato-, oxo- and hydroxo-. Complexation varies in freshwaters due to variations in the chloride concentration, pH, and alkalinity of the environment. Organic complexes are mainly stable formations between free metal ions and organic biological matter (Welbourn, 2003). Copper involvement in oxidation and reduction processes, in addition to adsorption/desorption and dissolution processes, causes changes to its speciation in water and sediments. Particulate forms of copper include oxides, sulphide precipitates, insoluble organic complexes, and copper adsorbed to clay or mineral solids. Soluble copper is that which passes through a small pore size filter (0.4 μ m) while colloidal matter consists of metal hydroxide precipitates and polypeptide material (Mansilla-Rivera *et al.*, 1999).

Various atomic spectrometry methods are used for the detection of copper in water, with inductively coupled plasma mass spectrometry having the lowest detection limit of 0.02 μ g/L (WHO, 2004). Removal methods to control copper in water include coagulation with aluminium or ferric salts which was predicted to have a 98% removal at pH 8, depending on the concentration of organic ligands. However, a study of 12 conventional water treatment plants in the U.S. found only a 49% copper reduction while other tests found no reduction in copper after conventional treatment (Health Canada, 1992). A more effective approach is lime precipitation and settling, or reverse osmosis and distillation (Health Canada, 1992).

Copper Uses

Copper has important uses in the chemical manufacturing, petrochemical processing, agriculture, and energy generation industries, all of which are extensive in the St. Clair River AOC, upstream from Walpole Island. Copper in the form of chemical compounds are used in these settings, often as copper salts, which act as reaction catalysts (West, 1982; Joseph, 1999).

Copper chloride is used in the petroleum industry for the catalytic oxidation and removal of mercaptan from oil and gas and is also used in ammoniacal solutions for the absorption of any carbon monoxide that may be present in a gas as an impurity. In the thermal energy generation industry, copper oxychloride added to coal produces a friable granular ash that can be readily removed, instead of burning to give hard masses of incombustible ash (West, 1982).

Copper is used extensively in agriculture and preservation as a fungicide, algacide, insecticide, and antimicrobial agent (Health Canada, 1992). Bordeaux mixture (copper sulphate, lime, water) is used to control approximately 300 diseases susceptible to copper-based fungicides. Other copper compounds are also used in the formulation of pesticides including copper oxide, copper chloride, and copper oxychloride. Copper carbonate is a fungicide for the treatment of wheat and sorghum seed and is also an intermediate in the production of other copper compounds. Copper, most commonly cuprous oxide in the form of powders and flakes, are used in paint formulations for the submerged portions of freshwater and marine structures to prevent biofouling. Copper is also used as a preservative for timber and fabric by making them resistant to insects and protected from fungus. There are three copper based products in use for the preservation of timber products—chromated copper arsenate (CCA), ammoniacal copper arsenate, and copper naphthenate. Both Canada and the U.S. have phased out the use of CCA in residential applications over the past decade but it is still in use for industrial and commercial applications (Joseph, 1999). Copper and various copper compounds are registered for use in pesticides in Canada. Canada's Pest Management Regulatory Agency (PMRA) pesticide database indicates that there are currently 34 pesticide applications with copper as an active ingredient and 96 registered products (PMRA, n.d.). The USEPA and WHO acute hazard rating for copper pesticides are varied but the most widely used form, copper sulphate, is classified as moderately hazardous, based on oral and dermal exposure concentrations for the LD₅₀ value in rats (Pesticide Action Network, 2010).

Organic and inorganic copper compounds fulfill an important catalytic role in the synthesis of organic chemicals which are essential to the manufacturing of a vast array of intermediate and end products in the chemical and plastics industry. Copper compounds are an important ingredient

of catalytic preparations for making a large number of organic compounds such as aldehydes, ketones, amides, carboxylic acids, and higher alcohols, which are subsequently used to synthesize polymers, pharmaceuticals, solvents, and food additives. Cupric oxide is used as a chemical intermediate in the production of synthetic fibres and semi-conductors and as a catalyst in the reduction of organic compounds. Cupric acetate is used in the rubber industry as a catalyst in a reaction for the vulcanization of rubber and related polymers (West, 1982; Joseph, 1999). Copper acetylide is used as a catalyst in the vinylation and ethynylation reactions of acetylene to produce the organic semi conductor, polyacetylene. Furthermore, through the discovery of organometallic copper compounds, a new field has opened up for the use of copper. Copper organometallic compounds are replacing magnesium organometallic compounds in organic synthesis for polymer production (Joseph, 1999).

Human Health Concerns

Copper is an essential element in human metabolism and is introduced mainly through food and drinking water (Health Canada, 1992). A minimum of 33 enzymes contain copper and function as redox catalysts or dioxygen carriers (Flemming and Trevors, 1989). Copper absorption in humans occurs mainly from the stomach and duodenum of the gastrointestinal tract. Approximately 80% of absorbed copper is bound to liver metallothionein and remainder is incorporated into cytochrome c oxidase or lysosomes (Health Canada, 1992). In spite of all the knowledge gained regarding copper metabolism in humans, there continue to be uncertainties in the exposure levels of copper and the levels at which effects may occur (Hancock and Pon, 1999). Acute copper poisoning symptoms include a metallic taste in the mouth, nausea, vomiting, diarrhoea, jaundice, and haemolysis. Terminal phases of poisoning include anuria, hypotension, and coma prior to death. These symptoms generally appear after 15-60 minutes and while limited chronic toxicity data exists, a dose of 5 mg/day results in gastrointestinal pain. The lowest observable effect level for copper occurred at 4mg/L, although background information on the study, such as amount of water consumed, sample collection, and analytical methods, is limited. The gastrointestinal effects of copper are influenced by exposure time and the concentration ingested and not just the total value consumed per day; however, a guideline value of 2 mg/day was established for copper in drinking water, which does not factor in supplemental intake from food (WHO, 2004). Copper concentrations in drinking water are exacerbated by the corrosion of copper pipes and copper alloy fittings, all of which is dependent on the physiochemical characteristics of the raw water (Hancock and Pon, 1999).

Copper was first regulated in 1993 by the WHO due to indications of chronic health effects. It was included in a list of parameters under "Health Significance," along with lead, arsenic, cadmium, and cyanide. The ruling came from copper's potential effects on infants, particularly those which were bottle-fed, and linked to a disease known as Indian Childhood Cirrhosis or Idiopathic Copper Toxicosis (Hancock *et al.*, 1999). Copper continues to be included on the provisional list of health significance parameters and currently under the WHO Rolling Revision of Drinking Water Quality Guidelines, they are investigating recent studies in rabbits which suggest a link between copper in drinking water and Alzheimer disease (WHO, 2010). Water supplied to the rabbits was well below the current WHO guideline of 2 mg/L; however, there are questions as to whether rabbits are an appropriate model. Additionally, there are suggestions to review the guideline value and text on copper with regard to toxicity in infants fed bottled formula (WHO, 2010). While copper has not been reviewed for carcinogenic effects, two studies reported an increased incidence of granulomas in the liver and malignant lung tumours in vineyard workers in France, Portugal, and Italy. The individuals were exposed to copper sulphate and lime sprays to control mildew. However, quantitative estimates could not be made from the data and the US EPA has classified copper as a Group D compound—inadequate data in humans and animals (Health Canada, 1992; Joseph, 1999).

A number of high risk groups for copper ingestion include individuals with glucose-6-phosphate dehydrogenase deficiencies and those with Wilson's disease, an inborn error whereby copper does not metabolize and accumulates in the brain, liver, and kidneys (Health Canada, 1992; WHO, 2004). Some evidence has shown that asymptomatic carriers of a defective Wilson disease gene also have abnormal retention of copper, although data are currently limited. Heterozygous carriers occur in an estimated 1 in 100 individuals and are therefore a potential population of concern for copper exposure in food and drinking water. Indian childhood cirrhosis, endemic Tyrolean infantile cirrhosis, and idiopathic copper toxicosis are complex disorders originating from genetic, developmental, and environmental factors but are also possibly linked to poor biliary excretion of copper. These disorders, resulting in enlarged liver, elevated copper in hepatic cells, pericellular fibrosis, and necrosis, generally lead to death (WHO, 2004). Uncertainty remains as to the long-term effects of copper exposure on these high risk populations, a group whose safety must be considered when establishing guidelines.

Copper in Aquatic Ecosystems

The vulnerability of aquatic environments to trace metal pollution is increased as a result of direct waste inputs and the added input from non-point sources such as runoff and atmospheric

deposition. Trace metals can enter the system via sewage discharges, urban and agricultural runoff, domestic and industrial wastewaters and direct discharges, surface runoff, and from natural processes in groundwater and sediments (Nriagu, 1990). Atmospheric sources of copper are removed and deposited back on earth via gravitational settling, dry deposition, rain, and snow (WHO, 2002).

The processes which guide oxidation and reduction of metals in aquatic environments are of great interest from a pollution aspect as these processes cycle metals and are important in determining the metal species present (Mansilla-Rivera *et al.*, 1999). The speciation of copper in water is important as it is the specific form of copper, not just its concentration that determines its bioavailability and therefore its toxicity. The two oxidation states of copper in natural water are the cupric ion and cuprous ion. The cupric ion predominates in natural waters and forms stable complexes with both organic and inorganic ligands. The cuprous ion is unstable in aqueous solution and rapidly changes to the cupric ion (Mansilla-Rivera *et al.*, 1999).

It has been demonstrated that it is the free cupric ion that is most toxic to organisms and that most cupric salts readily dissolve in water to give the cupric ion in the hydrated form of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ (Mansilla-Rivera *et al.*, 1999). In some cases, other inorganic copper forms can be toxic such as CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$ (Mansilla-Rivera *et al.*, 1999). In the environment, copper partitions into three phases: aqueous (free ionic and soluble complexes); solid (particulates, soils and sediments); and biological (adsorbed and incorporated). The form of copper, its bioavailability, and mobility in water, are determined by three main processes: complexation to ligands, precipitation of associate ions, and adsorption to living and non-living particulate matter. The main inorganic ligands in most natural freshwaters are hydroxyl and carbonate ions. Organic ligands include nitrogenous excretion products, amino acids, polyphenols, and humic and fluvic acids, which reduce the toxicity of copper (Flemming and Trevors, 1989).

Desorption of copper from the sediments is a long-term concern to aquatic life, even after sources of pollution have been removed. The concentrations of copper or the adsorbent, pH, as well as the type and concentrations of ligands and competing ions in solution can all affect the strength of adsorption. Studies have shown that the presence of certain ligands that form stable soluble copper complexes (copper-nitrogen) and high concentrations of competing cations (Mg^{2+} , Ca^{2+}) will cause desorption of copper from sediments. Another factor which may affect partitioning and increase levels of dissolved copper is the competitive presence of dissolved organic carbon. Kramer *et al.* (2004) found that the presence of natural organic matter such as humic and fulvic acids strongly complex with free cupric ions and decrease the bioavailability, uptake, and ecotoxicity of

copper in *D. magna*. In humic-rich waters, the free cupric ion concentration was estimated at $\approx 10^{-11}$ M, whereas in medium to low dissolved organic carbon waters the $[\text{Cu}^{2+}]$ was $\approx 10^{-10}$ M.

In comparison to mammals, copper is increasingly toxic to aquatic life and increases sensitivity in fish and invertebrates depending on the surface-area-to-volume ratio, respiratory rates, and flow rates over gills. As these factors increase, copper uptake is also increased. Sub-lethal effects in salmon, such as altered growth, reproduction, and behaviour were detected at concentrations of $5\mu\text{g/L}$ while another study indicated some lakes to be devoid of fish at copper concentrations greater than $60\mu\text{g/L}$ (Flemming and Trevors, 1989). Copper sulphate has been used widely as an algicide. An *in situ* study applied 0.01 mg/L of copper to a lake, causing a temporary reduction in chlorophyll which subsequently recovered in five days. An increase to 0.04 mg/L however resulted in further reduction of chlorophyll and no indication of phytoplankton recovery (Flemming *et al.*, 1989). The high toxicity of copper to phytoplankton has implications for aquatic system ecology as phytoplankton are primary producers and, once removed, can seriously disrupt the integrated food web, causing an increase in problems up the trophic chain.

Copper and Past Bioassays using Daphnia magna

The form of copper which is toxic to aquatic organisms is generally the soluble form. The most toxic forms in fish and *D. magna* were the cupric ion and inorganic complex, CuOH^+ ; however, the hydrolysis product, $\text{Cu}_2(\text{OH})_2^{2+}$, was also toxic in some cases. Carbonate-copper complexes did not appear to be toxic to fish or *D. magna* (Mansilla-Rivera *et al.* 1999). While precipitated forms of copper (oxides, phosphates, and carbonates) are assumed to be non-toxic and unavailable, precipitated copper was found to be toxic to algae. Copper bound to organic ligands is less available and is therefore generally less toxic in aquatic organisms. Certain ligands have been found to enhance toxicity: serine and citrate in the case of estuarine bacteria; copper citrate in the case of algae; and copper bound to amino acids in the case of *Daphnia*. The increase in toxicity is due to facilitated metal uptake by the organisms or rapid assimilation of the organic compound (Mansilla-Rivera *et al.* 1999).

The behavioural effects of copper have been investigated using *Daphnia*. Michels *et al.* (1999) found that *Daphnia* exhibited significantly less phototactic behaviour in the presence of sublethal concentrations of copper. The detection limit reported for copper, using phototactic behaviour, was 0.045mg/L , lower than the LC_{50} (24h) value of 0.054mg/L . Untersteiner *et al.* (2003) found that the average time of swimming participation and average swimming velocity decreased with increasing copper concentration and exposure time. At six hours of exposure, the

EC₅₀ value for the behavioural parameter swimming velocity was 30.35 ppb, lower than common LC₅₀ values. Flicklinger *et al.* (1982) evaluated the chronic effects of filtration rate and negative phototactic behaviour of *D. magna* to concentrations at and below the no-effects level of 40 µg/L. Organisms exposed to ≥20 µg/L of copper had a reduction in filtration rate and body length of neonates, and exhibited negative phototaxis. Hodsen *et al.* (1979) summarized the LC₅₀ (48 h) values for many invertebrates and found a wide range in the acute toxicity values for *Daphnia* species, ranging between 5 and 86 µg/L.

Rationale for Use of Copper

Copper is toxic to aquatic life and presents negative health affects in humans when ingested over 4mg/L. The most toxic form of copper is the cupric ion, which is the most prevalent form in water. It can present significant risk to consumers, particularly those of high-risk groups. Copper emissions into the aquatic environment have increased over time. While copper may become incorporated into sediments, this form does not act as a permanent sink and therefore even historical deposits of copper pollution can be reintroduced into the water column. An EWBS may contribute to the early detection of copper and the contaminant class of trace metals. Testing of the sub-acute behavioural responses of *D. magna* is important in the determination of the organism's suitability for the detection of low and pulse levels of contaminant classes, including metals.

Copper as copper (II) sulphate was chosen for use in this bioassay experiment for a number of reasons. The heavy metal was identified as a contaminant of concern from the Walpole Island study site, following extensive research into the site's precarious location downstream from heavy industrialization. The choice of copper also satisfied the metal contaminant requirement necessary for the development of the EWBS. Additionally, copper (II) sulphate is the form of copper commonly used in past research (Winner, 1985; Kangarot *et al.*, 1986; Cooper *et al.*, 2009) and copper salts readily dissolve in water to give the free cupric ion which is recognized as being the most toxic form to aquatic life, and predominates in natural waters. LC₅₀ (48h) values previously obtained for *Daphnia* ranged from 37.3-93 µg/L (Kangarot *et al.*, 1986; Cooper *et al.*, 2009).

