

Characterization and Tracking of
Contaminants in Oil Tar Sediments and
Assessment of Water Treatment
Technologies for Their Removal

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Between 1920 and 1950 an oil gasification plant operated on a property adjacent to Kettle Creek about 0.2 km from the mouth of Port Stanley harbour on Lake Erie, Ontario, Canada. Oil tar wastes from the gasification plant were stored on the site until it was eventually abandoned in 1987. At that time the Ontario Ministry of the Environment (MOE) determined that the site was contaminated with heavy metals and polycyclic aromatic hydrocarbons (PAHs) and that some of this waste had been flowing into Kettle Creek through the George Street drain in the village of Port Stanley for an undetermined period of time. The site was completely remediated in 1995 and the flow of contaminated water from the drain ceased. However, sediment sampling revealed the presence of heavy metals and PAHs in Kettle Creek, the inner and outer harbours, and in Lake Erie. From a drinking water source protection perspective, there was an interest in identifying the oil tar contaminants and assessing contaminated sediment transport within the Elgin Area Water Treatment Plant intake protection zones (IPZs). The effectiveness of conventional treatment processes currently available within Elgin Area Water Treatment Plant (WTP) in removing these contaminants was also evaluated.

According to historical monitoring data from various compartments including soil, sediment, groundwater and surface water, three types of contaminants were identified, including heavy metals (Sb, As, Cd, Cr, Cu, Fe, Pb, Ni, Se, V and Zn), PAHs and volatile organics (benzene, toluene, phenols). Due to extremely low toxicity and exposure probability, some unregulated contaminants (iron, vanadium, zinc, phenol and some PAHs) were removed from the final contaminant list and were not discussed from the perspective of treatment.

A technique developed by the USEPA to characterize and track contaminant plumes in water, the fingerprint analysis of leachate contaminants (FALCON), was for the first time investigated for its suitability as a tool to assist with the interpretation of contaminated sediment transport in surface water originating from a former oil/coal gasification plant and its potential to help assess drinking water intake protection zones. A source fingerprint based

on 4 heavy metals (As, Cr, Pb, Ni) and 6 polycyclic aromatic hydrocarbons (PAHs) from 12 sampling sites in a contaminant-impacted harbour was generated. This source fingerprint of the contaminated harbour sediments was then compared to 48 fingerprints generated at other sites in the vicinity of two intake protection zones of a drinking water treatment plant. The source fingerprint did not match fingerprints of sites upstream from the contaminant input source in the creek which fed the small harbour and other potential contamination sources to the east and west in the lake. However, the source fingerprint did match most sites in an outer harbour and some outside the harbour break walls, including sediments collected from within the drinking water intake pipe ~3 km to the east of the harbour. A high correlation between water intake sediments and the source fingerprint demonstrated that contaminated sediments have reached water intake. However, no exceedances of the target contaminants were reported in intake surface water in the period from 1990 – 2010. It was also found that the correlation between the source fingerprint and those in the intake has been decreasing over the period for which data are available, confirming the success of remediation efforts.

Surface water monitoring has demonstrated that PAH concentrations are lower than detection limits and only iron (Fe) exceeds the Ontario Drinking Water Quality Standards (ODWQS) aesthetic objective. The concentrations of oil tar contaminants in treated water were all below the MOE regulated concentrations, indicating that the current Elgin Area Water Treatment Plant configuration is effectively removing any oil tar contaminants present in raw water. Critical raw water concentrations (CRWCs), which represent maximum raw water concentrations that can reliably be removed by the Elgin WTP, were predicted for each oil tar contaminant. The probability of each contaminant exceeding the CRWC was then estimated using a Log Pearson Type III distribution. Copper was found to be the contaminant with the highest exceedance probability. A point system was designed to evaluate the cost-effectiveness of other treatment alternatives and to select the most appropriate of these to improve the robustness of the WTP. Granular activated carbon (GAC) was determined to be the most cost-effective compared to other techniques and hence is considered as the most suitable technique to be implemented in the plant in order to improve its robustness as it relates to dissolved heavy metal species and PAHs.

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List of Abbreviations

| | |
|--------|--|
| A | Aeration |
| AA | Activated Alumina |
| ABC | Association of Boards of Certification |
| AO | Aesthetic Objectives |
| AOPs | Advanced Oxidation Processes |
| AVF | Area Vulnerability Factor |
| BH | Borehole |
| BTX | Benzene, Toluene, Xylene |
| C | Coagulation |
| CCME | Canadian Council of Ministers of the Environment |
| CEF | Cost-Effectiveness Factor |
| CEQG | Canadian Environmental Quality Guidelines |
| CF | Cost Factor |
| CFS | Coagulation Flocculation Sedimentation |
| CRWC | Critical Raw Water Concentration |
| DWSP | Drinking Water Surveillance Program |
| EAPWSS | Elgin Area Primary Water Supply System |
| EBA | Event Based Approach |
| EF | Effectiveness Factor |
| EPA | Environmental Protection Agency |
| FALCON | Fingerprint Analysis of Leachate Contaminants |
| FMECA | Failure Mode and Effect and Criticality Analysis |
| FPT | Federal Provincial Territorial |
| FQG | Fill Quality Guidelines |
| FTA | Fault Tree Analysis |
| G | Skewness |
| GAC | Granular Activated Carbon |
| IARC | International Agency for Research on Cancer |

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|----------------|--|
| IPCS | International Programme on Chemical Safety |
| IMAC | Interim Maximum Allowable Concentration |
| IPZ | Intake Protection Zone |
| ISQG | Interim Freshwater Sediment Quality Guidelines |
| IX | Ion Exchange |
| KC | Kettle Creek |
| LR | Little River |
| LEL | Lowest Effect Level |
| LP | Log Pearson |
| MAC | Maximum Allowable Concentration |
| MCL | Maximum Contaminant Level |
| MO | Metal Oxides |
| MOE | Ministry of Environment |
| MOEE | Ministry of Environment and Energy |
| NF | Nanofiltration |
| NPL | National Priorities List |
| O ₃ | Ozonation |
| ODWQS | Ontario Drinking Water Quality Standards |
| OG | Operational Guidance |
| PAC | Powdered Activated Carbon |
| PO | Pre-Oxidation |
| PS | Precipitation Softening |
| PWQMN | Provincial Water Quality Monitoring Network |
| RO | Reverse Osmosis |
| Ro | Overall Removal Efficiency |
| SCADA | Supervisory Control and Data Acquisition |
| SEL | Severe Effect Level |
| SS | Surface Soil |
| SVF | Source Vulnerability Factor |

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|-------|--|
| SWD | Surface Water Depth |
| TP | Test-pit |
| TPAH | Total PAHs |
| TT | Treatment Technique |
| TOC | Total Organic Carbon |
| To | Transfer Function |
| UF | Ultrafiltration |
| USWRC | U.S. office of Water Data Coordination |
| WHO | World Health Organization |
| WTP | Water Treatment Plant |

Chapter 1

Introduction

1.1 Problem Statement

Between 1920 and 1950 an oil gasification plant operated on a property adjacent to Kettle Creek about 0.2 km from the mouth of Port Stanley harbour on Lake Erie, Ontario, Canada. There is also some evidence to suggest that coal gasification also occurred on the site. Oil/coal tar wastes from the gasification plant were stored on the site until it was eventually abandoned in 1987. At that time the Ontario Ministry of the Environment (MOE) determined that the site was contaminated with heavy metals and polycyclic aromatic hydrocarbons (PAHs) and that some of this waste had been flowing into Kettle Creek through the George Street drain in Port Stanley for an undetermined period of time. The site was completely remediated in 1995 and the flow of contaminated water from the drain ceased.