4.2 Methodology

4.2.1 *Daphnia magna* Culturing

Daphnia magna were cultured and maintained following protocols developed by Environment Canada (1996), the USEPA (2002) and the Organisation for Economic Co-operation and Development (2004). Two cultures of *D. magna* were maintained in two glass 9-L aquaria. Dechlorinated tap water was used for culture water after sitting aerating for 48 hours. Water

temperature remained at room temperature (18-20°C) throughout the entire experimental period. An aquarium bubbler was used to gently aerate water and maintain dissolved oxygen levels. The aquaria were housed beneath a laminar-flow hood (Canadian Cabinets, model number H4-MW-97-C-30) to prevent dust and debris from settling into the *Daphnia* cultures. Under the laminar hood, fluorescent lights with a light intensity of approximately 500 lux operated on a timed light: dark cycle of 16: 8 hours.

D. magna were fed three times per week a mixture of Roti-Rich Invertebrate Food (Ward's Natural Science, 88V5910) and *Pseudokirchneriella subcapitata* algae. During each feeding period 500µl of the invertebrate food was and periodic supplementation of *P. subcapitata* was administered. Feeding volumes were adjusted according to visual monitoring of water clarity, and the amount of algae consumed. Excess food and debris were removed using a 1.5mL sterile transfer pipette and dechlorinated water was added three times a week to compensate for water loss due to evaporation. As populations within the aquaria grew to numbers greater than 200 individuals, neonates, or offspring less than 24 hours old, were transferred to a new aquarium using a sterile transfer pipette to avoid overcrowding and stress.

4.2.2 Washing Procedures

Prior to use, all glassware, including test vessels and aquaria and measuring equipment, were thoroughly washed to remove traces of chemicals from previous use so not to affect the test organisms. The wash procedure was based on those described by the USEPA (2002). Glassware was initially soaked for 15 minutes in Extran soap solution and scrubbed to remove residue. Remaining soap was rinsed with tap water, and washed in 10% v/v hydrochloric acid, which was subsequently rinsed three times using distilled water. Glassware was then inverted to dry prior to use.

4.2.3 Metal Solution

Metal stock solutions were prepared on the day of each experiment by dissolving analytical grade copper (II) sulphate in distilled water for a concentration of 1.0g/L.

4.2.4 Behaviour Bioassay

Swimming behaviour bioassays using *D. magna* were exposed to four treatments including test concentrations of 50, 100, and 500ug/L, determined from literature bioassays, and a reference treatment. 200mL square glass test vessels were used, containing 150mL of each test solution. Previous studies indicated the LC₅₀ values for copper and *Daphnia* ranged from 37.3-93µg/L (Kangarot *et al.*, 1986; Cooper *et al.*, 2009). Hodsen *et al.* (1979) summarized the LC₅₀ (48 h) concentrations for many invertebrates and found a wide range in values for *Daphnia* species between 5 and 86ug/L. An increased concentration was also chosen in order to determine if

elevated concentrations of copper would greatly impact swimming behaviours and also to aid in the presentation of concentration and time dependencies.

As required by Environment Canada protocol, neonates were used for the test. Neonates were removed from the culture approximately a day prior to the bioassay and placed in a large beaker. They were used on the following day when they were approximately 24 hours old (Environment Canada, 2000). Five daphnids were placed in each test vessel using appropriate transfer procedure and ten replicates of each test concentration were used in the bioassay. Additionally, ten reference treatments containing dechlorinated water were used to examine behaviour under normal conditions. Vessels were arranged randomly in order to reduce possible discrepancies due to external factors such as lighting, temperature, and other abiotic factors within the laboratory.

The changes in swimming behaviour were determined based on personal observations throughout the duration of the experiment. These observations were made after 0, 1, 2, 3, 4, 5, and 6 hours of exposure with approximately three minutes of viewing time per vessel. Three behavioural parameters were observed: 1) immobility of the daphnids; 2) changes in the organisms swimming height in the water column; and 3) changes in the swimming style.

Normal, active daphnids display a high level of activity and are constantly swimming in the water column. Immobility is classified as no visible movement or swimming activity 15 seconds after stirred with a glass rod.

Normal daphnid swimming behaviour is described as spending no extended time at the surface or the bottom of the vessel, and using the entire water column for the primary purpose of foraging for food patches. Affected behaviour shows changes in swimming height in the water column. There is an overall decline in vertical movement; the majority of daphnids remained at the bottom of the vessel and only a few remained stuck at the top, possibly due to their inability to overcome surface tension. Often, individual daphnids rest at the bottom as they try to conserve energy that has been lost due to overcoming toxic effects.

Normal daphnid swimming style is classified as swimming in straight, directional lines and exhibiting slight vertical displacements called hopping. Affected changes in swimming style are characterized as: swimming with jerky, short strokes as individuals attempt to keep themselves propelled in the water; the presence of looping and twirling behaviour; and using the vessel bottom for propulsion.

Changes in individual behaviours over time and concentration were evaluated by first determining what percentage of the organisms displayed the altered behaviour in each replicate,

then averaging all replicates of a test concentration. A non-parametric Kruskal- Wallis test was then performed to determine if there was a significant difference between the four treatments in the overall bioassay model. Additionally, a non-parametric Mann- Whitney test was performed to determine if each individual test concentration had an effect on the individual movement behaviours when compared to the reference treatment over the six-hour experimental period. As this experiment used data from discrete time points, statistical differences were calculated for three representative time points in the six- hour experiment, at times 2, 4, and 6 hours.

4.3 Results and Discussion

The use of swimming behaviour as a sensitive endpoint to sublethal metal concentrations such as copper and cadmium has been demonstrated by numerous studies (Wolf *et al.*, 1998; Micheals *et al.*, 1999; Kieu *et al.*, 2001). Changes in swimming behaviour occur as a result of stress on the physiology of the organism. Previous researchers have ranked a number of potentially useful behavioural endpoints, three of which were chosen for use in the current bioassay experiments. Immobility, swimming height in the water column and swimming style were examined in *Daphnia magna* behaviour (Marshall, 2009), and their utility in the development of an EWBS is discussed. Changes in swimming behaviour were observed at exposures to varying concentrations (50µg/L, 100µg/L, and 500µg/L) of copper as a contaminant.

4.3.1 Immobility

In the copper bioassay, at time (t) = 2, there was no significant difference when comparing immobility of organisms between the reference and the 50 µg/L treatment (p= 1.000), the 100 µg/L treatment (p= 1.000), and the 500 µg/L treatment (p= 0.062). At this time, immobility was only noted in the 500 µg/L treatment (Figure 11). At t=4, no significant difference was observed when comparing the number of organisms immobilized in the reference and the 50 µg/L treatment (p= 1.000) or 100 µg/L treatment (p= 0.167). A significant increase was seen in the highest concentration, the 500 µg/L treatment (p= 0.000). There were no changes in immobility noted in the reference or 50 µg/L treatment (Figure 11). At the final time point, t=6, there was a significant difference between the reference and all treatments: 50 µg/L treatment (p= 0.009), 100 µg/L treatment (p= 0.008), and 500 µg/L treatment (p= 0.000).

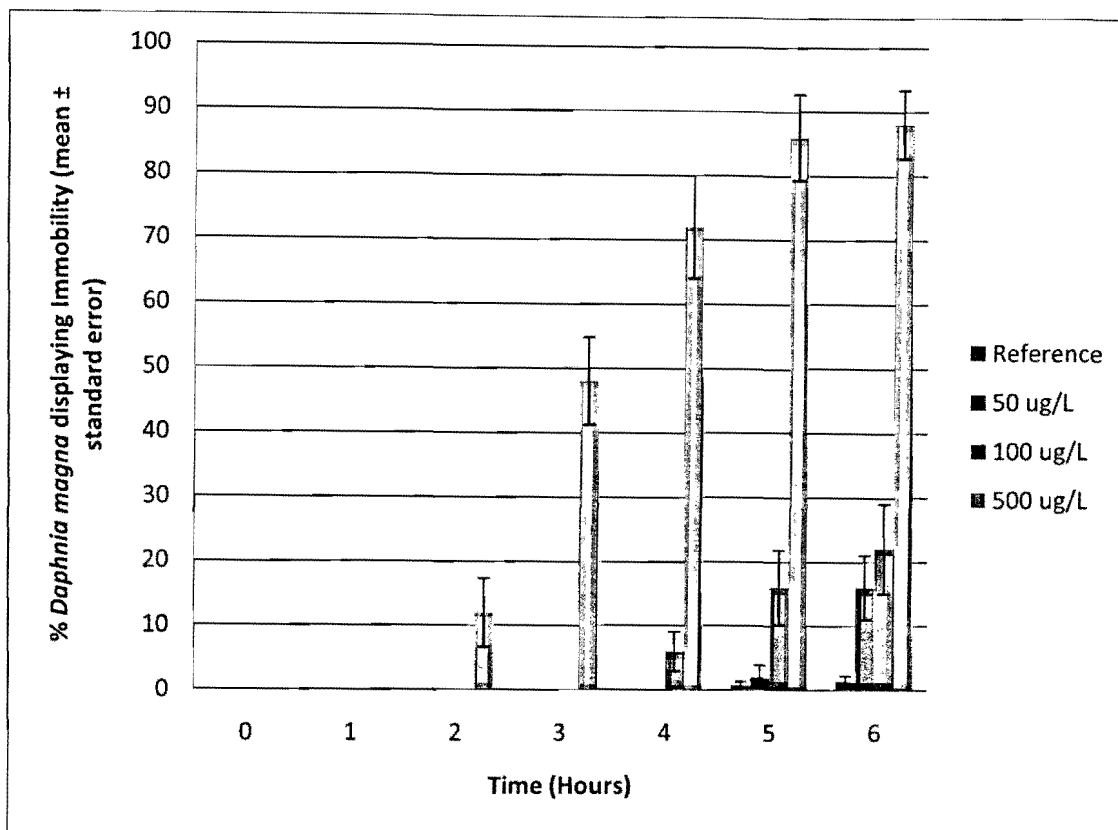


Figure 11: Average percentage of immobilized *Daphnia magna* in three treatments of copper and a reference, over a six hour period.

Organism immobility was noted in response to exposure to all treatments of copper (Figure 11). The majority of reference organisms demonstrated activity throughout the experiment, with a single case of immobility occurring in the latter hours. Responses were concentration- and time-dependent; higher concentrations of copper resulted in a greater percentage of organisms immobilized and an earlier onset of immobility. A concentration- and time-dependent response within a short timeframe indicates that immobility as a daphnid response to copper exposure may be highly appropriate for future modeling in the development of EWBS. Baillieul and Blust (1999) suggest that, for routine measurements of sublethal effects of copper stress, immobility as a response is useful because this behaviour displays sensitivity to the metal and its determination requires less expertise than more complex behaviours. However, the result of the present study possibly indicates that the immobility response does not present itself for four or five hours, unless environmental concentrations are high. This time frame may not allow adequate warning time for users of the EWBS.

There are a number of potential causes for *Daphnia* immobility. Swimming activity is closely related to the energy status of *Daphnia* and is highly energetically demanding. Changes in the

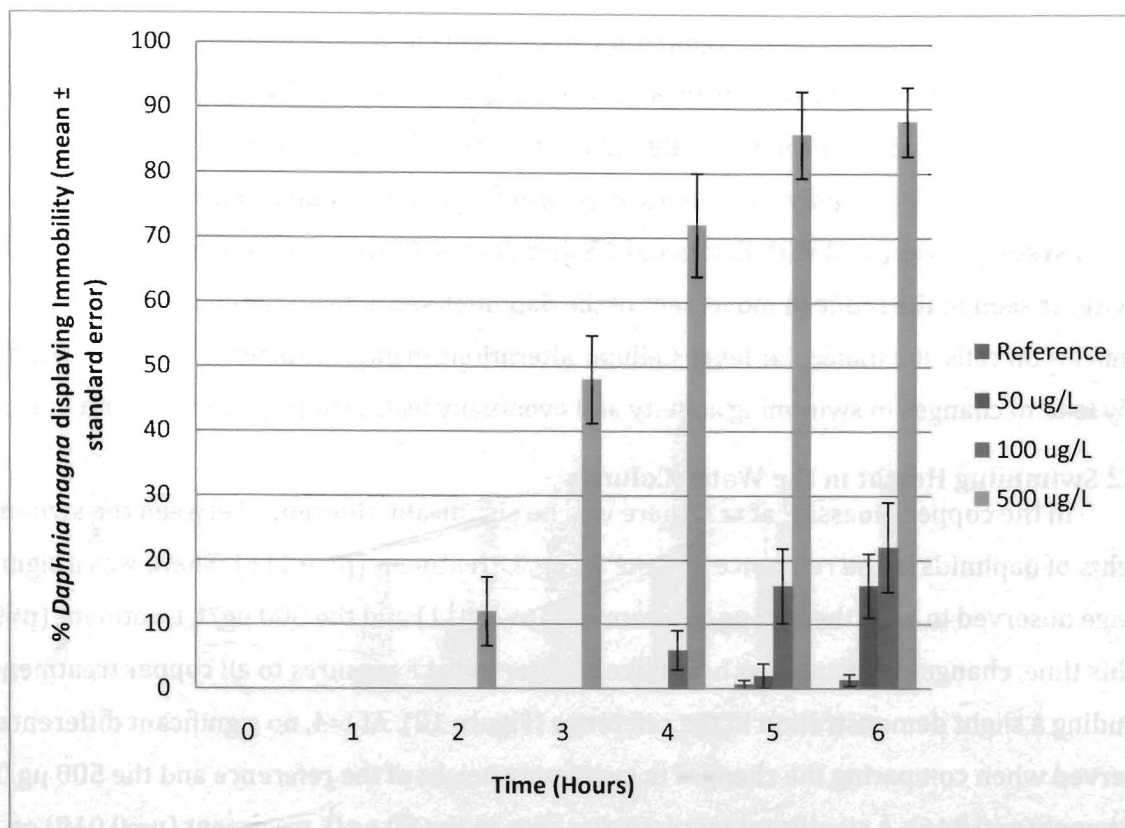


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external environment, natural (pH, temperature) or chemical, induce stress on the organisms. Increasing energy to compensate for the effects of stress on essential biological processes limits the available energy for activities not directly related to survival, such as swimming (Wolf *et al.*, 1998; Schmidt *et al.*, 2005). Secondly, immobility may result from direct impact on the muscle and sensory systems associated with locomotion. Schmidt *et al.* (2005) attribute inhibition of muscle activity, as seen in the reduced movement of the daphnids secondary antennae, to the effect of chemicals on cells at a molecular level. Cellular alterations in enzyme activity, for example, could likely lead to changes in swimming activity and eventually lead to immobility (Schmidt *et al.*, 2005).

4.3.2 Swimming Height in the Water Column

In the copper bioassay, at $t=2$, there was no significant difference between the swimming heights of daphnids in the reference and the 50 $\mu\text{g/L}$ treatment ($p=0.116$). There was a significant change observed in both the 100 $\mu\text{g/L}$ treatment ($p=0.011$) and the 500 $\mu\text{g/L}$ treatment ($p=0.001$). At this time, changes in swimming height were observed at exposures to all copper treatments, including a slight demonstration in the reference (Figure 12). At $t=4$, no significant difference was observed when comparing the changes in swimming height of the reference and the 500 $\mu\text{g/L}$ treatment ($p=0.246$). A significant increase was seen in the 50 $\mu\text{g/L}$ treatment ($p=0.010$) or 100 $\mu\text{g/L}$ treatment ($p=0.000$). At this time, changes in swimming height were observed at exposures to all copper concentrations, including a slight change in the reference (Figure 12). At $t=6$, no significant change was observed in the swimming height of the organisms in the 500 $\mu\text{g/L}$ treatment ($p=0.450$). There was a significant difference noted between the reference and the 50 $\mu\text{g/L}$ treatment ($p=0.028$) and the 100 $\mu\text{g/L}$ treatment ($p=0.000$).