PAHs and heavy metals are not easily dissolved in water but readily bind to sediments. The oil/coal tar contaminated sediments continue to be transported downstream in Kettle Creek toward Port Stanley harbor and extend from the Port Stanley harbor into Lake Erie. Sediment sampling has revealed the presence of heavy metals and PAHs in Kettle Creek, the inner and outer harbours, and in Lake Erie. Through prevailing Lake Erie littoral drift, those contaminated sediments could potentially be transported to the Elgin Area water treatment plant (WTP) intake and adversely impact the water quality for the Elgin Area Primary Water Supply System (EAPWSS), which supplies drinking water to approximately 94,400 customers. From a source protection perspective, there was an interest in assessing contaminated sediment transport within the Elgin Area Water Treatment Plant intake protection zones (IPZs).

1.2 Research Objectives and Scope

Kettle Creek has been identified as a potential source of contamination due to the presence of oil/coal tar contaminated sediment originating from a former gasification complex. The oil/coal tar contaminants potentially impact sediment quality and the raw water quality at EAPWSS intake area. Through a review of consultant reports and relevant literature,

potential contaminants in oil/coal tar were identified and evaluated on the basis of health impacts. The first objective of this research was to characterize the contaminated sediment through a novel fingerprinting technique and attempt to describe the migration of this sediment within a drinking water intake protection zone. The second objective of this research was to systematically evaluate the potential effectiveness of the Elgin Area WTP in removing selected contaminants should they appear in raw water. Alternative technologies were identified and discussed

1.3 Thesis Organization

Chapter 2 starts with a discussion of intake protection zones and their vulnerabilities. Then the source and fate of anthropogenic contaminants including heavy metals and PAHs are discussed and compared. Potential health impacts of selected contaminants are then comprehensively reviewed and identified. Target contaminants are also classified on the basis of their varying degree of health impacts.

Chapter 3 begins with a review of some background information of EAPWSS, including area characterization, climate, Kettle Creek Watershed, Lake Erie, Port Stanley Harbor and contamination history. Section 3.2 reviews the available soil, sediment, groundwater and surface water monitoring data within the study area to qualitatively evaluate the contribution of oil tar contaminant sediments to downstream sites and the water intake. A contaminant list with drinking water regulation/guideline standards is provided for those potential oil/coal tar contaminants. Finally, Section 3.3 provides a review of design parameters for existing treatment units at Elgin Area WTP.

Chapter 4 focuses on providing a quantitative assessment of contribution of oil/coal tar contaminated sediments to local contamination using an USEPA-developed empirical statistical method known as the fingerprint analysis of leachate contaminants (FALCON) method. Based on sediment sampling data, the pathway of oil/coal tar contaminated sediments is tracked to demonstrate the potential of contaminated sediments to impact intake protection zones of Elgin Area. The results of FALCON analysis are also validated by comparing with the results obtained based on hydrodynamic analysis.

A review of promising treatment alternatives for oil tar contaminants is provided in Chapter 5. The efficiency of the Elgin Area WTP was evaluated for PAHs and heavy metals and those, which if present in raw water, could not be removed through existing conventional processes. Critical raw water concentration and Log Pearson type III distribution analysis are used to calculate the guideline exceedance probabilities of oil tar contaminants and quantitatively evaluate the treatment efficiency of the current Elgin Area WTP processes (as it relates to heavy metals and PAHs). The cost-effectiveness of other treatment alternatives currently not available in Elgin Area WTP is also investigated using a point system. The most cost-effective technology is recommended to ensure the quality of treated drinking water and to provide increased robustness in the existing water treatment plant.

Important conclusions and recommendations are made in Chapter 6.

Chapter 2

Literature Review

2.1 Intake Protection Zones (IPZs) and Water Safety

Following recent drinking water disease outbreaks, regulators, consultants, and municipal drinking water providers have come to recognize even more that the provision of safe water extends beyond simply treating water and instead should be considered as a set of guiding principles to protect, improve, or restore water quality from the source to the tap. Source water protection is a key element in this plan.

2.1.1 Water Intakes and Intake Protections Zones

The Ontario Ministry of the Environment (MOE) (2010) defines a surface water intake as being “the structure through which surface water (water from lakes and rivers) is drawn for drinking water.” According to the nature of a water source, a municipal surface water intake can be fit into one of four categories (Type A – D) (Ontario MOE, 2010). Type A intakes are defined as “intakes located in the Great Lakes.” Type B intakes are those which are located “in connecting channels.” A type C intake is defined as one “located in rivers where neither the flow nor direction of water at the intake is affected by a water impoundment structure.” Type D intakes include all others such as intakes within inland lakes.

An intake protection zone (IPZ) includes “the areas of land and water that surround municipal water intakes that may be vulnerable to contamination” (Ontario MOE, 2010). Based on the degree of vulnerability, IPZs can be further classified into three main categories (IPZ-1, IPZ-2, and IPZ-3).

2.1.1.1 Intake protection zone categories

An IPZ-1 includes the primary area immediately adjacent to the intake (Ontario MOE, 2010). Due to geographic proximity to the intake, contaminants of concern entering IPZ-1 would undergo little to no dilution or sequestration before reaching the intake. An IPZ-1 is typically a zone around the intake with a radius of 1 km.

The Ontario MOE (2010) defines an IPZ-2 as a secondary protective zone that extends upstream from an IPZ-1 in the case of lakes, taking into account currents. Large quantities of contaminants discharged within an IPZ-2 may not be sufficiently diluted or sequestered before reaching the intake. An IPZ-2 includes either water courses or inland water bodies that may contribute water to an intake within a travel time determined based on the minimal response time required by water treatment plant operators to respond to a contamination event (Ontario MOE, 2010). The travel time is generally considered to be no more than a minimum 2-hour time-of-travel (Ontario MOE, 2010).

An IPZ-3 includes a protective area that may contribute contaminants to the intake under extreme conditions (Ontario MOE, 2010). The event based approach (EBA) has been designated as the common methodology to delineate an IPZ-3. Through an EBA, activities that significantly threaten the water intake area must be identified. Then the IPZ-3 boundary can be delineated based on travel time of contaminants released from extreme activities (e.g. 100-year storm event) (Ontario MOE, 2009).

2.1.2 Vulnerability of IPZs

The degree of vulnerability is assessed by a vulnerability score (Ontario MOE, 2009). The IPZ with a higher vulnerability score is considered to be more vulnerable to contamination. The vulnerability score is expressed as the product of the area vulnerability factor (AVF) and the source vulnerability factor (SVF) which are described below.

The area vulnerability factor (AVF) can be evaluated by assessing various factors, including percentage of the area that is composed of land, land cover, soil type, permeability, slope of setbacks, and hydrological/hydrogeological conditions within the area that contribute water to the area via transport pathways (Ontario MOE, 2010). An AVF is quantified by a decision matrix established based on the above factors. Generally, the IPZ that is closer to the water intake has the higher AVF value.

The source vulnerability factor (SVF) can be evaluated by assessing relevant factors, including the depth of the intake, distance of the intake from land, and historical water

quality concerns at the intake. Similarly, a decision matrix developed based on the above factors can be used to quantify a SVF.

Anthropogenic contaminants, which originate from various industries and are widely distributed in different compartments (e.g. water, sediment, soil), can potentially migrate into drinking water intake protection zones resulting in the need for more robust treatment. This is especially the case for persistent contaminants such as heavy metals and PAHs in sediments, as they are refractory to natural degradation processes (e.g. biological, chemical) due to their inert nature and/or high toxicity. Despite being associated with sediment, persistent contaminants can still potentially partition into the water phase. As well, extreme events (e.g. floods) and anthropogenic activities (e.g. dredging) can expose deeper buried contaminants to the water/sediment interface, or simply suspend lighter sediments which are then drawn into the intake. Therefore, it is necessary to understand the characteristics and fate of those anthropogenic contaminants to better monitor and control them.

2.2 Sources and Fate of Selected Anthropogenic Contaminants

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals are two highly persistent organic and inorganic contaminants in natural environment, respectively. Because of their wide distribution and their toxicity to humans and ecosystems, these two contaminants have received considerable attention. It is also widely reported that heavy metals usually coexist with PAHs in the environment due to their common sources such as automobile exhaust and oil gasification (Wang et al., 2004; Morillo et al., 2008).

The coexistence of these two groups of contaminants amplifies the potency of the contamination and increases the difficulty of contamination control. Heavy metals may inhibit or decelerate the biodegradation of PAHs by naturally-occurring microorganisms (Wang et al., 2004). For example, Wild et al. (1991) reported that PAHs were more resistant to biochemical degradation in soil amended with nickel-rich sludge. Therefore, it is important to understand the environmental behavior of both groups of contaminants in order to better control and mitigate potential contamination.

2.2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

2.2.1.1 Introduction to PAHs

Due to their carcinogenicity, mutagenicity, and ecotoxicity (Mumtaz et al., 1996), some polycyclic aromatic hydrocarbons (PAHs) have been included in priority pollutant lists in the USEPA and European Union.

Table 2.1 USEPA priority PAHs list (Manoli and Samara, 1999)

| PAHs | Vapor Pressure (Torr) | Solubility in Water (mg/L) | K _{ow} | Carcinogenic Potency IARC/US EPA * classification |
|------------------------|---|----------------------------|-------------------|---|
| Acenaphthene | 10 ⁻³ – 10 ⁻² at 20°C | 3.4 at 25°C | 21000 | |
| Acenaphthylene | 10 ⁻³ – 10 ⁻² at 20°C | 3.93 | 12000 | |
| Fluorene | 10 ⁻³ – 10 ⁻² at 20°C | 1.9 | 15000 | |
| Naphthalene | 0.0492 | 32 | 2300 | |
| Anthracene | 2×10 ⁻⁴ at 20°C | 0.05 – 0.07 at 25°C | 28000 | 3 |
| Fluoranthene | 10 ⁻⁶ – 10 ⁻⁴ at 20°C | 0.26 at 25°C | 340000 | 3 |
| Phenanthrene | 6.8×10 ⁻⁴ at 20°C | 1.0 – 1.3 at 25°C | 29000 | 3 |
| Benzo[α]anthracene | 5×10 ⁻⁹ at 20°C | 0.01 at 25°C | 4×10 ⁵ | 2A/B2 |
| Benzo[b]fluoranthene | 10 ⁻¹¹ to 10 ⁻⁶ at 20°C | – | 4×10 ⁶ | 2B/B2 |
| Benzo[k]fluoranthene | 9.6×10 ⁻⁷ at 20°C | – | 7×10 ⁶ | 2B |
| Chrysene | 10 ⁻¹¹ to 10 ⁻⁶ at 20°C | 0.002 at 25°C | 4×10 ⁵ | 3/B2 |
| Pyrene | 6.9×10 ⁻⁹ at 20°C | 0.14 at 25°C | 2×10 ⁵ | 3 |
| Benzo[ghi]perylene | ~10 ⁻¹⁰ | 0.00026 at 25°C | 10 ⁷ | 3 |
| Benzo[α]pyrene | 5×10 ⁻⁹ | 0.0038 at 25°C | 10 ⁶ | 2A/B2 |
| Dibenzo[α,h]anthracene | ~10 ⁻¹⁰ | 0.0005 at 25°C | 10 ⁶ | 2A/B2 |
| Indeno[1,2,3-cd]pyrene | ~10 ⁻¹⁰ | | 5×10 ⁷ | 2B/B2 |

2A/B2: Probably carcinogenic to humans/probable human carcinogen;

2B: Possibly carcinogenic to humans;

3: Not classifiable as to human carcinogenicity;

Blank: Not tested for human carcinogenicity.

*IARC: International Agency for Research on Cancer; USEPA: US Environmental Protection Agency

PAHs are comprised of two or more aromatic rings fused together and generally appear as a complex mixture rather than single contaminant (Mumtaz et al., 1996). As semi-

volatile and persistent pollutants, PAHs can undergo long-range migration. Their refractory properties allow PAHs to be ubiquitous contaminants in the environment and they have been detected in atmosphere, water, soil, sediments, food and other matrices (Mumtaz et al., 1996; Mostafa et al., 2009).

Sixteen PAHs have been identified by USEPA as being contaminants of concern due to their higher concentrations at National Priorities List (NPL) hazardous waste sites, greater potential for human exposure, detrimental impacts on human health, and the availability of toxicity data (Mumtaz et al., 1996; Manoli and Samara, 1999). The chemical structures, physiochemical constants, and estimated carcinogenic potency of these 16 PAHs are summarized in Table 2.1 (Manoli and Samara, 1999).

In drinking water supply systems, chlorination may result in the formation of oxygenated and chlorinated PAHs which are more toxic compared to the parent PAHs (Shiraishi et al., 1985).

2.2.1.2 Sources of PAHs

Unlike other anthropogenic organic contaminants, most PAHs have no practical use in industry. Only a few PAHs are used in the production of medicines, dyes, plastics and pesticides, and construction materials (e.g. asphalt) (Mumtaz et al., 1996). The sources of PAHs can be classified into three main categories, including diagenetic, petrogenic, and pyrogenic sources (Mostafa et al., 2009).

Diagenetic PAHs are those which are generated from biogenic precursors (e.g. plant terpenes) which can result in the formation of compounds such as retene and derivatives of chrysene and phenanthrene (Venkatesan, 1988; Silliman et al., 1998). Perylene, which is the most frequently detected diagenetic PAH, is mainly transformed from biogenic precursors through diagenetic processes (Mostafa et al., 2009).

Petrogenic PAHs, which are components of petroleum and other fossil fuels, result from diagenetic processes at relatively low temperatures over geologic time scales (Boeham et al., 2001). Petrogenic sources include the release of petroleum and/or petroleum products during transportation, oil spills, and natural oil seepage (McGroddy and Farrington, 1995;

Yang et al., 2008; Mostafa et al., 2009). The petrogenic PAHs can be classified into two categories based on molecular weight (Burgess et al., 2003). The low molecular weight PAHs are readily biodegraded by microorganisms in the environment whereas higher molecular weight PAHs are more likely to be removed from the water phase through sedimentation (Burgess et al., 2003).

Pyrogenic sources typically include those resulting from incomplete but high-temperature, short-duration combustion of fossil fuels (e.g. oil, gas, and coal), pyrolysis of organic materials, and fires (e.g. forest, prairie) (McGroddy and Farrington, 1995; Mumtaz et al., 1996; Yang et al., 2008). These pyrogenic PAHs result from the breakdown of organic matter to lower molecular weight radicals during pyrolysis (Neff, 1979). Soot carbon is another byproduct during pyrolysis due to agglomeration of pericondensed PAHs.