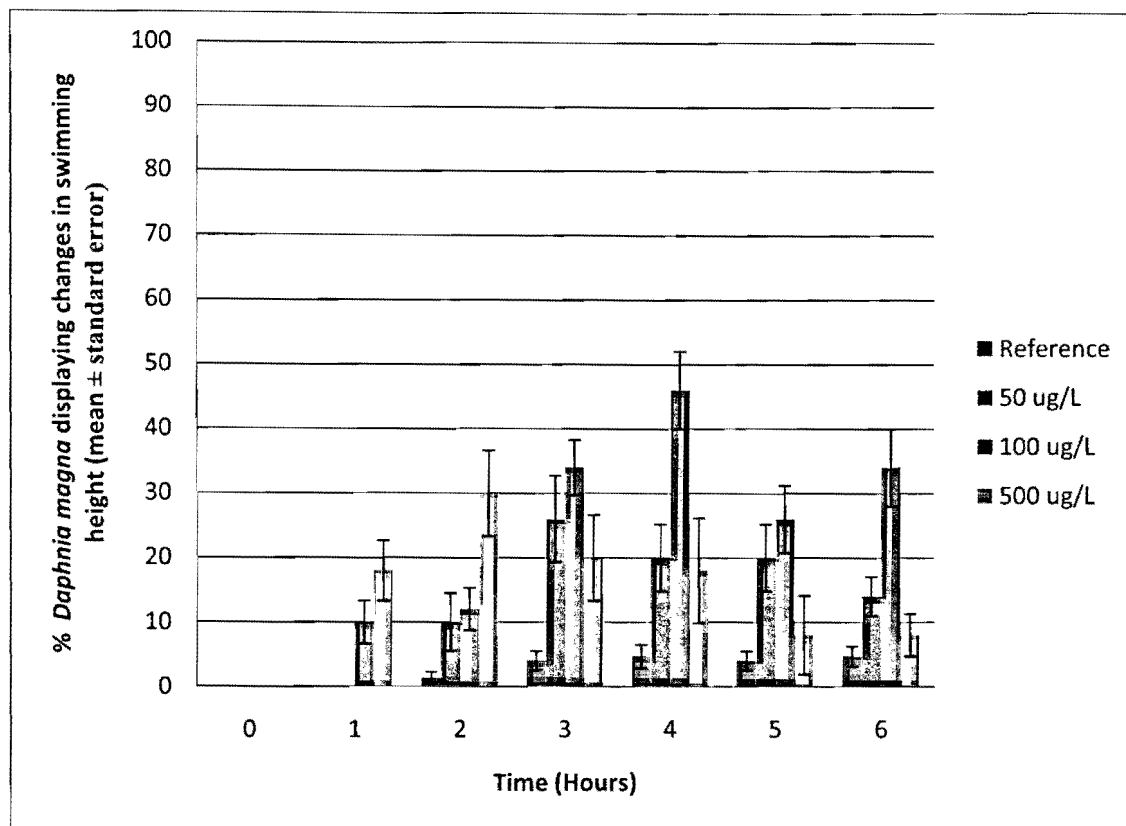


Figure 12: Average percentage *Daphnia magna* displaying changes in swimming height in three treatments of copper and a reference, over a six hour period.

An increase in the average percentage of organisms showing changes in swimming height in the water column was seen in all copper treatments during the first three hours of the experiment. After this time point, the average number of organisms showing changes in swimming height decreased for the lowest and highest concentrations (50µg/L and 500µg/L) and fluctuated for the median concentration (100µg/L). Therefore, no consistent pattern of time or concentration dependence was noted after three hours with respect to the percentage of organisms affected. The timeframe from the start of abnormal behaviour to the peak of the behaviour showed a short-term, sub-acute response to copper exposure. However, after the peak in behaviour, copper exposure continued to increase and changes in swimming height as an endpoint became less precise. At the highest copper concentration, it was particularly evident that the number of organisms showing changes in swimming height decreased after three hours of copper exposure. This was related to the immobilization of the organisms. As exposure time increased, more organisms in the copper treatment became immobilized and were therefore unable to move in the water column. This indicates that changes in swimming height in the water column may be a good indicator of high concentrations of copper following short-term exposure, but after three hours of exposure

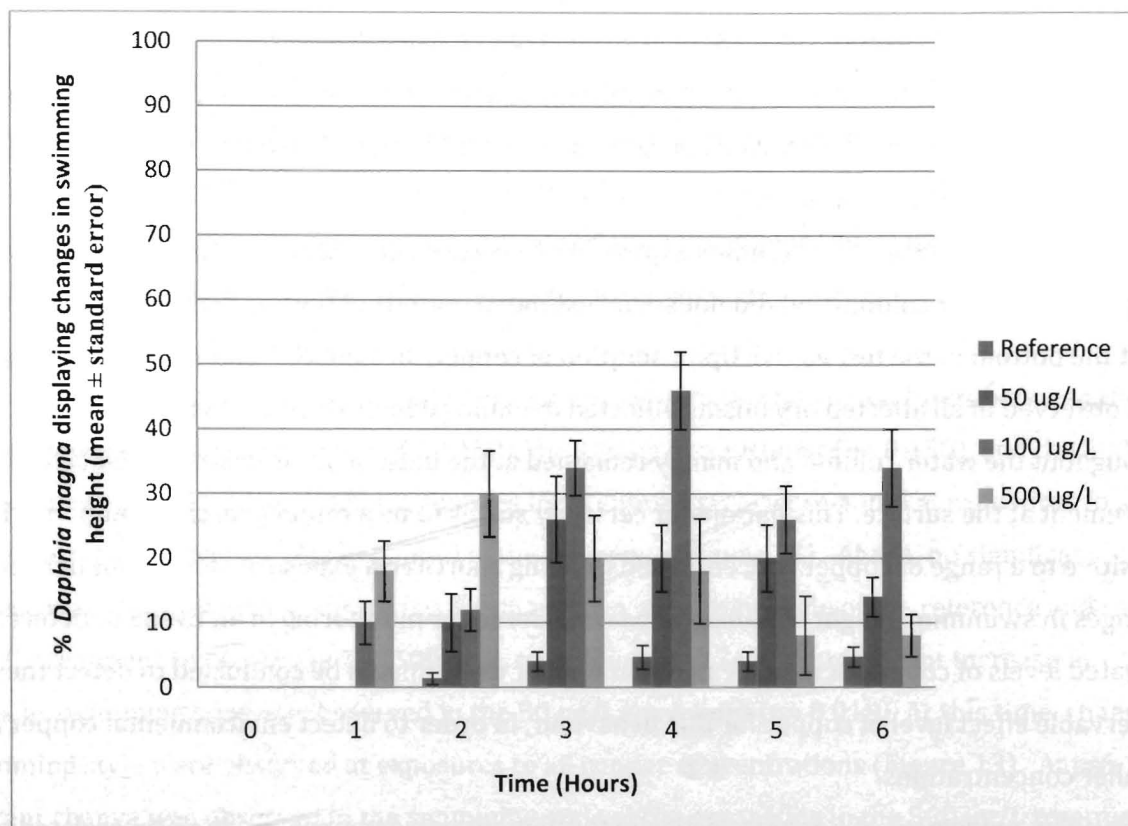


Figure 12: Average percentage *Daphnia magna* displaying changes in swimming height in three treatments of copper and a reference, over a six hour period.

An increase in the average percentage of organisms showing changes in swimming height in the water column was seen in all copper treatments during the first three hours of the experiment. After this time point, the average number of organisms showing changes in swimming height decreased for the lowest and highest concentrations (50µg/L and 500µg/L) and fluctuated for the median concentration (100µg/L). Therefore, no consistent pattern of time or concentration dependence was noted after three hours with respect to the percentage of organisms affected. The timeframe from the start of abnormal behaviour to the peak of the behaviour showed a short-term, sub-acute response to copper exposure. However, after the peak in behaviour, copper exposure continued to increase and changes in swimming height as an endpoint became less precise. At the highest copper concentration, it was particularly evident that the number of organisms showing changes in swimming height decreased after three hours of copper exposure. This was related to the immobilization of the organisms. As exposure time increased, more organisms in the copper treatment became immobilized and were therefore unable to move in the water column. This indicates that changes in swimming height in the water column may be a good indicator of high concentrations of copper following short-term exposure, but after three hours of exposure

immobility becomes a more sensitive indicator of copper stress. These results correspond with those obtained by Micheals *et al.* (1999). Sublethal concentrations of Cu^{2+} in a standard medium cause a linear decrease in phototactic behaviour of daphnids after 3.30 hours with the strongest relationship seen after four hours.

During the bioassay, daphnids exposed to reference conditions moved throughout the height of the water column and did not spend extended periods of time at the surface of the water or at the bottom of the test vessel. Upon addition of copper, an overall decline in vertical movement was observed in all affected organisms. Affected daphnids demonstrated less movement throughout the water column and mainly remained at the bottom of the vessel or displayed little movement at the surface. This parameter certainly seems to be a rapidly-reached endpoint that is sensitive to a range of copper concentrations, during short-term exposure. It is recommended that changes in swimming height of *D. magna* be considered for monitoring in an EWBS to detect elevated levels of copper. It is suggested that further experiments be conducted to detect the lowest observable effect level of copper for this behaviour, in order to detect environmental copper at smaller concentrations.

The movement of *Daphnia* vertically throughout the water column is closely related to diel vertical migration and phototaxis. Diel vertical migration is an important component of zooplankton swimming behaviour in which the organism moves deeper in the water column during the day and rises to the surface during the night (Dodson *et al.*, 1995). This has advantages for feeding—to take advantage of warmer surface waters, and for predator avoidance, as *Daphnia* are less likely to be seen at the surface at night. Diel vertical migration has been observed in previous studies in the presence of predator smells (kairomones), which anthropogenic chemicals have been known to mimic (Dodson *et al.*, 1991; Micheals *et al.*, 1999; Kieu *et al.*, 2001). Other studies have also observed that *Daphnia* spatial orientation and phototactic response is changed when exposed to sub-lethal concentrations of chemicals (Dodson *et al.*, 1995).

Numerous studies have recommended the use of phototactic behaviour of *Daphnia* to detect sub-lethal concentrations of contaminants (Martins *et al.*, 2007; Micheals *et al.*, 1999). This behaviour is an oriented direction towards a light source. A decrease in light intensity from above will cause the daphnids to ascend and a decrease will lead them to return lower in the water column (Flicklinger *et al.*, 1982; Kieu *et al.*, 2001; Martins *et al.*, 2007). This response is a result of integrated effects on the nervous and muscular system (Martins *et al.*, 2007). Schmidt *et al.* (2005) observed that a typical reaction of daphnids under chemical stress was a rapid change in the preferred swimming depth, to the surface, followed by sinking to the bottom of the test vessel. They

saw a relationship between the position at the bottom of the water column and the increasing number of daphnids with very limited antennal movement. These losses of biological function are suggested to be a result of inhibition or activation of certain enzymes (Schmidt *et al.*, 2005). Researchers have found the behaviour of daphnids to become significantly less phototactic in the presence of sublethal concentrations of copper and have recommended its use for continuous biomonitoring (Flickinger *et al.*, 1982; Micheals *et al.*, 1999; Kieu *et al.*, 2001).

4.3.3 Swimming Style

At t=2, there was no significant difference in the swimming style of daphnids between the reference and the 50 µg/L treatment (p= 0.450), the 100 µg/L treatment (p= 0.450), and the 500 µg/L treatment (p= 0.209). At this time, changes in swimming style were noted at exposures to all copper treatments as well as slight changes in the reference (Figure 13). At t=4, no significant difference was observed when comparing the changes in swimming style of the reference and the 100 µg/L treatment (p= 0.363) or the 500 µg/L treatment (p=0.363). A significant increase in changes in swimming style was observed in the 50 µg/L treatment (p= 0.018). At this time, changes in swimming style were observed at exposures to all copper concentrations (Figure 13). At t=6, no significant change was observed in the swimming style of the organisms in the 500 µg/L treatment (p= 1.000) or the 50 µg/L treatment, although significance was quite close (p=0.062). There was a significant change noted between the reference and the 100 µg/L treatment (p= 0.018). Changes in swimming style were only observed in the 50 µg/L and 100 µg/L treatments at this time point (Figure 13).

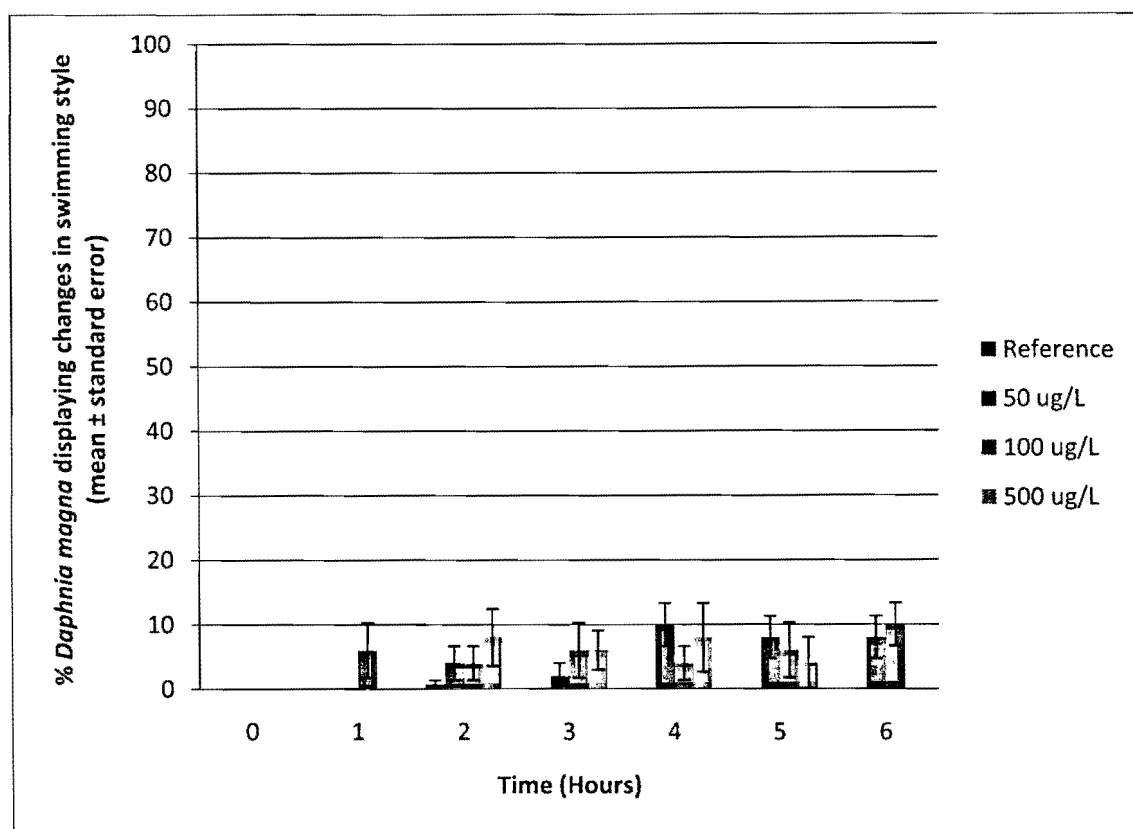


Figure 13: Average percentage *Daphnia magna* displaying changes in swimming style in three treatments of copper and a reference, over a six hour period.

It is difficult to draw conclusions regarding the applicability of changes in swimming style for use in an EWBS due to the overall low percentage of changes observed in all of the copper treatments (Figure 13). There was no relationship observed over concentration or time and therefore this behaviour cannot be recommended for the detection of copper in an EWBS. Changes in the swimming style of daphnids were observed as short, jerky strokes and erratic directional movements. Also included was spinning behaviour and using the bottom of the test vessel for propulsion.

Previous studies have identified components of swimming behaviour presented by daphnids upon exposure to acutely toxic levels of contaminants. When undisturbed, *Daphnia* typically swim by hopping as indicated by the number of antennae beats per second. Movement through an aqueous medium requires the power to resist sinking which comes from muscle strength opposing the force of gravity and sinking velocity (Dodson *et al.*, 1991). The spinning response is characterized by a tendency to swim quickly and erratically in a horizontal plane rather than using normal hopping behaviour (Dodson *et al.*, 1991; Dodson *et al.*, 1995). Spinning behaviour has most likely adapted as "escape" behaviour and it has been observed by daphnids

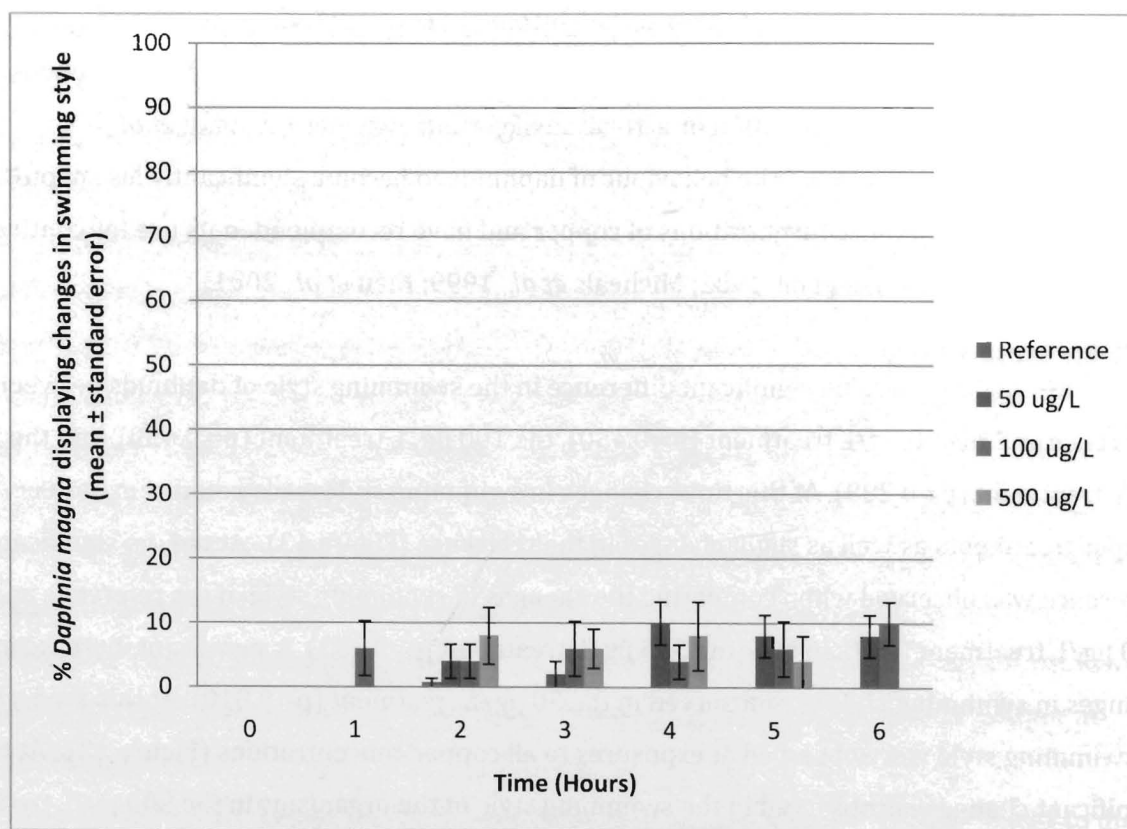


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when escaping fish (Dodson *et al.*, 1995). However, spinning quickly begins to reduce energy resources. In a study using cyclopoid copepods, the energy expended by violent power strokes in escape reactions is about 400 times that of a normal, undisturbed copepod swimming behaviour (Dodson *et al.*, 1995). This has important implications for survival as it increases encounter rates with predators and reduces foraging efficiency. Spinning is thought to be a representation of non-adaptive symptoms from impaired central nervous system function, induced by predator kairomones or anthropogenic chemicals (Dodson *et al.*, 1995).

Upon exposure to a contaminant, the potential response of an organism is a change in its behaviour due to damage to its visual or chemoreceptors (Ren *et al.*, 2009). The first behavioural response of organisms to stress is avoidance behaviour. It is an adaptation behaviour by which organisms try to escape the pollution source using higher behaviour strength. Normal escape behaviour involves short bursts of swimming with a few quick, powerful hops (Dodson *et al.*, 1995) and can possibly explain swimming behaviour characterized as erratic with the use of jerky, short strokes. Avoidance is an important defence mechanism but cannot be maintained for long periods of time as it requires excessive amounts of energy. If a stress is drastic, continued exposure will become incompatible with life and the organism will lose mobility (Ren *et al.*, 2009).

A decrease in swimming velocity is identified as one of the most useful parameters for measuring swimming behaviour in *Daphnia* (Dodson *et al.*, 1995; Baillieul *et al.*, 1999; Untersteiner, Kahapka and Kaiser, 2003). Velocity is an important component of locomotion that is controlled by the muscle activity of the secondary antennae and is related to the organism's ability to resist sinking in the water column. Since locomotion involves coordination with the nervous and muscular systems, it is predicted that copper has integrative effects (Untersteiner *et al.*, 2003). A study, using the metal cadmium, showed that the beat frequency of the secondary antennae, which is responsible for swimming activity in *Daphnia*, decreased with increasing cadmium concentrations due to neurological failure (Baillieul *et al.*, 1999). The decrease of velocity can also be explained as a result of reduced fitness from the effect of the metal on metabolism, resulting in less energy produced (Wolf *et al.*, 1998). This has important implications for survival as it increases encounter rates with predators and decreases foraging efficiency.

The organism's use of the bottom of the vessel for propulsion can be explained by its reduction in energy due to stress on its physiology. The organism has less energy for muscle activity that would be used for locomotion and for overcoming friction of water when swimming. Using the vessel for propulsion is an attempt to overcome this obstacle, often followed by resting at

the bottom. Schmidt *et al.* (2005) observed that decreased motility resulted in a sinking of daphnids to the bottom in order to conserve energy.

4.4 Summary and Conclusion of *Daphnia magna* Behavioural Bioassay

The results of the *Daphnia* swimming behaviour bioassays reveal that not all behaviours are useful for detection of copper sensitivity. The concentration and the exposure time affect the reliability of the responses as a modelling component for a multi-organism EWBS. The behavioural responses showing the greatest sensitivities can be considered as those representing the greatest stress responses and should be considered first for integration into an EWBS.

Immobility of organisms in response to copper was concentration- and time-dependent, presenting a clear endpoint with short-term exposure. However, in comparison to other behavioural endpoints, immobility does not occur until later in the experiment, unless at the highest test concentration and therefore does not give sufficient warning time to the systems users.

Changes in swimming height in the water column manifested themselves very early after initial copper exposure. This indicates a very short-term response that can provide warning to users more quickly than using immobility responses. However, the response is only concentration and time dependent up to a certain point, after which the percentages of changes in swimming height become erratic and less precise; therefore, immobility becomes a more sensitive response to copper stress.

It is difficult to conclude the effectiveness of change in swimming style as a response to copper stress. This behaviour was not observed in a sufficient percentage of *Daphnia* at any of the test concentrations and there was no concentration or time dependence observed.

In conclusion, it is useful to rank, in order of importance, the three behavioural endpoints of swimming height, immobility, and swimming style for potential use in an EWBS. Change in swimming height is considered the most beneficial, as demonstrated by its early manifestation after initial copper exposure. Immobility becomes the second most useful endpoint since its dependence on copper concentration and time takes longer to provide sufficient warning and is therefore less useful. The third endpoint, changes in swimming style, is not recommended for use, at least not for detection of copper contaminants, as there was no conclusive behaviour change in any of the test concentrations completed in this research.

5.0 Research Summary and Future Applications

The current thesis contributed a number of objectives in the development of an EWBS. The research team was introduced to Canada's inconsistent drinking water jurisdictional background, enabling early understanding of the political climate into which the system will eventually be incorporated. A case study site of vulnerable water supply was identified for possible application of the EWBS and associated research highlighted a subset of Canada's population which can truly benefit from this holistic technology. Lastly, the use of the metal class of contaminants was initiated in laboratory bioassays and evaluated for their utility in an EWBS, using the behavioural responses of *Daphnia magna* upon exposure to copper.

In order to bring the EWBS research to the next level, behavioural response data gathered will be statistically processed and used in a multi-variable statistical model that is simultaneously being developed by another researcher. This model will build a library of responses to various types of contaminants, and will be incorporated into the multi-organism EWBS. Bioassays have now been conducted for several classes of contaminants including heavy metals, pesticides, and organo-metals. In order to build a response library and strengthen existing modeling, further research is required for PAHs, pathogens, endocrine disruptors, and other potential contaminant classes of interest. The laboratory methods conducted in this thesis will contribute to greater ease in future laboratory bioassays with regard to experimental setup and monitored behaviours.

The next step in the process will be the introduction of the proposed EWBS, as a detection system for contaminants and pathogens, in a water treatment facility. The system is designed to provide timely information on water quality changes, and will do so in a cost-effective manner that requires low maintenance and minimal training. These features are especially attractive for use within small, rural, and remote communities, where funding and available personnel are often major issues of concern.

Field application of this system will initially take place at the region of Niagara's Decew WTP in Thorold, ON. If the behaviour of bioassay organisms is consistent in the field, and if the behaviour changes can be used with the incorporated models to detect specific classes of contaminants and at relevant concentrations, then the multi-species biomonitoring system can be successfully implemented. Data produced from the system will eventually be linked, in some way, to policy development and possible enforcement purposes. These aspects have potential legislative and economic implications. It is critical that the data and deduced conclusions are as free of error as is possible, and, since a perfect system is not attainable, an acceptable error rate must be determined. Acceptable error relates to quality assurance, and ensures scientifically sound testing and monitoring procedures that produce accurate results (De Zwart, 1995). It will be important

that the determined acceptable error rate for vulnerable communities be low, as the system will be most useful within a vulnerable setting.

Once successfully implemented *in situ* at a water treatment plant, the next step is to introduce the technology nationwide, particularly in marginalized and vulnerable areas of water supply, such as First Nations reserves and rural communities. The challenge lies in building trusting relationships with these users and in instilling their confidence in this technology. The EWBS strives to be scientifically rigorous and environmentally relevant, and since it does not use expensive chemical testing or complex equipment, is therefore useful for communities where expertise is limited and cost savings are critical. The successful application of this early-warning biomonitoring system hinges on its location within a watershed and the positive impact it can have on water protection for at-risk populations.

This research study specifically examined the implementation of the early-warning biomonitoring system in the context of marginalized communities, and in particular, the Walpole Island First Nations reserve. Historically, Canada's First Nations have been faced with "third world" drinking water standards, and generally do not receive the same level of protection as do their fellow Canadians. The development of a relationship with these marginalized people during this study provided an opportunity to introduce the EWBS technology to a subset of the population that truly needs it. It also supported the fulfillment of the research team's primary goal of ensuring safe drinking water.

The EWBS is consistent with First Nation ideals of environmental protection. First Nations' people have a commitment to nature and to the environment, which coincides with the basic, natural ideals of the early-warning biomonitoring system. This congruency enhances understanding and support of the technology, and a greater likelihood of acceptance into First Nations drinking water frameworks. As cited on the website of the Assembly of First Nations, "Water problems and challenges are connected and should be addressed in a holistic manner" (Assembly of First Nations, n.d.). The early-warning biomonitoring system is truly holistic in its approach, analogous to the "miner's canary" once used to test air quality of mines. As previously stated, the greatest challenge of system implementation at the local level will lie in the building of trusting relationships with eventual users and, at a national level, with the integration of biomonitoring requirements in federal legislation.

One aspect of the completed research focused on the assessment of the drinking water frameworks in place for all levels of government nationwide. The critical finding was a pattern of inconsistency across the board in relation to legislation, ministerial, and departmental

responsibility, testing procedures, and boil water advisory notifications. Based on these findings and the negative resulting impacts, it is clear that a necessary step in moving forward involves policy-based changes that will mandate all drinking water facilities in Canada, or those of particular vulnerability, to use biomonitoring technology as a supplement to traditional chemical and physical testing. However, this step relies on government's recognition and proactive interest in legally mandating the provision of clean drinking water. The federal government must also direct a focused effort towards the improvement of drinking water management in First Nation communities, and solidify that with the development of enforceable standards.

EWBS technology will be a useful tool in source water protection. In Ontario, the 2006 *Clean Water Act*, along with the previously assented *Safe Drinking Water Act*, help to control and regulate drinking water and ensure that community stakeholders are able to identify potential risks to drinking water supply, and to take action to reduce or eliminate these risks. The *Clean Water Act* has set in motion the development of source water protection plans, although many have yet to be implemented. In ideal situations, a number of people and sectors such as municipalities, conservation authorities, landowners, farmers, industry, community groups, and members of the public work together to meet this common goal. The EWBS, once fully developed and tested at the field level, will be available to these diverse groups for fulfillment of source water protection plans.

In addition to drinking water system implementation, the system may eventually be suitable for other branches of pollution detection, including industrial effluent toxicity monitoring and ambient toxicity monitoring. Effluent toxicity monitoring can be applied for both the management of water quality and the detection for pulses of contaminants. EWBS use in this setting is best suited for industries that claim fishable and swimmable effluent, as raw effluent could potentially overwhelm the organisms. The EWBS can aid in compliance testing, the prevention/reduction of effects occurring in receiving water bodies, and in the early-warning of accidental spills directly from the source. Ambient toxicity tests evaluate receiving waters and sediments, and are useful in conjunction with effluent toxicity tests. The EWBS can reveal or confirm existing toxic conditions in the receiving water, and may reveal the location of unknown point-source or diffuse discharges. The system may also be used to evaluate the persistence of chemicals, and the combined effects of multiple discharges from various point sources. This type of monitoring aids in the management of ambient water quality, rather than providing a sudden alarm function, as is the case with spills.

EWBS technology has the capacity to play a critical role in the current state of water quality issues in Canada and worldwide. The *United Nations ICESCR* has yet to be realized by much of the

World's population. Even more challenged are marginalized populations who must be guaranteed that their voices are heard, and that their needs are viewed as important. The EWBS will be useful in areas of particular environmental stress; it will provide added protection that is relatively low in cost and simple in its concept. These unique attributes contribute to the system's suitability for use in developing countries where drinking water and sanitary conditions tend to cause overwhelming suffering through adverse health, political, financial, and social effects. It must also be recognized that these same effects can be identified at varying levels of severity within our own developed country. The EWBS is an innovative, practical, and cost-effective environmental tool that will help improve the uneven distribution of clean water, an essential human right, both here at home and across the world.