There is a strong relationship between PAH source and geographical distribution (Burgess et al., 2003). Usually, the pyrogenic PAHs are found to be dominant in the aquatic environment. PAH contaminants generated from these three major sources have distinctive chemical attributes (Mostafa et al., 2009). Pyrogenic PAHs are found to be more strongly bound to particles compared to petrogenic PAHs and hence unlikely to participate in sorption and desorption processes. Additionally, pyrogenic PAHs are less bioavailable and biodegradable than petrogenic PAHs (McGroddy and Farrington, 1995).

2.2.1.3 Fate of PAHs in the Aquatic Environment

As a consequence of their low aqueous solubility and high hydrophobicity, PAHs in aquatic environments are typically rapidly bound to particles and ultimately deposit as sediments. Therefore, sediments in various water bodies including rivers, lakes, and oceans act as important sinks for PAHs (Yang et al., 2008; Khairy et al., 2009; Orecchio et al., 2010). These particle-associated PAHs are readily mixed within the surficial sediment through various physical and biological processes. Those natural processes, including sediment resuspension, biogeochemical activities, and bioturbation (displacement and mixing of sediments and solutes by benthonic organisms), play an important role in determining the migration and fate of PAHs (Yang et al., 2008; Orecchio et al., 2010). Sediment

resuspension, which is mainly caused by hydrodynamic processes (e.g. wave, tides and currents) and anthropogenic activities (e.g. dredging, boating), can directly result in release of PAHs from entrained sediments into the water phase and hence increase their bioavailability.

The partition behavior of PAHs between surface sediments and porewaters (sediment interstitial water) can be described using sediment-porewater partition model proposed by McGroddy and Farrington (1995). The sediment-porewater partition process is also a determining factor in the fate and ecotoxicological risk of PAHs. Partition coefficients are defined to describe the tendency of PAHs release from sediment to porewater (McGroddy and Farrington, 1995) and can be used to predict PAH distribution in sediments (Yu et al., 2009).

2.2.2 Heavy Metals

2.2.2.1 Introduction

Heavy metals of health concern include antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc (Glanze, 1996). The acceleration of industrialization and urbanization increases the chance of those heavy metals being released into the natural environment. Currently, some major heavy metals with high health risk (e.g. arsenic, cadmium, chromium, lead, mercury) have been detected in various compartments within ecosystem such as water, soil and sediments (Audry et al., 2004; Singh et al., 2005; Zhang et al., 2009). Due to the wide distribution and acute and/or chronic health impacts, all those heavy metals have been included in the list of priority pollutants of the WHO, USEPA, European Union, and Health Canada.

2.2.2.2 Sources of Heavy Metals

Heavy metals mainly originate from natural geological processes and anthropogenic activities. Geological weathering of soils and rocks is the most important natural source of heavy metals while anthropogenic sources include industrial, agricultural, municipal, and

residential activities (Audry et al., 2004; Singh et al., 2005; Hang et al., 2009). Industrial processes using metals as raw materials (e.g. smelting, mining, electroplating), releases from oil/coal gasification and other oil spills are the main contributors to heavy metal contamination (Singh et al., 2005; Hang et al., 2009).

2.2.2.3 Fate of Heavy Metals in the Aquatic Environment

Heavy metals in the aquatic environment can exist in colloidal, dissolved, and particulate form (Audry et al., 2004; Peng et al., 2009). When introduced into the aquatic environment, heavy metals can be bound to different compartments within sediments in various ways, including physio-chemical adsorption on sediments, clogging in amorphous materials, complexation with organic matter, and bioaccumulation in benthic organisms (Tessler et al., 1979; Jain and Sharma, 2001; Yu et al., 2001; Singh et al., 2005). Therefore, sediments can act either as carriers or sinks for heavy metals (Singh et al., 2005). The concentration of trace metals in sediments is influenced by particle size and composition of the sediments (Jain and Sharma, 2001). Jain and Sharma (2001) also concluded that the fine-grained sediment fraction, organic matter, and Fe/Mn hydrous oxides within the sediments are the largest sinks for heavy metals and play the major role in their transport.

Compared to PAHs, heavy metals cannot be degraded or destroyed through natural processes and hence tend to be enriched in sediment by organisms and/or other compartments (Peng et al., 2009). It is reported that under some conditions more than 99% of heavy metals introduced into a river can be retained in river sediments in various compartments (Salomons and Stigliani, 1995). Sediments will change from a sink to a source of heavy metals through various processes, including geochemical processes, bioturbation, resuspension of sediments due to anthropogenic activities (e.g. dredging), and diffusion between water-sediment interfaces (van den Berg et al., 2001). Therefore, heavy metals will mobilize among compartments and some metals tend to re-enter the overlying water, increasing their bioavailability and contamination risk.

2.2.3 Contaminated Sediments

Due to their special biogeochemical properties, some anthropogenic contaminants (e.g. PAHs and heavy metals) can directly combine with sediments through various processes (e.g. adsorption) when introduced into the aqueous environment. These contaminants will be confined within sediments (particulates) which will eventually settle to the bottom of a river or lake under favorable hydrodynamic conditions. Sediment movement driven by hydrodynamic processes in surface water is responsible for the migration and dispersion of PAHs and heavy metals to the downstream or surrounding areas. During sediment movement, the sediments are continuously mixing both vertically and horizontally through biological and physical forces and hence the contaminants are dispersed internally. Anthropogenic activities such as dredging and boating can also significantly impact the distribution and migration velocity of the contaminated sediments.

2.3 Properties and Health Impacts of PAHs and Heavy Metals

2.3.1 Properties and Health Impacts

The physico-chemical properties of potential contaminants significantly influence their availability, toxicity, and the selection of treatment alternatives. In sufficiently high concentrations PAHs and heavy metals may cause acute health effects, while in other instances chronic exposure over a longer period (typically years) may increase cancer risk. The physico-chemical properties and health effects of the target contaminants are summarized as follows.

2.3.1.1 Antimony (Sb)

Antimony is found in the environment in the form of trivalent (III) and pentavalent (V) species. The main anthropogenic sources of antimony include the production of ceramics, fire retardants, additives, medicine, pigments, semiconductors, special alloys, and storage batteries (King, 1994; WHO, 2008). The toxicity potency depends on the form of antimony and the pentavalent species is reported to be less toxic compared to trivalent species (WHO, 2008). Soluble antimony (III) salts can cause genotoxic effects in vitro and in vivo (WHO,

2008). Inhalation exposure to antimony was reported to be responsible for pneumonitis, fibrosis, bone marrow damage and carcinomas (Kang et al., 2000). The International Agency for Research on Cancer (IARC) has classified antimony trioxide in Group 2B (possible human carcinogen) and antimony trisulfide in Group 3 (not classifiable as to its carcinogenicity to humans) (IARC, 2010).