References

- Adamowicz, S.J., Gregory, T.R., Marinone, M.C., & Hebert, P.N. (2002). New insights into the distribution of polyploid *Daphnia*: The Holarctic revisited and Argentina explored. *Molecular Ecology*, 11, 1209–1217.
- Alberta Environment. (n.d.). *Drinking Water*. Retrieved from: <http://www.environment.alberta.ca/01220.html>
- Alberta Environment. (n.d.). *Frequently Asked Questions*. Retrieved from: <http://environment.alberta.ca/apps/RegulatedDWQ/Faqs.aspx#FAQ4>
- Alberta Environment. (n.d.). *Source Water Protection*. Retrieved from: <http://environment.alberta.ca/1485.html>
- Alberta Environment. (2004). *Alberta Water Act*. Retrieved from: http://www.albertawater.com/index.php?option=com_content&view=article&id=54&Itemid=60
- Alberta Environment. (2006). *Standards and Guidelines for Municipal Waterworks, Wastewater and Storm Drainage Systems*. Retrieved from: <http://environment.gov.ab.ca/info/library/6979.pdf>
- Alberta Environment. (2010). *Advisories and warnings currently in effect*. Retrieved from: <http://www.environment.alberta.ca/forecasting/advisories/>
- Allan, I. J., Vrana, B., Greenwood, R., Mills, G. A., Roig, B., & Gonzalez, C. (2006). Review a “toolbox” for biological and chemical monitoring requirements for the European Union’s water framework directive. *Talanta*, 69, 302–322.
- Allen, H.E., & Hansen, D.J. (1996). The importance of trace metal speciation to water quality criteria. *Water Environment Research*, 68(1), 42–54.
- American Water Works Association. (2005). *Microfiltration and Ultrafiltration Membranes for Drinking Water*. First Edition. 2005. American Water Works Association. Denver, CO
- American Water Works Association. (2008). Microfiltration and ultrafiltration membranes for drinking water. *American Water Works Association Journal*, 100 (12), 84
- Assembly of First Nations (n.d.). *First Nations Water Initiative*. Retrieved from: <http://www.afn.ca/article.asp?id=2844>
- Aurilio, A.C., Mason, R.P., & Hemond, H.F. (1994). Speciation and fate of arsenic in three lakes of the aberjona watershed. *Environmental Science & Technology*, 28, 577–505.
- Baillieul, M., & Blust, R. (1999). Analysis of the swimming velocity of cadmium-stressed *Daphnia magna*. *Aquatic Toxicology*, 44, 245–254.
- Bakker, Karen (ed.). (2007). *Eau Canada: the Future of Canada’s Water*. Vancouver: UBC Press

- Barlow, S. (2004). *Scientific Facts on Arsenic*. Prepared for GreenFacts. Retrieved from: <http://www.greenfacts.org/en/arsenic/index.htm>
- Beltran, F. J., Ovejero, G., & Acedo, B. (1993). Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide. *Water Research*, 27(6), 1013-1021.
- Bossuyt, B.T.A., & Janssen, C.R., (2005). Copper regulation and homeostasis of *Daphnia magna* and *Pseudokirchneriella subcapitata*: Influence of acclimation. *Environmental Pollution*, 136, 135-144.
- British Columbia Guide to Watershed Law and Planning. (n.d.). *Canada Water Act*. Retrieved from: <http://www.bcwatersheds.org/issues/water/bcgwlp/n7.shtml>
- British Columbia Ministry of Environment. (2008). *Water Stewardship Division Strategic Plan 2008*. Retrieved from: http://www.env.gov.bc.ca/wsd/water_rights/cabinet/WSDstratplan.pdf
- British Columbia Ministry of Healthy Living and Sport. (n.d.). *Drinking Water Protection Act*. Retrieved from: <http://www.hls.gov.bc.ca/protect/dwact.html>
- British Columbia Ministry of Healthy Living and Sport. (2002). Final Report: *Panel Review of British Columbia's Drinking Water Protection Act*. Retrieved from: http://www.hls.gov.bc.ca/protect/pdf/dwrp_final.pdf
- British Columbia Ministry of Healthy Living and Sport. (2007). *Drinking Water Officers Guide*. Prepared by Drinking Water Leadership Council. Retrieved from: http://www.hls.gov.bc.ca/protect/dwoguide_updated_approved%202007.pdf
- Chan, C. 1993. St. Clair River Head and Mouth Water Quality Monitoring, 1987-89. *Water Pollution Research Journal of Canada*, 28(2), 451-71.
- Chen, P.H., Jenq, C.H., & Chen, K.M. (1996). Evaluation of granulated activated carbon for removal of trace organic compounds in drinking water. *Environment International*, 22(3), 343-359.
- Christensen, R. (2006). *Waterproof 2*. Prepared for the Sierra Legal Defence Fund. Retrieved from: <http://www.ecojustice.ca/publications/reports/waterproof-2-canadas-drinking-water-report-card/attachment>
- City of Cincinnati. (n.d.). *Greater Cincinnati water works*. Retrieved from: <http://www.cincinnati-oh.gov/water/pages/-3283/>
- City of Whitehorse. (n.d.). *Watershed Management Plan*. Retrieved from: http://www.city.whitehorse.yk.ca/index.asp?Type=B_BASIC&SEC=%7B3244D095-8D1E-4D17-9248-EA49B9AAA2A8%7D
- Claus, C. (1976). Effect of 2,4-D on Survival and Reproduction of *Daphnia magna* Straus. *Meded Rijksuniv Gent Fak Landbouwkde Toegep Biol Wet*, 41(2, Pt.2), 1467-1475.
- Consolidation of Public Water Supply Regulations*. R.R.N.W.T. 1990,c.P-23. *Public Health Act*. Retrieved from: <http://www.canlii.org/en/nu/laws/regu/rrnwt-nu-1990-c-p-23/latest/part-1/rrnwt-nu-1990-c-p-23-part-1.pdf>

- Copper Development Association. (n.d.). *General, Atomic and Crystallographic Properties and Features of Copper*. Retrieved from:
<http://www.copper.org/resources/properties/atomic/homepage.html>
- Corapcioglu, M. O., & Huang, C. P. (1987). The adsorption of heavy metals onto hydrous activated carbon. *Water Research*, 21(9), 1031-1044.
- The Council of Canadians. (2006). *Five Things You Should Know About Canada's Position on the Right to Water*. Retrieved from:
http://www.canadians.org/water/documents/Right_to_Water_0206.pdf
- The Council of Canadians (2008). *A Federal Perspective on Water Quantity Issues*. Prepared by Environment Canada. Retrieved from:
<http://www.canadians.org/water/documents/FederalWaterQuantity.pdf>
- De Schamphelaere, K.A.C., Forrez, I., Dierckens, K., Sorgeloos, P., & Janssen, C.R. (2007). Chronic toxicity of dietary copper to *Daphnia magna*. *Aquatic Toxicology*, 81, 409-418.
- De Zwart, D. (1995). *Monitoring Water Quality in the Future, Volume 3: Biomonitoring*. Prepared for: The Netherlands National Institute for Public Health and the Environment. Retrieved from:
<http://rivm.openrepository.com/rivm/handle/10029/10424>
- Dodson, S.I. (1990). Predicting diel vertical migration of zooplankton. Prepared by the American Society of Limnology and Oceanography, Inc. *Limnology and Oceanography*, 35(5), 1195-1200.
- Dodson, S.I. & Hanazato, T. (1995). Commentary on effects of anthropogenic and natural organic chemicals on development, swimming behaviour, and reproduction of *Daphnia*, a key member of aquatic ecosystems. *Environmental Health Perspectives*, 103(Suppl 4), 7-11.
- Dodson, S.I., Hanazato, T. & Gorski, P.R. (1995.) Behavioural responses of *Daphnia pulex* exposed to Carbaryl and Chaoborus Kairomone. *Environmental Toxicology and Chemistry*, 14, 43-50.
- Dodson, S.I., & Ramcharan, C. (1991). Size-specific swimming behaviour of *Daphnia pulex*. *Journal of Plankton Research*, 13, 1367-1379.
- Drinking Water Protection Act*, S.B.C. 2001, c. 9. Retrieved from:
http://www.bclaws.ca/Recon/document/freeside/--%20D%20--/Drinking%20Water%20Protection%20Act%20SBC%202001%20c.%209/00_01009_01.xml
- Drinking Water Protection Regulation*. 200/2003. Retrieved from:
http://www.bclaws.ca/Recon/document/freeside/--%20D%20--/Drinking%20Water%20Protection%20Act%20SBC%202001%20c.%209/05_Regulations/10_200_2003.xml
- Drinking Water Quality Standards Regulation* 41/ 2007. Retrieved from:
<http://www.gov.mb.ca/waterstewardship/odw/reg-info/acts-reg/041-d101.07.pdf>

- Drinking Water Regulation. 2007/139. Public Health Act. O.I.C.* Retrieved from: http://www.gov.yk.ca/legislation/regs/oic2007_139.pdf
- Drinking Water Safety Act. S.M. 2002, c.36.* Retrieved from: <http://web2.gov.mb.ca/laws/statutes/2002/c03602e.php>
- Drinking Water Safety Regulation 40/2007.* Retrieved from: <http://www.gov.mb.ca/waterstewardship/odw/reg-info/acts-regs/040-d101.07.pdf>
- Drinking Water Systems Regulation. 170/03.* Retrieved from: http://www.e-laws.gov.on.ca/html/regs/english/elaws_regs_030170_e.htm#BK31
- Drinking Water and Wastewater Facility Operating Regulations, 2004.* Retrieved from: <http://www.gov.pe.ca/law/regulations/pdf/E&09-04.pdf>
- Ebert, D. (2005). *Daphnia magna* images. Retrieved from: <http://www.ncbi.nlm.nih.gov/bookshelf/br.fcgi?book=daph&part=ch2>
- Eggertson, L. (2008). Investigative report: 1766 boil-water advisories now in place across Canada. *Canadian Medical Association Journal*, 178 (10), 1261-63
- Eisler, R. (1988). *Arsenic hazards to fish, wildlife, and invertebrates: A synoptic review.* Prepared for the U.S. Fish and Wildlife Service. Retrieved from: http://www.pwrc.usgs.gov/infobase/eisler/chr_12_arsenic.pdf
- Environment Canada. (1996a). *Biological test method: Acute lethality test using Daphnia spp.*
- Environment Canada (1996b). *The State of Canada's Environment.* Retrieved from: <http://www.ec.gc.ca/soer-ree/English/soer/1996Report/Doc/1-6-6-5-3-3-4-1.cfm>
- Environment Canada. (2000). *Biological test method: Reference method for determining acute lethality of effluents to Daphnia magna.* 2nd ed.
- Environment Canada. (2004). *Drinking Water Case Study: Edmunston, New Brunswick.* Retrieved from: <http://www.ec.gc.ca/eau-water/default.asp?lang=En&n=DFF500EF-1#Section1>
- Environment Canada. (2007). *National Pollutant Release Inventory Pollution Data Library.* Retrieved from: http://www.ec.gc.ca/pdb/websol/querysite/results_e.cfm?opt_report_year=2007
- Environment Canada. (2008). *Threats to Sources of Drinking Water and Aquatic Ecosystem Health in Canada: Waterborne pathogens.* Retrieved from: <http://www.ec.gc.ca/INRE-NWRI/default.asp?lang=En&n=235D11EB-1&offset=2&toc=show>
- Environment Canada. (2009a). *Federal Water Policy.* Retrieved from: <http://www.ec.gc.ca/eau-water/default.asp?lang=En&n=D11549FA-1#part6>
- Environment Canada (2009b) *Summary of NPRI Reporting Requirements for 2009.* Retrieved from: <http://www.ec.gc.ca/inrp-npri/default.asp?lang=En&n=27269DFC-1>

- Environment Yukon. (2010). *Water Resources*. Retrieved from:
<http://www.environmentyukon.gov.yk.ca/monitoringenvironment/aboutwaterresources.php>
- Environmental Management and Protection Act. C. E-10.21*. 2002. Retrieved from:
<http://www.qp.gov.sk.ca/documents/english/Statutes/Statutes/e10-21.pdf>
- European Commission. (2009). *The Drinking Water Directive*. Retrieved from:
http://ec.europa.eu/environment/water/water-drink/index_en.html
- Expert Panel on Safe Drinking Water for First Nations. (2006). *Report of the Expert Panel on Safe Drinking Water for First Nations*. Retrieved from: http://www.sdw-eps.gc.ca/rsrsc/volume_1_e.pdf
- Federation of Canadian Municipalities. (n.d.). *About the Quality of Life Reporting System*. Retrieved from: <http://www.fcm.ca/english/View.asp?mp=477&x=1043>
- Fjallborg, B., Li, B., Nilsson, E., & Dave, G. (2006). Toxicity identification evaluation of five metals performed with two organisms (*Daphnia magna* and *Lactuca sativa*). *Archives of Environmental Contamination and Toxicology*, 50, 196–204.
- Flemming, C.A., & Trevors, J.T. (1989). Copper toxicity and chemistry in the environment: A review. *Water, Air, and Soil Pollution*, 44, 143-158.
- Flickinger, A.L., Randall, J.F., Winner, R.W., & Skillings, J.H. (1982). Filtration and phototactic behavior as indices of chronic copper stress in *Daphnia magna* Straus. *Archives of Environmental Contamination and Toxicology*, 11, 457-463.
- Government of Northwest Territories. (2005). *Managing Drinking Water Quality in the Northwest Territories*. Retrieved from:
<http://www.maca.gov.nt.ca/operations/water/docs/waterframework.pdf>
- Goyal, M., Rattan, V.K., Aggarwal, D., & Bansal, R.C. (2001). Removal of copper from aqueous solutions by adsorption on activated carbons. *Colloids and Surface A: Physicochemical and Engineering Aspects*, 190, 229–238.
- Grayman, W.M., Deininger, R.A., & Males, R.M. 2001. *Design of Early Warning and Predictive Source-Water Monitoring Systems*. American Water Works Association (AWWA) Research Foundation, AWWA, Denver, Colo.
- Great Lakes Environmental Center. 2005. *Great Lakes Connecting Channels 2005 Annual Data Report*. Prepared for Michigan Department of Environmental Quality. Retrieved from:
http://www.michigan.gov/documents/deq/wb-swas-trend-05ccreport_203311_7.pdf
- Green, U., Kremer, J.H., Zillmer, M. & Moldaenke, C. (2003). Detection of chemical threat agents in drinking water by an early warning real-time biomonitor. *Environmental Toxicology*, 18, 368-374.
- Gullick, R.W., Grayman, W.M., Deininger, R.A. & Males, R.M. 2003. Design of early-warning monitoring systems for source waters. *Journal AWWA*, 95 (11), 58-72.

- Hancock, B.A., & Pon, M.R.L. (1999). *Proceedings of the Copper 99-Cobre 99 International Conference: October 10-13, 1999, Phoenix, Arizona, USA*. Warrendale, Penn: Minerals, Metals, and Materials Society
- He, W., Megharaj, M., & Naidu, R. (2009). Toxicity of tri- and penta-valent arsenic, alone and in combination, to the cladoceran *Daphnia carinata*: The influence of microbial transformation in natural waters. *Environmental Geochemistry and Health*, 31, 133-141.
- Health Canada. (1992). *Copper*. Retrieved from: <http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/copper-cuivre/index-eng.php>
- Health Canada. (2006). *Arsenic*. Retrieved from: <http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/arsenic/index-eng.php>
- Health Canada. (2007). *Procedure Manual for Safe Drinking Water in First Nations Communities South of 60°*. Retrieved from: http://www.watertraining.ca/drinkingwater/pdf/DW_English.pdf
- Health Canada. (2008). *Guidelines for Canadian Drinking Water Quality Summary Table. Federal-Provincial-Territorial Committee on Drinking Water*. Retrieved from: http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/water-eau/sum_guideres_recom/summary-sommaire-eng.pdf
- Health Canada. (2009). *Water Quality*. Retrieved from: <http://www.hc-sc.gc.ca/ewh-semt/water-eau/index-eng.php>
- Health Canada. (2010). *First Nations, Inuit, and Aboriginal Health: Drinking water and wastewater*. Retrieved from: <http://www.hc-sc.gc.ca/fniah-spnia/promotion/public-publique/water-eau-eng.php>
- Herbert, C.P. (2009). *Poisons in the Water: First Nations Community-Based Participatory Research partnership*. Prepared for Participatory Research at McGill. Retrieved from: http://pram.mcgill.ca/i/CHerbert-Poison_in_the_Water16oct2009.pdf
- Hill, C., Furlong, K., Bakker, K. & Cohen, A. (2008). Harmonization versus subsidiary in water governance: a review of water governance and legislation in the Canadian provinces and territories. *Canadian Water Resources Journal*, 33(4), 315-332
- Indian & Northern Affairs Canada (INAC). (2005). *Walpole Island First Nation to Build \$10 million Water Treatment Facility*. Retrieved from: <http://www.ainc-inac.gc.ca/ai/mr/nr/s-d2005/2-02747-eng.asp>
- INAC. (2006a). *Design Guidelines for First Nations Water Works*. Retrieved from: <http://www.inac-ainc.gc.ca/h2o>
- INAC. (2006b). *Protocol for Safe Drinking Water in First Nations Communities*. Retrieved from: <http://www.ainc-inac.gc.ca/enr/wtr/pubs/sdw/sdw-eng.pdf>

- INAC. (2007). *Summative Evaluation of the First Nations Water Management Strategy*. Retrieved from: <http://www.ainc-inac.gc.ca/ai/arp/aev/pubs/ev/efnw08/efnw08-eng.asp>
- INAC. (2008a). *Fact Sheet: First Nations and Inuit Health in Canada*. Retrieved from: <http://www.ainc-inac.gc.ca/ai/mr/is/fnihb-eng.asp>
- INAC. (2008b). *Government of Canada Announces Next Important Steps To Improve Drinking Water In First Nations Communities*. Retrieved from: <http://www.ainc-inac.gc.ca/ai/mr/nr/j-a2008/2-3019-eng.asp?p1=209557&p2=6293>
- INAC. (2008c). *Plan of Action for Drinking Water in First Nations Communities - Progress Report*. Retrieved from: <http://www.ainc-inac.gc.ca/enr/wtr/pubs/prpf/pad09/pad09-eng.asp>
- INAC. (2008d). *Water Management*. Retrieved from: <http://www.ainc-inac.gc.ca/nth/wa/wm-eng.asp>
- INAC. (2009). *First Nations Water and Wastewater Action Plan - Progress Report*. Retrieved from: <http://www.ainc-inac.gc.ca/enr/wtr/pubs/prpf/pad09/pad09-eng.asp>
- International Joint Commission. (2006). *Report on Spills in the Great Lakes Basin with a Special Focus on the St. Clair-Detroit River Corridor*. Retrieved from: <http://www.ijc.org/php/publications/pdf/ID1594.pdf>
- Isfeld, H. (2009). *Boil Water Advisory Mapping Project: An Exploration and Review of Available Data*. Prepared for the Prairie Women's Health Centre of Excellence. Retrieved from: <http://www.pwhce.ca/pdf/boilWater.pdf>
- Johansen, D. (2002). *Bulk Water Removals, Water Exports and the NAFTA*. Retrieved from: <http://dsp-psd.pwgsc.gc.ca/Collection-R/LoPBdP/BP/prb0041-e.htm>
- Joseph, G., Kundig, J.A.C. (1999). *Copper: Its Trade, Manufacture, Use, and Environmental Status*. Materials Park, OH: ASM International
- Juang, R.S., & Shiau, R.C. (2000). Metal removal from aqueous solutions using chitosan-enhanced membrane filtration. *Journal of Membrane Science*, 165, 159–167.
- Khalfan, A. & Kiefer, T. (2008). *Why Canada must Recognize the Human Right to Water and Sanitation*. Retrieved from: <http://www.righttowater.info/pdfs/canada-must-recognise-right-to-water.pdf>
- Kieu, N.D., Michels, E. & De Meester, L. (2001). Phototactic behavior of *Daphnia* and the continuous monitoring of water quality: Interference of fish kairomones and food quality. *Environmental Toxicology and Chemistry*, 20, 1098-1103.
- Kleywegt, S., Smyth, S-A., Parrott, J., Schaefer, K., Lagacé, E., Payne, M., Topp, E., Beck, A., McLaughlin, A. and K. Ostapyk (eds). 2007. *Pharmaceuticals and Personal Care Products in the Canadian Environment: Research and Policy Directions*. NWRI Scientific Assessment Report Series, No.8, p.53.

- Kramer, K.J.M., Jak, R.G., Van Hattum, B., Hooftman, R.N., & Zwolsman, J.J.G. (n.d.). Copper toxicity in relation to surface water-dissolved organic matter: biological effects to *Daphnia magna*. *Environmental Toxicology and Chemistry*, 23 (12), 2971-2980.
- Krewski, D., Balbus, J., Butler-Jones, D., Haas, C., Isaac-Renton, J., Roberts, K., *et al.* (2002). Managing Health Risks From Drinking Water-A Report to the Walkerton Inquiry. *Journal of Toxicology & Environmental Health: Part A*, 65(21), 1635-1823.doi:10.1080/00984100290071711
- Kurniawan, T.A., Chana, G.Y.S., Lo, W., Babel, S. (2006). Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*, 118, 83-98.
- Lake St. Clair Canadian Watershed Coordination Council (2005). *The Lake St. Clair Canadian Watershed Draft Technical Report: An examination of current conditions*. Retrieved from: http://www.bkejwanong.com/StClairMgmt/Draft%20Report/Cover_1.pdf
- Liao, C., & Gurol, M.D. (1995). Chemical oxidation by photolytic decomposition of hydrogen peroxide. *Environmental Science and Technology*, 29, 3007-3014.
- Lide, D. (ed.).(2009). *CRC Handbook of Chemistry and Physics*. Cleveland, OH: CRC Press.
- Logsdon, G.S., Horsley, M.B., Freeman, S.D.N., Neemann, J.J., & Budd, G.C. (2006). Filtration processes: a distinguished history and a promising future. *American Water Works Association*, 98(3), 150-154, 157-162.
- Mackenzie, C.A., Lockridge, A., & Keith, M. (2005). Declining sex ratio in a first nation community. *Environmental Health Perspectives*, 113(10).
- Manitoba Water Stewardship. (n.d.). *Water Stewardship Fund*. Retrieved from: http://www.gov.mb.ca/waterstewardship/water_info/wsf/index.html#objectives
- Marshall, G.C. (2009). *Assessing behavioural and physiological responses of three aquatic invertebrates to atrazine and tributyl tin in a multi-species, early-warning biomonitoring technology*. Unpublished master's thesis. Ryerson University. Toronto, ON.
- Martins, J., Soares, M.L., Saker, M.L., Oliva-Teles, L. & Vasconelos, V.M. (2007). Phototactic behavior in *Daphnia magna* straus as an indicator of toxicants in the aquatic environment. *Ecotoxicology and Environmental Safety*, 67, 417-422.
- Martins, J., Teles, O.L., & Vasconcelos, V. (2007). Assays with *Daphnia magna* and *Danio rerio* as alert systems in aquatic toxicology. *Environment International*, 33, 414-425.
- McCarthy, L.H., Bostan, I.V., Laursen, A.E., Gilbride, K., Marshall, G., & Pearce, C. 2008. *Protecting Canada's Drinking Water: Developing Real-time Early-Warning Biomonitoring Technology*. Ryerson University, Toronto, ON.
- Melamed, D. (2004). *Monitoring arsenic in the environment: A review of science and technologies for field measurements and sensors*. Prepared for the Office of Solid Waste and Emergency Response. U.S. EPA. Retrieved from: http://www.physics.harvard.edu/~wilson/arsenic/measurement/EPA_review.pdf

- Micheals, E., Leynen, M., Cousyn, C., De Meester, L. & Ollevier, F. (1999). Phototactic behaviour of *Daphnia* as a tool in the continuous monitoring of water quality: Experiments with a positively phototactic *Daphnia magna* clone. *Water Resources*, 33(2), 401-408.
- Micheals, E., Semsari, S., Bin, C. & De Meester, L. (2000). Effect of sublethal doses of cadmium on the phototactic behavior of *Daphnia magna*. *Ecotoxicology and Environmental Safety*, 47: 261-265.
- Newfoundland and Labrador (NL) Department of Environment and Conservation. (n.d.). *Newfoundland and Labrador Water Resources Portal*. Retrieved from: <http://maps.gov.nl.ca/water/>
- NL Department of Environment and Conservation. (2009). *Drinking Water Safety in Newfoundland and Labrador Annual Report: Rural Reactions and Remedies*. Retrieved from: http://www.env.gov.nl.ca/Env/env/waterres/Surfacewater/DWS-Report/2009/DWQ_Annual_Report_2009.pdf
- NL Department of Environment and Conservation. (2009). *Policy for Drinking Water Quality Monitoring and Reporting for Public Water Supplies*. Retrieved from: <http://www.env.gov.nl.ca/Env/env/waterres/Policies/PDWR09-1.asp>
- The North Battleford Water Inquiry. (2002). *Report of the Commission of the Inquiry*. Retrieved from: <http://www.justice.gov.sk.ca/nbwater/inquiry/inquiry.htm>
- Northwest Territories Health & Social Services. (2007). *Drinking Water Quality*. Retrieved from: http://www.hlthss.gov.nt.ca/pdf/brochures_and_fact_sheets/environmental_health/2007/english/nwt_drinking_water_sampling_and_testing_requirements.pdf
- North West Territories Municipal and Community Affairs. (n.d.). *Northwest Territories Drinking Water Quality Database*. Retrieved from: <http://www.maca.gov.nt.ca/operations/water/homepage.asp>
- North West Territories Regional Health Office. (n.d.). *Water Supply System Regulations Information*. Retrieved from: http://www.hlthss.gov.nt.ca/pdf/brochures_and_fact_sheets/environmental_health/2009/english/water_supply_system_regulations.pdf
- Nova Scotia Environment and Labour. (2005a). *A Drinking Water Strategy for Nova Scotia*. Retrieved from: <http://www.gov.ns.ca/nse/water/docs/NSWaterStrategyReport.pdf>
- Nova Scotia Environment and Labour. (2005b). *Guidelines for Monitoring Public Drinking Water Supplies*. Retrieved from: <http://www.gov.ns.ca/nse/water/docs/consultation.Guidelines.for.Monitoring.Public.Drinking.Water.Supplies.pdf>
- Nova Scotia Environment and Labour. (2009). *Boil Water Advisories*. Retrieved from: <http://www.gov.ns.ca/nse/water/boiladvisory.asp>
- Nriagu, J.O. (1990). Global metal pollution: Poisoning the biosphere? *Environment*, 32(7), 6-11, 28-33

- Nunavut Water Board. (n.d.). *Conserving Nunavut's Freshwater*. Retrieved from: <http://www.nunavutwaterboard.org/en/home>
- Nutrient Management Act*. S.O. 2002, c. 4. Retrieved from: http://www.e-laws.gov.on.ca/html/statutes/english/elaws_statutes_02n04_e.htm
- Office of the Auditor General of Canada. (2005). *Report of the Commissioner of the Environment and Sustainable Development: Drinking Water in First Nations Communities*. Retrieved from: http://www.oag-bvg.gc.ca/internet/English/parl_cesd_200509_05_e_14952.html#ch5hd3a
- Office of the High Commissioner for Human Rights. (1976). *International Covenant on Economic, Social and Cultural Rights: Article 11*. Retrieved from: http://www.unhchr.ch/html/menu3/b/a_ceschr.htm
- Ontario Ministry of the Environment (OMOE). (2005). *Environmental Compliance in the Petrochemical Industry in the Sarnia Area*. Retrieved from: <http://www.ene.gov.on.ca/programs/5069e.pdf>
- OMOE. (2009a). *Clean Water Act*. Retrieved from: <http://www.ene.gov.on.ca/en/water/cleanwater/cwa-factsheets.php>
- OMOE. (2009b). *Drinking Water Surveillance Program*. Retrieved from: <http://www.ene.gov.on.ca/en/water/dwsp/>
- Ontario Ministry of Natural Resources (2009). *Guide to Eating Ontario Sport Fish (2009-2010)*. Retrieved from: <http://www.ene.gov.on.ca/en/water/fishguide/index.php>
- Organisation for Economic Co-operation and Development. (2004). *OECD Guideline for testing of chemicals: Daphnia sp., acute immobilization test*. Retrieved from: <http://www.oecd.org/dataoecd/17/21/1948249.pdf>
- Papa, B. & Edwards, S. (2004). *The Source Water Protection Primer*. Prepared for Pollution Probe. Retrieved from: <http://www.pollutionprobe.org/Reports/swpprimer.pdf>
- Perrow, C. (2007). *The Next Catastrophe*. Princeton, New Jersey. Princeton University Press.
- Pesticide Action Network (PAN). (n.d.). *Copper Sulfate (Pentahydrate)*. Retrieved from: http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC33541#Ecotoxicity
- Pesticide Action Network (PAN). (2010). *Canada Pesticide Registration*. Retrieved from: http://www.pesticideinfo.org/Detail_Country.jsp?Country=Canada&offset=0
- Pest Management Regulatory Agency. (n.d.). *Product Registry*. Retrieved from: http://pr-rp.pmr-arla.gc.ca/portal/page?_pageid=34,6928,34_6956&_dad=portal&_schema=PORTAL&letter=C
- Potable Water Regulation 93-203*. Retrieved from: <http://www.gnb.ca/0062/PDF-regs/93-203.pdf>
- Potable Water Regulation 277/2003*. Retrieved from: <http://environment.alberta.ca/1485.html>

- Poynton, H.C., Varshavsky, J.R., Chang, B., Cavigliolo, G., Chan, S., Holman, P.S., Loguinov, A.V., & Vulpe, C.D. (2007). *Daphnia magna* ecotoxicogenomics provides mechanistic insights into metal toxicity. *Environmental Science and Technology*, 41 (3), 1044-1050.
- Prince Edward Island Ministry of Environment. (n.d.). *Drinking Water Strategy: 10 Points to Purity*. Retrieved from: <http://www.gov.pe.ca/photos/original/10points2purity.pdf>
- Public Health Act. S.N.W.T. 2007,c.17; SI-007-2009. Retrieved from: <http://www.justice.gov.nt.ca/PDF/ACTS/Public%20Health.pdf>
- Regulation Respecting the Quality of Drinking Water, R.Q. c. Q-2, r.18.1.1. Retrieved from: http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=2&file=/Q_2/Q2R18_1_1_A.htm
- Remedial Action Plan (RAP). (1991). *St. Clair River Remedial Action Plan Report Stage 1*. Retrieved from: <http://www.friendsofstclair.ca/pdf/rap1.pdf>
- RAP. (1995). *St. Clair River Remedial Action Plan Report. Stage 2*. Retrieved from: <http://www.friendsofstclair.ca/pdf/rap2.pdf>
- RAP. (2005). *St. Clair River Remedial Action Plan Progress Report*. Retrieved from: http://www.friendsofstclair.ca/pdf/StClair_RAP_Report_complete.pdf
- Ren, Z.M., Li, Z.L., Zha, J.M., Rao, K.F., Ma, M., Wang, Z. & Fu, R.S. (2009). The avoidance responses of *Daphnia magna* to the exposure of organophosphorus pesticides in an on-line biomonitoring system. *Environmental Modelling and Assessment*, 14, 405-410.
- Riddell, D. J., Culp, J.M., & Baird, D.J. (2005). Behavioural responses to sublethal cadmium exposure within an experimental aquatic food web. *Environmental Toxicology and Chemistry*, 24(2), 431-441.
- Rosen, B.P., & Liu, Z. (2009). Transport pathways for arsenic and selenium: A mini review. *Environment International*, 35, 512-515.
- Safe Drinking Water Foundation. (n.d.(a)) *The Boil Water Advisory Quest*. Retrieved from http://www.safewater.org/PDFS/resourceswaterqualityinfo/Boil_Water_Adv_Quest.pdf
- Safe Drinking Water Foundation. (n.d.(b)). *Purpose of Drinking Water Quality Guidelines and Regulations*. Retrieved from: <http://www.safewater.org/PDFS/PurposeofDrinkingWaterQualityGuidelinesRegulations.pdf>
- Safe Drinking Water Foundation. (2008). *First Nations Drinking Water Position Paper*. Retrieved from: <http://www.safewater.org/PDFS/PositionPaper.pdf>
- Sarnia Lambton Environmental Association. (2005). *Wastewater Treatment- Physical/Chemical*. Retrieved from: <http://www.sarniaenvironment.com/pdf/SLEA-Monograph-W3.pdf>
- SaskH2O. (2009a). *My Drinking Water*. Retrieved from: <http://www.saskh2o.ca/MyDrinkingWater.asp>