2.3.1.2 Arsenic (As)

The oxidation states of arsenic include -3, 0, +3 and +5 (Smedley et al., 2002). The predominant and most stable species of arsenic is As (V)/arsenate in aerobic surface waters but As(III)/arsenite predominates in moderately reducing anaerobic groundwaters (Malik et al., 2009). Arsenic has been widely used in the manufacture of alloys, desiccants, pesticides, glass, pharmaceuticals, pigments, and wood preservatives (Chong et al., 2007). The most toxic form is arsine (AsH_3), followed by As(III)/arsenite, As(V)/arsenate and organic arsenic compounds (WHO, 2008). Arsenic exposure is responsible for hyper- and hypopigmentation, peripheral neuropathy, peripheral vascular disease, dermal lesions, keratosis, liver fibrosis as well as bladder, lung, and skin cancers (Brandhuber and Amy, 1998; Kang et al., 2000; Chong et al., 2007; WHO, 2008). The IARC has classified inorganic arsenic in Group 1 (human carcinogen) (IARC, 2010).

2.3.1.3 Cadmium (Cd)

Cadmium ions have low tendency of hydrolysis at $\text{pH} \leq 8$ and at $\text{pH} \geq 11$ and therefore mainly exist as the hydroxo-complex (Mohan and Singh, 2002). Anthropogenic sources of cadmium include batteries, fertilizers, plastics, and steel industries as well as coal utilization for energy production (Diaz-Somoano et al., 2006; WHO, 2008). The source of daily exposure to cadmium mainly comes from food (WHO, 2008). High levels of cadmium accumulated in human body can induce chronic pulmonary problems, diarrhea, erythrocyte destruction, muscular cramps, nausea, renal degradation, salivation, and skeletal deformity (Mohan and Singh, 2002). The WHO (2008) also reports that cadmium toxicity mainly targets the kidneys. The IARC has classified cadmium and cadmium compounds in Group 2A (probably carcinogenic to humans) (IARC, 2010).

2.3.1.4 Chromium (Cr)

Chromium is commonly present in the form of hexavalent and trivalent species. Cr(III) is believed to be more stable and Cr(VI) is a strong oxidizing agent (Barceloux, 1999a). The main anthropogenic sources of chromium include chrome tanning, electroplating, dyes, paints, and paper industries as well as aluminum manufacturing (Gupta et al., 2001). It is reported that hexavalent form is more toxic compared to trivalent species (Smith and Lec, 1981; WHO, 2008). Barceloux (1999a) also concluded that Cr(III) has low toxicity and has a low tendency to be adsorbed onto gastrointestinal tract. Exposure to Cr(VI) can cause allergic contact dermatitis, digestive and lung carcinoma as well as irritation and corrosion of skin and respiratory tract (Barceloux, 1999a; Gupta et al., 2001). Food is the major source of chromium intake (WHO, 2008). Chromium ingestion may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage (Browning, 1969; Gupta et al., 2001). The IARC has categorized chromium(VI) species in Group 1 (human carcinogen) and chromium(III) in Group 3 (not classifiable as to its carcinogenicity to humans) (IARC, 2010).

2.3.1.5 Copper (Cu)

As a transition metal, copper has three oxidation states including 0, +1, and +2. Anthropogenic sources include metal plating, mining, smelting as well as the application of algicides, fertilizers, and sewage sludge (Barceloux, 1999b; WHO, 2008). Copper is an essential element in human nutrition and is the third most abundant trace element in the body (Flemming and Trevors, 1989; Barceloux, 1999b; WHO, 2008). However, high concentrations of copper can result in adverse health effects such as stomach upset and cause an objectionable taste to the water (Ontario MOE, 2006a). It is also reported that copper sulfate is responsible for irritation of gastrointestinal tract but chronic copper toxicity is rare and primarily targets the liver or kidney (Barceloux, 1999b; USEPA, 2009). The WHO (2008) reported that food and water are two main sources of copper exposure.

2.3.1.6 Iron (Fe)

As an essential element in human nutrition, minimum daily iron requirement, which depends on age, sex, physiological status and iron bioavailability, ranges from about 10 to 50 mg/day

(WHO, 2008). The Provisional Maximum Tolerable Daily Intake (PMTDI) is set as 0.8 mg/kg of body weight to avoid excessive iron storage (WHO, 2008). 10% of this PMTDI is allocated to drinking water and generates a value of approximately 2 mg/L, below which iron does not pose any adverse effect to human health and/or affect taste and appearance of drinking water (WHO, 2008). The application of iron coagulants and pipe corrosion are two potential sources of iron in drinking water (WHO, 2008). Iron can also be naturally elevated in some groundwater sources. High levels of iron in drinking water may impart a brownish color to water and generate a bitter, astringent taste in water (Ontario MOE, 2006a).

2.3.1.7 Lead (Pb)

Lead is present in the form of sulphide, cerussite and galena in the natural environment (Acharya et al., 2009). Based on toxicity data, Pb(II) is the form of lead which is highly toxic and should be targeted. Pb(II) is widely used in various industrial applications such as coal combustion, explosives manufacturing, fuels, gasoline additives manufacturing such as tetra ethyl lead (TEL), photographic material, printing pigments, storage battery manufacture, and television tube (Sabry et al., 2007; Acharya et al., 2009). High levels of lead (II) are directly or indirectly related to anemia, chills, diarrhea, headache, infertility and abnormalities in pregnant women, dysfunction of kidney, reproductive system, and liver, brain, mental retardation, reduction in hemoglobin formation, tissue damage of brain, nervous disorders, and death under extreme circumstances (Gupta et al., 2001; Singh et al., 2008; Acharya et al., 2009). Infants are believed to be the most sensitive subgroup of the population to the lead exposure (WHO, 2008). The IARC has categorized lead and inorganic lead in Group 2B (possible human carcinogen) (IARC, 2010).

2.3.1.8 Nickel (Ni)

The predominant species of nickel in natural waters at pH 5 – 9 is $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ (IPCS, 1991). Other species such as metallic nickel, nickel sulfides, and nickel oxides have poor water solubility (Barceloux, 1999c). Nickel is mainly used in the manufacture of stainless steel and alloys (WHO, 2008). Acute nickel toxicity is mainly caused by nickel carbonyl and typical symptoms include irritation of the respiratory tract, interstitial pneumonitis, and cerebral

edema (Barceloux, 1999c). The IARC has categorized inhaled nickel compounds in Group 1 (human carcinogen) and metallic nickel in Group 2B (possible human carcinogen) (IARC, 2010). Drinking water and food are two primary exposure sources (Barceloux, 1999c).

2.3.1.9 Selenium (Se)

There are various selenium species, including elemental selenium (0), selenide (-2), selenite (+4), selenite (+6) and organic selenium such as selenomethionine and selenocysteine (Tamari, 1998; Barceloux, 1999d). The predominant species found in drinking water is usually the divalent anion Se(II) (American Society of Civil Engineers, 1998). The main anthropogenic sources include ceramic, pharmaceutical, photoelectric cell, pigment, rectifier, rubber, semiconductor, and steel industries (Barceloux, 1999d). As an essential element for humans, daily intake of selenium is recommended as approximately 1 µg/kg of body weight for adult (WHO, 2008). When daily intake exceeds 0.8 mg, chronic exposure to selenium can exert toxic effects on nails, hair and the liver (WHO, 2008). The toxicity of most Se species is low and depends mainly on the chemical form (Barceloux, 1999d). However, there is no evidence of carcinogenic, genotoxic and teratogenic effects in humans under long-term selenium exposure. Food is the main exposure pathway of selenium (WHO, 2008).