- SaskH2O.(2009b). *Water Information Partners-Roles and Responsibilities*. Retrieved from:
<http://www.saskh2o.ca/RolesAndResponsibilities.asp>
- Saskatchewan Ministry of Environment. (2006). *Saskatchewan Drinking Water Quality Standards and Objectives*. Retrieved from:
<http://www.environment.gov.sk.ca/adx/asp/adxGetMedia.aspx?DocID=765,758,253,94,88,Documents&MediaID=330&Filename=Drinking+Water+Quality+Standards+and+Objectives.pdf&l=English>
- Schmidt, K., Steinberg, C.E.W., Staaks, G.B.O. & Pflugmacher, S. (2005). Influence of xenobiotic mixture (PCB and TBT) compared to single substances on swimming behaviour or reproduction of *Daphnia magna*. *Acta Hydrochimistria and Hydrobiologia*, 33, 287-300.
- Sharma, S.K., Petrushevski, B., & Amy, G. (2008). Chromium removal from water: A review. *Journal of Water Supply: Research and Technology—AQUA*, 57(8), 541-553.
- Shih, T.C., Wangpaichitr, M., & Suffet, M. (2003). Evaluation of granular activated carbon technology for the removal of methyl tertiary butyl ether (MTBE) from drinking water. *Water Research*, 37, 375-385.
- Smedley, P.L., & Kinniburgh, D.G. (2002). A review of the source, behaviour, and distribution of arsenic in natural waters. *Applied Geochemistry*, 17, 517-568.
- Statistics Canada. (2008). *Canadian Environmental Sustainability Indicators: Freshwater Quality Indicators – Data Sources and Methods; Future Improvements*. Retrieved from
<http://www.statcan.gc.ca/pub/16-256-x/16-256-x2008000-eng.pdf>
- Sustainable Development Institute. (n.d.). *Walpole Island First Nation: Where the Waters Divide*. Retrieved from:
http://www.sustainabledevelopmentinstitute.org/InvasiveSpecies/Walpole_Island_First_Nation_EAB_Presentation.pdf
- Szalinska, E., Haffner, D.G., & Drouillard, K.G. (2007). Metals in the sediments of the Huron-Erie corridor in North America: Factors regulating metal distribution and mobilization. *Lakes & Reservoirs: Research and Management*, 12, 217-236.
- Terra, N.R., & Feiden, I.R. (2003). Reproduction and survival of *Daphnia magna* straus, 1820. (crustacea:cladocera) under different hardness conditions. *Acta Limnologica Brasiliensia*, 15(2), 51-55. Retrieved from:
[http://ecologia.icb.ufmg.br/~joseneto/Acta_Limnologica/PDF15\(2\)/Art7_15\(2\).pdf](http://ecologia.icb.ufmg.br/~joseneto/Acta_Limnologica/PDF15(2)/Art7_15(2).pdf)
- Tisler, T., & Zagorc-Koncan, J. (2002). Acute and chronic toxicity of arsenic to some aquatic organisms. *Bull. Environ. Contam. Toxicol*, 69, 421-429.
- Trach, R.J. (1996). *Ultraviolet/oxidation treatment*. Prepared for the Ground-Water Remediation Technologies Analysis Center. Retrieved from:
http://www.cluin.org/download/toolkit/uvox_o.pdf
- United Nations. (2006). *Water for Life Decade. Factsheet on Water and Sanitation*. Retrieved from:
<http://www.un.org/waterforlifedecade/factsheet.html>

- United Nations Economic & Social Council. (2002). *General Comment No. 15: the Right to Water*. Retrieved from: <http://www.unhcr.ch/html/menu2/6/cescr.htm>
- United States Environmental Protection Agency (USEPA). (1999). *Wastewater Technology Fact Sheet: Ultraviolet Disinfection*. Retrieved from: <http://www.epa.gov/owm/mtb/uv.pdf>
- USEPA. (2002). *Methods for Measuring Acute Toxicity of Effluents and Receiving waters to freshwater and marine organisms*. Retrieved from: <http://www.epa.gov/waterscience/methods/wet/disk2/>
- USEPA. (2004). *Safe Drinking Water Act: Drinking Water Monitoring, Compliance and Enforcement*. Retrieved from: http://www.epa.gov/safewater/sdwa/pdfs/fs_30ann_monitoring_web.pdf
- USEPA. (2005). *Membrane Filtration Guidance Manual*. Retrieved from: http://www.epa.gov/safewater/disinfection/lt2/pdfs/guide_lt2_membranefiltration_final.pdf
- University of Iowa. (2001). *Daphnia magna* image. Retrieved from: http://www.uhl.uiowa.edu/publications/archive/hotline/2001/2001_09/sponsors.xml
- Vancouver Island Health Authority. (n.d.). *Guidelines for the Approval of Water Supply Systems*. Retrieved from: <http://www.viha.ca/NR/rdonlyres/BA469B79-2A46-4215-8E8F-515619A16DAC/0/GUIDELINESFORTHEAPPROVALOFWATERWORKS.pdf>
- VanWynsberghe, R. (2000). Sustainability in proximity to industry: the case of critical events in Walpole Island. *American Indian Culture and Research Journal*, 24, 95-128.
- VanWynsberghe, R. (2002). *AlterNatives: Community, Identity, and Environmental Justice on Walpole Island*. Boston, MA: Allyn and Bacon
- Visser, M. (2005). Walpole Island water tower photo credit. Retrieved from: <http://www.eureka4you.com/wtower-on-w/WalpoleIsland.htm>
- The Water Chronicles. (2008). *A guide to Canada's drinking water*. Retrieved from: <http://www.water.ca/sat-82308.asp#bc>
- Water Quality Regulation 82-126. Retrieved from: <http://www.gnb.ca/0062/regs/82-126.htm>
- The Water Regulations. 2002. Chapter E-10.21 Reg. 1. Retrieved from: <http://www.qp.gov.sk.ca/documents/english/Regulations/Regulations/e10-21r1.pdf>
- Water and Wastewater Facilities and Public Drinking Water Supplies Regulations 181/2009. Retrieved from: <http://www.gov.ns.ca/just/regulations/regs/envwaste.htm>
- Welbourn, R.H. (2003). *The effect of copper and manganese on phytoplankton in the Grand River (Southern Ontario), Lake Erie and Pacific Ocean ecosystems*. Unpublished Master's thesis. Ryerson University, Toronto, ON.
- West, E.G. (1982). *Copper and its Alloys*. New York, NY: Halsted Press

- Winter, J. (2000). *Effects of Golf Course Construction and Operation on the Aquatic Environment of the Precambrian Shield*. Prepared for the Trent University Golf Course Research Group and the Ontario Ministry of the Environment. Retrieved from:
http://www.chebucto.ns.ca/ccn/info/Science/SWCS/INFO/GOLF-COURSES/winter_golf.html
- Wolf, G., Scheunders, & P., Selens, M. (1998). Evaluation of the swimming activity of *Daphnia magna* by image analysis after administration of sublethal cadmium concentrations. *Comparative Biochemistry and Physiology Part A*, 120, 99–105.
- World Health Organization (WHO). (2004). *Copper in Drinking Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality*. Retrieved from:
http://www.who.int/water_sanitation_health/dwq/chemicals/copper.pdf
- WHO. (2007). *Chemical Safety of Drinking Water: Assessing Priorities for Risk Management*. Retrieved from: http://whqlibdoc.who.int/publications/2007/9789241546768_eng.pdf
- WHO. (2008). *Guidelines for Drinking-Water Quality*. Third edition. Retrieved from:
http://www.who.int/water_sanitation_health/dwq/fulltext.pdf
- WHO. (2010). *Chemical Hazards in Drinking Water-Copper*. Retrieved from:
http://www.who.int/water_sanitation_health/dwq/chemicals/copper/en/
- Yuasa, A. (1998). Drinking water production by coagulation-microfiltration and adsorption-ultrafiltration. *Water Science and Technology*, 37(10), 135-146.

Appendices

Appendix A. Sierra Legal Defence Fund's 2006 national drinking water report card

NATIONAL DRINKING WATER REPORT CARD (2006)			
Jurisdiction	Comments (source protection comments not included)	2001	2006
Alberta	GOOD: treatment standards; contaminant standards; accredited labs for water quality testing; operator certification. NEEDS IMPROVEMENT: testing. LACKING: public reporting.	B	B
British Columbia	GOOD: accredited labs for water quality testing; operator certification. NEEDS IMPROVEMENT: treatment standards; contaminant standards; testing; public reporting.	D	C+
Manitoba	GOOD: accredited labs for water quality testing; operator certification; public reporting (planned). NEEDS IMPROVEMENT: treatment standards; contaminant standards; testing.	C-	C+
Newfoundland	GOOD: testing; government tests water quality; public reporting. NEEDS IMPROVEMENT: treatment standards; contaminant standards. LACKING: operator certification.	D	C-
New Brunswick	GOOD: accredited labs for water quality testing. NEEDS IMPROVEMENT: treatment standards; testing. LACKING: contaminant standards; water treatment system design regulation; operator certification; public reporting.	C-	D
NW Territories	GOOD: contaminant standards; testing; accredited labs for water quality testing; public reporting. NEEDS IMPROVEMENT: treatment standards. LACKING: operator certification.	C	C+
Nova Scotia	GOOD: treatment standards; contaminant standards; testing; accredited labs for water quality testing; operator certification. LACKING: public reporting.	B-	B
Nunavut	GOOD: contaminant standards; accredited labs for water quality testing. NEEDS IMPROVEMENT: treatment standards; testing. LACKING: operator certification; public reporting.	C	C
Ontario	GOOD: treatment standards; contaminant standards; testing; accredited labs for water quality testing; operator certification; public reporting.	B	A-
PEI	GOOD: testing; accredited labs for water quality testing; operator certification. NEEDS IMPROVEMENT: public reporting (but plans in works). LACKING: treatment standards; contaminant standards.	F	C-
Quebec	GOOD: treatment standards; contaminant standards; testing; accredited labs for water quality testing; operator certification. NEEDS IMPROVEMENT: public reporting (reports at the regional level only).	B	B+
Saskatchewan	GOOD: accredited labs for water quality testing; operator certification; public reporting. NEEDS IMPROVEMENT: treatment standards; contaminant standards; testing.	C	B-
Yukon†	GOOD: contaminant standards; testing; accredited labs for water quality testing; operator certification. NEEDS IMPROVEMENT: treatment standards. LACKING: public reporting.	D-	C††
Federal Government	NEEDS IMPROVEMENT: evaluation and regulation of chemicals; formulation of standards for guidelines. LACKING: First Nations drinking water safety; binding minimum drinking water standards; recognition of a right to clean drinking water; tracking national drinking water data, trends and best practices.	Not graded	F
Note: †Based on detailed proposed legislation. ††Will be higher if reforms are implemented.			

Source: Christensen, 2006

Appendix B. Drinking water parameters tested in each province/territory as outlined in legislations and guidelines

Testing Parameters	NL	PEI	NS	NB	QC	ON	MB	SK	AB	BC	YK	NWT	NT
Inorganics													
Aluminum	x	x	x						x		x	x	
Ammonia	x								x				
Antimony	x	x	x	x	x	x			x				
Arsenic	x	x	x	x	x	x	x	x	x		x	x	x
Barium	x	x	x	x	x	x		x	x		x	x	x
Boron	x	x	x	x	x	x		x	x		x		
Bromate		x			x				x				
Bromide	x												
Cadmium	x	x	x	x	x	x		x	x		x	x	x
Calcium	x	x	x						x		x		
Chloramines--total		x			x				x				
Chloride	x	x	x	x					x		x	x	x
Chromium	x	x	x	x	x	x		x	x		x	x	x
Copper	x	x	x	x	x				x		x	x	x
Cyanide					x			x	x			x	x
Fluoride	x	x	x	x	x	x	x	x	x		x	x	x
Glyphosate					x	x			x				
Iron	x	x	x	x					x			x	x
Lead	x	x	x	x	x	x	x	x	x		x	x	x
Magnesium	x	x	x						x		x		
Manganese	x	x	x	x					x			x	x
Mercury	x			x	x	x		x	x		x	x	
Nickel	x												
Nitrate	x	x	x	x	x	x	x	x	x		x	x	x
Nitrite	x				x	x			x		x		
Phosphorus (total)	x	x											
Potassium	x	x	x								x		
Radon													
Selenium	x	x	x	x	x	x		x	x		x	x	x
Silver		x							x				x
Sodium	x	x	x	x		x			x		x	x	
strontium		x											
Sulphate	x	x	x	x					x		x	x	x
Sulphide (as H ₂ S)									x				
Uranium	x	x	x	x	x	x	x	x	x		x	x	
Vanadium		x											
Zinc	x	x	x						x		x	x	x
Organics													
Alachlor						x							
Aldicarb						x							
Aldrin + dieldrin						x							
Alkyl benzene sulfonate													x
Atrazine + metabolites					x	x		x	x				
Azinphos-methyl					x	x							
Bendiocarb						x							
Benzene		x		x	x	x	x	x	x				
Benzo[a]pyrene		x		x	x	x		x	x				
Bromoxynil					x	x		x	x				
Carbaryl					x	x							
Carbofuran					x	x		x					
Carbon tetrachloride		x		x	x	x		x	x				
Chlordane						x							
Chlorpyrifos					x	x		x	x				
Cyanazine					x	x			x				
DDT + metabolites						x							
Diazinon					x	x			x				
Dicamba					x			x	x				
1,2-Dichlorobenzene		x		x	x	x		x	x				