2.3.1.10 Vanadium (V)

In aqueous environment, vanadium exists in the +3, +4 and +5 oxidation states (Tubafard et al., 2010). The major anthropogenic sources that contribute to water contamination by vanadium include ceramic, glass, metallurgy, photography, petroleum, rubber, and textile industries (Vega et al., 2003; Naeem et al., 2007). Generally, vanadium compounds have relatively low toxicity (Barceloux, 1999e). Pentavalent vanadium is more toxic and the toxicity of vanadium increases as the valence increases (Barceloux, 1999a). Long-term exposure can cause bronchospasm, conjunctivitis, cough, diarrhea, fatty infiltration of the liver, increased intestinal motility, local irritation of eyes and upper respiratory tract, nasal hemorrhage, sensory, variable fevers, vomiting, and wheezing (Barceloux, 1999a; Tubafard et al., 2010). Because only sufficient evidence in experimental animals for the carcinogenicity has been found, the IARC has classified vanadium pentoxide in Group 2B

(possible human carcinogen) (IARC, 2010). Food is the major exposure source to vanadium (Barceloux, 1999e; WHO, 2008).

2.3.1.11 Zinc (Zn)

Zinc is present in the form of sulfide, carbonate, silicate and oxide in the natural environment (Mohan and Singh, 2002). The hydrolysis of zinc is negligible under $\text{pH} < 7$. The main anthropogenic sources include chemicals, fiber, metals, paper, pulp, and viscose rayon yarn manufacturing processes (Mohan and Singh, 2002). As an essential trace element found in all food and potable water, zinc involves a variety of cellular processes including bone formation, DNA synthesis, behavioral responses, and reproduction (Barceloux, 1999f). PMTDI is set as 1 mg/kg of body weight. It is reported that daily zinc requirement ranges between 15 – 20 mg/day for adult (WHO, 2008). However, high concentrations of zinc can cause undesirable taste in water and a taste threshold concentration is set as 4 mg/L (as zinc sulfate) (WHO, 2008). Barceloux (1999f) also reported that high concentrations of zinc can cause adult respiratory distress syndrome, acute renal tubular necrosis, chemical pneumonitis, interstitial nephritis, and irritation and corrosion of the gastrointestinal tract (Barceloux, 1999f).

2.3.1.12 Benzene

The main anthropogenic sources of benzene include the petrochemical and petroleum refining industries (Gist and Burg, 1997). High concentrations of benzene compounds primarily exert adverse effects on the central nervous system and can cause kidney disease, respiratory allergies, skin rashes and urinary tract disorders (Gist and Burg, 1997; WHO, 2008). Lower concentrations of benzene compounds mainly affect haematopoietic system (WHO, 2008). Benzene is also a well-known human carcinogen (WHO, 2008). The IARC has classified benzene in Group 1 (human carcinogen) (IARC, 2010).

2.3.1.13 Toluene

Toluene ($\text{C}_6\text{H}_5\text{CH}_3$) is widely used either as a solvent in various industries such as coatings, gums, oils, paints, and resins or as raw material for chemical and rubber production (WHO,

2004). Toluene can rapidly volatilize from water column to air and biodegradation and sorption are less important for toluene removal (WHO, 2004). The IARC has classified toluene in Group 3 (not classifiable as to its carcinogenicity to humans) (IARC, 2010). However, it is reported that inhalation of toluene can cause impairment of the central nervous system and irritation of mucous membranes as well as embryotoxic and fetotoxic effects in laboratory animals and humans (WHO, 2008).

2.3.1.14 Phenols

Phenols (4AAP) represent an aggregate measure of compounds with a phenol-like or “phenolic” structure by employing the reagent 4-aminoantipyrine (4AAP) (USEPA, 2002a). The main anthropogenic sources of phenols include chemical, mineral (non-metallic), paper, plastic, pulp, petroleum refining, steel, and wood industries (Health Canada, 2000; Ispas et al., 2010). Phenols are not significantly adsorbed onto suspended or bottom sediment in water and can be removed through biodegradation in water as well as photooxidation in the air (Health Canada, 2000). Health Canada (2000) has concluded that phenol is not considered to be “toxic” because it “is not entering the environment in a quantity or concentration or under conditions constituting or that may constitute a danger in Canada to human life or health.” However, high concentrations of phenol can cause irritation of skin, eyes and mucous membrane and is acutely toxic after both oral and dermal exposure (Health Canada, 2000). It is also noted that phenols can result in the formation of chlorophenols which can cause objectionable tastes and odors in drinking water but are unlikely to pose a significantly adverse impact on human health (Goulden et al., 1973; WHO, 2008). Food is the major exposure route for general population (Health Canada, 2000).

2.3.1.15 Polycyclic Aromatic Hydrocarbons (PAHs)

Natural and anthropogenic sources as well as physico-chemical properties of polycyclic aromatic hydrocarbons (PAHs) were discussed previously. PAHs include a mixture of complex hydrocarbons comprised of two or more fused benzenoid rings. Inhalation and dermal exposure to PAHs can cause cancer. Based on the available scientific information on

the carcinogenicity, the IARC has classified individual and mixture of PAHs in groups with different carcinogen potency (Table 2.2) (IARC, 2010; CCME, 2008).

Table 2.2 IARC classifications of the carcinogenicity of individual and mixtures of PAHs

| Group | Carcinogenic Effect | PAH Contaminants |
|-----------------|--|---|
| Group 1 | Human carcinogen | Coal tars, soots |
| Group 2A | Probably carcinogenic to humans | Benzo(a)anthracene; benzo(a)pyrene; dibenzo(a,h)anthracene; ideno(1,2,3-cd)pyrene |
| Group 2B | Possible human carcinogen | Benzo(b,c)fluoranthene; naphthalene |
| Group 3 | Not classifiable as to its carcinogenicity to humans | Acenaphthene; anthracene; benzo(g,h,i)perylene; chrysene; fluoroanthene; fluorene; phenanthrene; pyrene |

Source: CCME, 2008

2.3.2 Classification of Oil Tar Contaminants

The Ontario MOE has assigned predetermined scores for various contaminants based on their toxicity as illustrated in Table 2.3 (Ontario MOE, 2006b). The maximum score is 10 and higher scores indicate more adverse impacts of the contaminant. There are no toxicity scores (TS) for acenaphthene, antimony, chrysene, fluorine, selenium, and vanadium.

Table 2.3 Toxicity scores of oil tar contaminants

| Toxicity Score (0 = Low; 10 =High) | Contaminants |
|---|---|
| 10 | Arsenic; benzo(a)pyrene; dibenzo(a,h)anthracene |
| 7 | Benzene; benzo(a)anthracene; cadmium; chromium; lead |
| 4 | Benzo(b,c)fluoranthene; benzo(g,h,i)perylene; copper; fluoranthene; ideno(1,2,3-cd)pyrene; nickel; phenanthrene; pyrene |
| 2 | Anthracene; naphthalene; toluene; zinc |
| 0 | Phenols; iron |

Source: Ontario MOE, 2006b

IARC classifications were also used to set criteria to categorize oil tar contaminants into groups with different toxicity potency. IARC Group 1 and Group 2A contaminants, as well as contaminants that have toxicity scores higher than 6, were classified into Group I. All

Group 2B contaminants were classified into Group II. Oil tar contaminants in Group I and II are believed to pose the most risk and are designated as priority contaminants.

Those contaminants with scores less than 5 were classified into Group III, indicating they are of least concern from a human health effects perspective. Group III contaminants include essential elements for human nutrition, non-carcinogens (Group 3), and phenol. Essential elements including copper, iron, selenium, and zinc seldom exert adverse impacts on human health and were considered to have very low toxicity potency (at low concentrations). Phenol has been concluded to be non-toxic by Health Canada (2000) due to its low concentration and persistence in the natural environment. The classification criteria for each group are summarized in Table 2.4 and the contaminant list based on human health effects is summarized in Table. 2.5.