	NL	PEI	NS	NB	QC	ON	MB	SK	AB	BC	YK	NWT	NT
1,4-Dichlorobenzene		x		x	x	x		x	x				
1,2-Dichloroethane		x		x	x	x			x				
1,1-Dichloroethylene		x			x	x		x					
Dichloromethane		x		x	x	x		x	x				
2,4-Dichlorophenol,		x			x	x		x	x				
2,4-Dichlorophenoxyacetic acid					x	x		x					
Diclofop-methyl						x		x	x				
Dimethoate					x	x		x	x				
Dinoseb						x							
Diquat					x	x							
Diuron					x	x			x				
Ethylbenzene		x		x					x				
Haloacetic Acids-Total	x												
Heptachlor + heptachlor epoxide						x							
kjeldahl nitrogen	x												
Lindane (Total)						x							
Malathion					x	x		x	x				
Methoxychlor					x	x			x				
Methyl tertiary-butyl ether													
Metolachlor					x	x			x				
Metribuzin					x	x			x				
Monochlorobenzene		x			x	x		x	x				
Nitrilotriacetic acid									x				
Paraquat (as dichloride)					x	x							
Parathion					x	x							
Phenols													x
Pentachlorophenol		x		x	x	x		x	x				
Phorate					x	x							
Picloram					x	x		x	x				
Polychlorinated biphenyls (PCBs)						x							
Prometryne						x							
Simazine					x	x			x				
Temephos						x							
Terbufos					x	x			x				
Tetrachloroethylene		x		x	x	x	x	x	x				
2,3,4,6-Tetrachlorophenol		x			x	x		x	x				
Toluene		x		x					x				
Triallate						x			x				
Trichloroethylene		x		x	x	x	x		x				
2,4,6-Trichlorophenol		x			x	x		x	x				
2,4,5-Trichlorophenoxy acetic acid						x							
Trifluralin					x	x		x	x				
Trihalomethanes-total	x			x	x	x	x	x	x		x	x	
bromoform		x		x									
Bromodichloromethane (BDCM)		x		x			x						
chloroform		x		x									
chlorodibromomethane		x		x									
carbon chloroform extract													x
Vinyl chloride		x		x	x	x		x	x				
Xylenes--total		x		x					x				
Microbiological													
<i>Escherichia coli</i>	x	x	x	x	x	x	x		x	x	x	x	
Total coliforms	x	x	x	x	x	x	x	x	x	x	x	x	x
Fecal coliform					x			x		x			

	NL	PEI	NS	NB	QC	ON	MB	SK	AB	BC	YK	NWT	NT
Physical													
alkalinity	x	x	x								x	x	
Colour	x		x						x		x	x	x
Conductivity			x								x		
Hardness	x	x	x						x		x	x	
pH	x	x	x		x				x		x	x	
Total organic carbon/Dissolved OC	x		x						x		x	x	
Total dissolved solids (TDS)	x		x						x		x	x	x
Total suspended solids											x	x	
Turbidity	x	x	x	x	x	x	x	x	x		x	x	x
UV absorbance						x			x				

Appendix C. St. Clair River priority point sources & contaminants as identified by the Remedial Action Plan

Source	Facility/Production type	Contaminant
Cole Drain	Open ditch drainage system It receives stormwater runoff from undeveloped and developed land, waste disposal and product storage areas, treated and untreated runoff and industrial process effluent and cooling water.	Hexachlorobenzene, Hexachlorobutadiene, Pentachlorobenzene, Octachlorostyrene, Nickel
Dow Chemical	Organic chemical products: vinyl chloride monomer, propylene oxide, propylene glycols, polyglycols, chlorine, caustic soda, anhydrous hydrochloric acid, styrene, polystyrene, latex, ethylbenzene, chlorinated solvents, epoxy resins, and high density and low density polyethylene.	Copper, Zinc, Hexachlorobenzene
ESSO Petroleum	Petroleum refinery produces a complex combination of fuel products, packaging, lubricating oil, and petrochemical operations.	Arsenic, Phosphorus, Ethyl Lead, Mercury, 1,2-Dichloroethane, 1,1-Dichloroethane, Carbon Tetrachloride, 1,1,2-Trichloroethane, Tetrachloroethylene, Trichloroethylene, PAHs, Toluene
Marysville WWTP	Trickling filter secondary plant with chemical phosphorus removal	Phosphorus
Novacor Petroleum	Petrochemical refinery processes crude oil, condensate and natural gas liquids for the production of primary petrochemicals	Arsenic
Polysar	Produces nitrile-butadiene, styrene-butadiene, polybutadiene, and butyl and halobutyl rubbers	Benzene, Oil & Grease, Phosphorus
Port Huron WWTP	Activated sludge secondary treatment plant with chemical phosphorus removal	Cadmium, Phosphorus
Sarnia WPCP	Primary treatment facility with continuous phosphorus removal	Zinc, Cadmium, Iron, Mercury Phosphorus, Copper, Nickel, Lead,
Suncor	Crude oil processed into motor gasoline, light and heavy fuels, light aromatic products, liquefied gases, and solid sulphur.	Arsenic

Source: Adapted from RAP, 1995

Appendix D. Ontario Ministry of Environment "Sarnia Sweep" compliance checklist

Number	Company Name	**Spill Contingency and/or Prevention Plans	C of A for Wastewater Collection or Air Emission Control Equipment	C of A (Air or Wastewater) for altering equipment, systems, processes or structure	Chemical Handling, Storage and Identification
1	Air Liquide Canada Inc.	Y	Y	Y	Y
2	Air Products Canada Ltd.	Y	Y	N	Y
3	Base# Canada Inc.	Y	N	N	N
4	Bayer Inc.	Y	N	Y	Y
5	BP Canada Energy Resources Company	Y	N	Y	N
6	Cabot Canada Ltd.	N	N	N	Y
7	Chinook Corporation	Y	N	N	Y
8	Dow Chemical Canada Inc.	Y	N	N	N
9	Enbridge Pipelines Inc.	Y	N	N	Y
10	Entropex Corporation	Y	N	N	Y
11	Ethyl Canada	Y	N	N	Y
12	Fibrex Insulations Inc.	N	N	N	Y
13	ICI Canada Inc.	Y	N	N	Y
14	Imperial Oil Ltd.	Y	N	N	N
15	Invista (Canada) Company	N	Y	N	N
16	Katoen Natie Canada Company	not required	Y	Y	Y
17	Lanxess Inc. Butyl 1	Y	N	N	Y
18	Lanxess Inc. Butyl 2	Y	N	N	Y
19	Lanxess Inc. landfill	Y	Y	Y	not required
20	NOVA Chemicals (Canada) Ltd. Styrene II Tashmoo	N	N	N	Y
21	NOVA Chemicals (Canada) Ltd. Styrene I	Y	Y	Y	Y
22	NOVA Chemicals Corporation St. Clair	Y	N	N	N
23	NOVA Chemicals Corporation Corunna	Y	N	N	Y
24	NOVA Chemicals Corporation Moore	N	N	Y	X
25	Ontario Power Generation Incorporated	Y	Y	N	Y
26	Praxair Canada Inc. Courtright	Y	Y	N	Y
27	Praxair Canada Inc. Sarnia	N	Y	N	Y
28	Royal Polymers Limited	Y	Y	N	N
29	SCU Nitrogen Inc.	N	Y	N	N
30	Shell Canada Products Ltd.	Y	N	N	N
31	Sunoco Energy Products Inc.	Y	N	Y	Y
32	Terra International (Canada) Inc.	N	N	N	N
33	TransAlta Energy Corporation (Power Island)	Y	Y	N	Y
34	TransAlta Energy Corporation (South Block)	Y	Y	Y	Y
35	TransAlta Energy Corporation (North Block)	Y	Y	N	Y

Source: OMOE, 2005

Appendix E. Arsenic as a bioassay contaminant

Arsenic trioxide was initially chosen as the metal for use in the present study. However, once obtained, the powder would not dissolve in water. According to the *CRC Handbook of Chemistry and Physics*, 2.05 grams of arsenic trioxide should dissolve in 100 grams of water at 20°C (Lide, 2009). Unfortunately, it was not possible to dissolve 0.823 g/L needed for the experiment. In an attempt to increase solubility, the mixture was heated, mixed magnetically, and sonicated. Numerous source waters were tested as well as the water's pH. Faculty and staff members including S. O'Sullivan, K. Terry, and N. George (Ryerson University) were consulted in the process and were also unable to determine why the solute was not dissolving. The chemical supply company, Sigma, was contact and suggested the addition of hydrochloric acid to increase solubility; however, this in itself would have greatly impacted daphnid behaviour and therefore was not considered environmentally relevant. Recently, Ryerson University researcher G. Wolfaardt indicated experiencing similar issues with the dissolving of solutes and has suggested the university's water supply as a likely cause.

Arsenic is a metalloid that occurs in the environment in several oxidation states (-3, 0, +3 and +5) but in natural waters it mostly occurs in the inorganic form as oxyanions of trivalent arsenite or pentavalent arsenate (Smedley and Kinniburgh, 2002; Health Canada, 2006). In comparison to other oxyanion-forming elements, arsenic is among the most problematic in the environment due to its mobility over a range of redox conditions (Smedley *et al.*, 2002). Arsenic is a highly toxic, historical element that has caused great problems in drinking water worldwide. It is listed as a Group 1 carcinogen by the International Agency for Research on Cancer, indicating that it is carcinogenic to humans. Subsequently, the WHO and the USEPA established a drinking water guideline level of 0.01 mg/L. This level was also recently adopted by Health Canada, resulting in a reduction from 0.025 mg/L (Health Canada, 2008). Arsenic exposure is associated with increased incidences of cardiovascular and peripheral vascular disease, neurological disorders, diabetes and various forms of cancer (Rosen and Liu, 2008). In surface water, arsenite and arsenate combine with cations such as iron, to form salts that are dissolved or suspended in the water column. Eventually, these particles settle out and become incorporated into the sediments (Health Canada, 2006).

Arsenic occurs in the environment from various sources and until recently, arsenic was not routinely monitored in drinking water systems. The body of knowledge about its distribution in drinking water is not as well known as other drinking water constituents (Smedley and Kinniburgh, 2002). The WHO guideline values and national standards for arsenic are often exceeded in drinking water sources. In areas of arsenic contamination, drinking water can provide the greatest source of

arsenic to diet and its early detection is therefore critical. Arsenic is transported and distributed through the environment in a complex manner due to many chemical forms in which it can exist in and its continuous cycling through the air, water, and soil. Arsenic exists in the water column in a number of forms: arsenate, the pentavalent form; arsenite, the trivalent form; and as methylarsonic acid and dimethylarsonic acid, both organic arsenicals. In well-oxygenated surface water and sediments, arsenic is often present as arsenate. The oxidation state of arsenate and arsenite is interchangeable depending on the reducing or oxidizing conditions, pH, and biological processes within the environment. Fluctuation in these parameters can result in the release of arsenic that is adsorbed to particulate matter, causing increased arsenic concentrations in the water column (Barlow, 2004). The redox potential (Eh) and pH have the greatest influence on arsenic speciation. In lake and river waters, pentavalent arsenic tends to be the dominant species. Under oxidising conditions, H_2AsO_4^- is dominant at a low pH ($\text{less} \leq 6.9$) and HAsO_4^{2-} prevails at a higher pH. Under reducing conditions, at a $\text{pH} \leq 9.2$, the uncharged arsenite species H_3AsO_3^0 will dominate (Smedley *et al.*, 2002). Arsenic cannot be transformed to a non-toxic form as is the case with many organic pollutants; it can only be transformed into a form that is less toxic such as the transformation from its trivalent form to pentavalent form (Melamed, 2004).

Appendix F. *Daphnia magna* swimming bioassay: immobility

Percentage of *Daphnia* displaying immobility

50 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	0	0	20	40
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	20
Rep 6	0	0	0	0	0	0	20
Rep 7	0	0	0	0	0	0	20
Rep 8	0	0	0	0	0	0	20
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	40
Average	0	0	0	0	0	2	16
100 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	0	0	20	40
Rep 2	0	0	0	0	0	20	20
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	20	60	60
Rep 5	0	0	0	0	20	20	40
Rep 6	0	0	0	0	0	20	20
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	20	20	40
AVG	0	0	0	0	6	16	22
500 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	20	40	60	60
Rep 2	0	0	20	40	40	100	100
Rep 3	0	0	20	40	80	100	100
Rep 4	0	0	0	80	80	80	80
Rep 5	0	0	40	60	100	100	100
Rep 6	0	0	0	40	60	80	80
Rep 7	0	0	0	80	100	100	100
Rep 8	0	0	0	40	80	100	100
Rep 9	0	0	40	60	100	100	100
Rep 10	0	0	0	20	40	40	60
AVG	0	0	12	48	72	86	88

Reference	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	0	0	0	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	20	20
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	0
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	0	0	0	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	20
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	0	0	0	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	0
AVG	0	0	0	0	0	0.6666667	1.33333333

Appendix G. *Daphnia magna* swimming bioassay: height in the water column
Percentage of *Daphnia* displaying changes in swimming height in the water column

50 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	20	40	40	20	20
Rep 2	0	0	20	20	20	0	20
Rep 3	0	0	0	0	0	20	20
Rep 4	0	0	20	60	40	40	20
Rep 5	0	0	0	40	20	40	0
Rep 6	0	0	0	20	0	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	40	40	20	20	20
Rep 9	0	0	0	40	40	20	20
Rep 10	0	0	0	0	20	40	20
AVG	0	0	10	26	20	20	14
100 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	20	40	40	40	60
Rep 2	0	20	20	40	40	20	20
Rep 3	0	0	20	20	20	40	20
Rep 4	0	20	0	60	80	0	20
Rep 5	0	0	0	40	60	40	20
Rep 6	0	20	20	40	40	0	60
Rep 7	0	0	0	20	20	20	40
Rep 8	0	20	20	20	60	40	60
Rep 9	0	20	20	40	60	40	20
Rep 10	0	0	0	20	40	20	20
AVG	0	10	12	34	46	26	34
500 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	20	20	0	40	20	20
Rep 2	0	40	20	20	60	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	80	0	0	0	20
Rep 5	0	20	40	40	0	0	0
Rep 6	0	20	60	40	20	0	20
Rep 7	0	0	40	0	0	0	0
Rep 8	0	40	0	20	0	0	0
Rep 9	0	20	0	20	0	0	0
Rep 10	0	20	40	60	60	60	20
AVG	0	18	30	20	18	8	8

Reference	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	0	0	20	20
Rep 2	0	0	0	0	0	20	20
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	0	0	0	0	0
Rep 7	0	0	0	0	0	0	20
Rep 8	0	0	0	20	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	0
Rep 1	0	0	0	0	0	20	20
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	20	40	0	0
Rep 6	0	0	20	0	20	0	20
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	20	20	20	0
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	20	20	20	20
Rep 6	0	0	20	20	20	20	20
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	20	20	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	0
AVG	0	0	1.33333333	4	4.66666667	4	4.66666667

Appendix H. *Daphnia magna* swimming bioassay: swimming style
Percentage of *Daphnia* displaying changes in swimming style

50 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	0	0	0	0	20
Rep 3	0	0	0	0	0	0	20
Rep 4	0	0	20	20	20	20	0
Rep 5	0	0	0	0	20	20	0
Rep 6	0	0	0	0	20	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	20	0	20	0	0
Rep 9	0	0	0	0	0	20	20
Rep 10	0	0	0	0	20	20	20
AVG	0	0	4	2	10	8	8
100 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	0	0	0	20
Rep 2	0	0	20	0	0	0	0
Rep 3	0	0	20	0	0	0	20
Rep 4	0	40	0	20	20	40	20
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	0	0	0	0	0
Rep 7	0	0	0	0	20	20	0
Rep 8	0	20	0	0	0	0	0
Rep 9	0	0	0	40	0	0	20
Rep 10	0	0	0	0	0	0	20
AVG	0	6	4	6	4	6	10
500 µg/L	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	20	20	40	0	0
Rep 3	0	0	0	20	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	40	0	0	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	20	20	40	40	0
AVG	0	0	8	6	8	4	0

Reference	time 0	time1	time2	time3	time4	time5	time6
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	0	0	0	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	0
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	20	0	0	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	0
Rep 1	0	0	0	0	0	0	0
Rep 2	0	0	0	0	0	0	0
Rep 3	0	0	0	0	0	0	0
Rep 4	0	0	0	0	0	0	0
Rep 5	0	0	0	0	0	0	0
Rep 6	0	0	0	0	0	0	0
Rep 7	0	0	0	0	0	0	0
Rep 8	0	0	0	0	0	0	0
Rep 9	0	0	0	0	0	0	0
Rep 10	0	0	0	0	0	0	0
AVG	0	0	0.66666667	0	0	0	0