Table 2.4 Classification criteria of oil contaminants based on carcinogenicity potential* and toxicity score (TS)**

| Group | Classification Criteria |
|------------------|---|
| Group I | IARC Group 1 and Group 2A and $TS \geq 7$ |
| Group II | IARC Group 2B |
| Group III | IARC Group 3 and $TS \leq 4$ |

* CCME, 2008

** Ontario MOE, 2006b

Table 2.5 Classification of oil tar contaminants based on carcinogenicity potential* and toxicity score (TS)**

| Group | Contaminants |
|------------------|---|
| Group I | Arsenic; benzene; cadmium; chromium; lead; nickel; PAHs (oil/coal tar); benzo(a)anthracene; benzo(a)pyrene; dibenzo(a,h)anthracene; ideno(1,2,3-cd)pyrene |
| Group II | Antimony; vanadium; benzo(b,c)fluoranthene; naphthalene |
| Group III | Copper; iron; selenium; zinc; phenol; toluene; acenaphthene; anthracene; benzo(g,h,i)perylene; chrysene; fluoroanthene; fluorene; phenanthrene; pyrene |

* CCME, 2008

** Ontario MOE, 2006b

Chapter 3

Background Information

3.1 Elgin Area WTP and Intake

3.1.1 Area Characterization

The Elgin Area Water Treatment Plant (WTP), situated on the north shore of Lake Erie, is located in the Municipality of Central Elgin in Elgin County in southwestern Ontario, Canada (Figure 3.1). Port Stanley, which is located at the mouth of Kettle Creek, is situated approximately 2 km west of the Elgin Area WTP and is the largest community in the vicinity of WTP intake (Figure 3.2).



Figure 3.1 Regional Setting of the Elgin Area Primary Water Supply System

(Stantec Consulting Ltd., 2008)

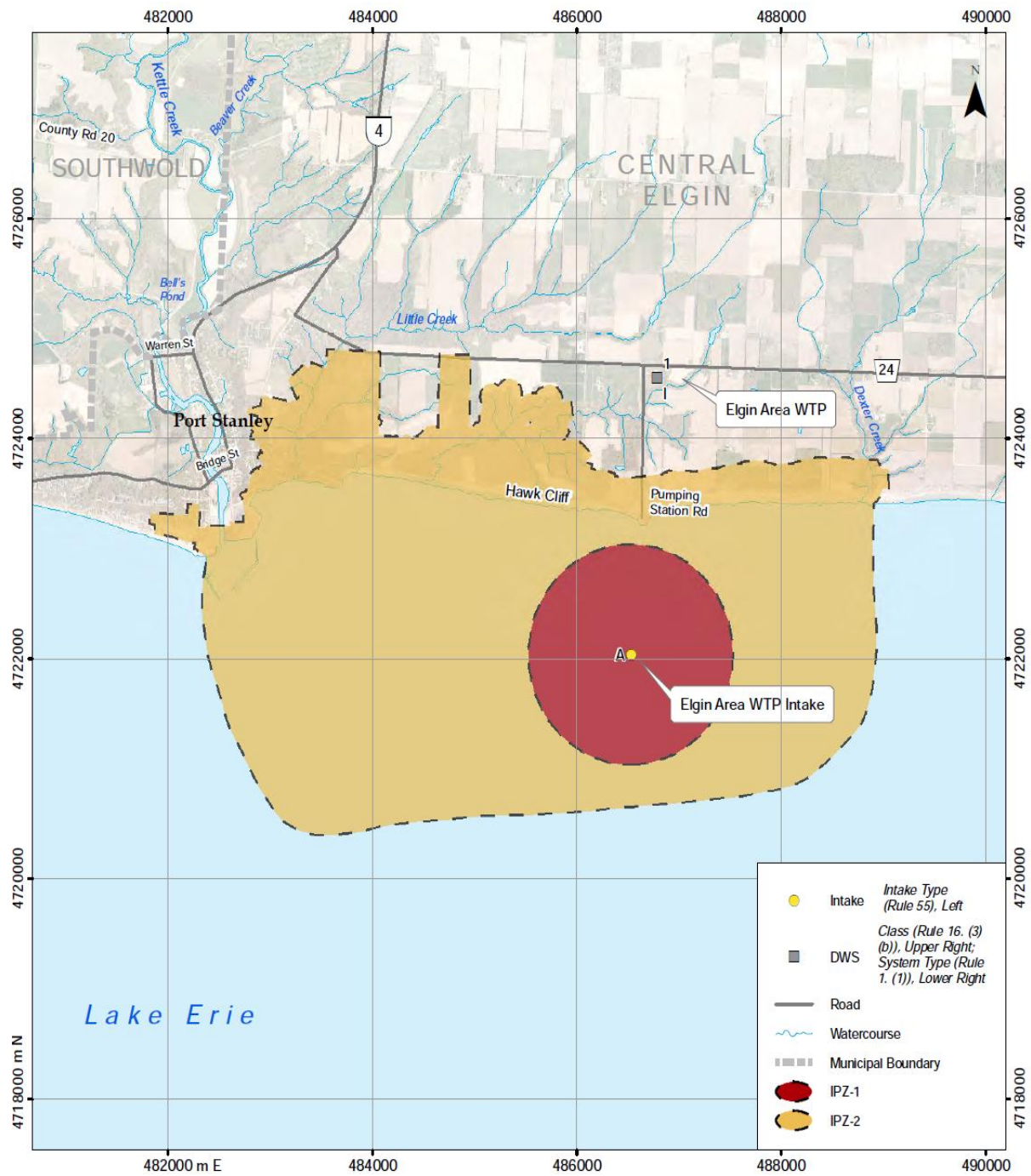


Figure 3.2 Intake Protection Zones for the Elgin Area WTP

(Stantec Consulting Ltd., 2009a)

The vulnerable areas for the Elgin Area WTP are delineated and illustrated in Figure 3.2, including Intake Protection Zone 1 (IPZ-1) and Intake Protection Zone 2 (IPZ-2). IPZ-1 is defined as the most vulnerable zone around the intake and delineated as a circle with a radius of 1000 m centered on the intake (Stantec Consulting Ltd., 2009a). IPZ-2 represents the local drainage zone and characterizes the influences of local water currents, shoreline features, and local tributaries on the water quality at the intake. IPZ-2 includes two main components including contributions from on-shore and in-water parts. The landward part includes some parts of shorelines and watercourses, constructed pathways along the shoreline and up-tributary watershed (Figure 3.2). The in-water part, which includes in-lake and along-shoreline (in-water) areas determined based on three-dimensional hydrodynamic modeling, represent wind and wave influences (Stantec Consulting Ltd., 2009b).

3.1.2 Climate

The study area is located within the Mixed Wood Plains ecozone, which can be further subdivided into 4 ecoregions including St. Lawrence Lowlands, Frontenac Axis, Manitoulin-Lake Simcoe and Lake Erie Lowland (Stantec Consulting Ltd., 2009b). The Elgin Area WTP is situated within Lake Erie Lowland ecoregion, which has humid, warm to hot summers and mild, snowy winters (Stantec Consulting Ltd., 2009b). The Port Stanley weather station, which is closest to the Elgin Area WTP, reported that the annual daily average temperature was 7.6°C during the period from 1971 to 1993 (Stantec Consulting Ltd., 2008). During this time period, precipitation was reported to be evenly distributed throughout the year and the average annual total precipitation was 1,040 mm (Stantec Consulting Ltd., 2009b).

3.1.3 Kettle Creek Watershed and Lake Erie

The Kettle Creek watershed, which is located in southwestern Ontario on the north central shore of Lake Erie, encompasses an area of approximately 520 km² and 83% of the watershed is influenced by agricultural operations (Stantec Consulting Ltd., 2008). The spring peak flow of Kettle Creek is approximately 16 m³/s but the summer flow is often less than 1 m³/s (Acres and Associated, 2001).

Lake Erie is located between the United States and Canada and is the most important water source in the study area. Some important characteristics of Lake Erie are summarized in Table 3.1.

Table 3.1 Lake Erie Characteristics

| Parameter | Value |
|------------------|------------------------|
| Water volume | 484 km ³ |
| Average depth | 19 m |
| Maximum depth | 64 m |
| Surface area | 25,700 km ² |
| Drainage area | 78,000 km ² |

Lake Erie is the shallowest and smallest of the Great Lakes. The lake circulation patterns within the Port Stanley area are generally towards the east for most of the year and the currents within the Port Stanley region are relatively strong compared to other areas of Lake Erie (Beletsky et al., 1999).

3.1.4 Port Stanley Harbour

Port Stanley Harbour is situated at the junction of Kettle Creek and Lake Erie (Figure 3.3) and can be divided into three distinctive areas, including the West Pier, East Pier and East Headland. The site layout of Port Stanley Harbour is illustrated in Figure 3.4



Figure 3.3 Aerial view of Port Stanley Harbour (Municipality of Central Elgin, 2009)

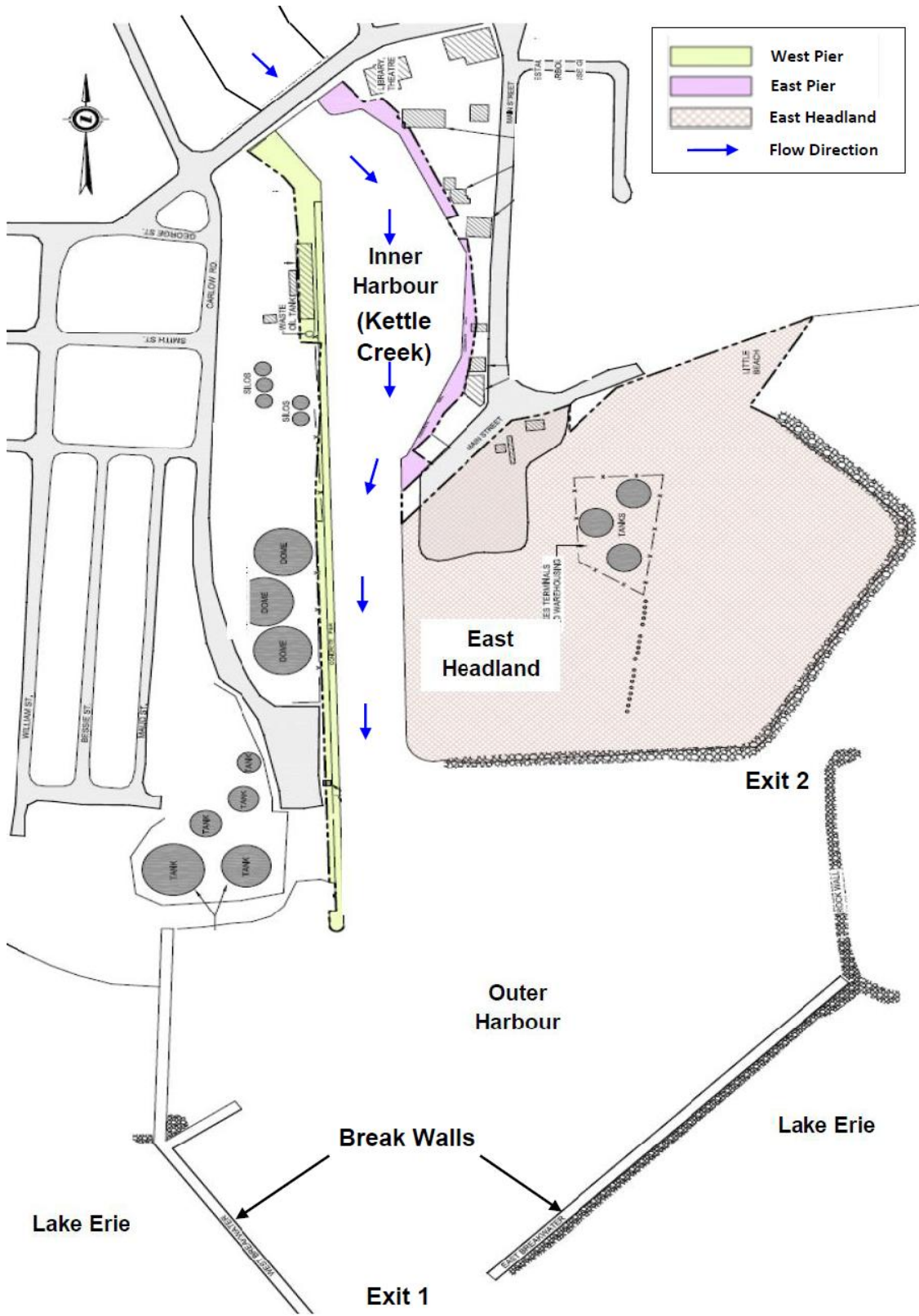


Figure 3.4 Site layout of Port Stanley Harbour (CH2MHILL, 2009b)

The West Pier, which consists of a narrow concrete pier structure, a grassed area, a gravel driveway/parking lot and one story building, is located to the west of Kettle Creek and is mainly used to transfer packaged foods only. Pipelines owned by McAsphalt Industries Ltd. were installed and transect the West Pier to transfer urea ammonium nitrate, fertilizer, and asphalt cement. The East Pier is also a narrow concrete pier that acts as an access road between Kettle Creek and the adjacent businesses. As the largest part of Port Stanley Harbour, the East Headland is a man-made feature constructed with dredged sediments. The former Public Utilities Commission facilities used to be located at East Headland and the main operation included storing, maintaining, and refueling diesel vehicles, and storage of salt utility poles, cold patch and asphalt emulsion (CH2MHILL, 2009a).

3.1.5 History of Contaminant Site

Due to the lack of historical maps and documents for the site, most of historical information for Port Stanley gasification complex site is unconfirmed. Both coal gasification and oil gasification processes were likely employed on the sites (Stantec Consulting Ltd., 2009b; Griffiths and Smith, 2010). Initially, the site was owned by the Southern Ontario Gas Company from the 1920s to the 1930s. During this period, it is believed that gas was generated from coal. From the 1930s to the 1950s, the gasification complex site was transferred to the Dominion Natural Gas Company. An oil gasification facility was constructed in the late 1940s and operated throughout the 1950s (Griffiths and Smith, 2010). Then, the facility was occupied by Shamrock Chemicals Limited (northern parcel) and Ultramar Canada Inc. (southern parcel) between the years 1970 and 1985. The main product of Shamrock Chemicals was solid fertilizer using spent sulphuric acid.

This former oil/coal gasification complex was located at Port Stanley along Carlow Road near Kettle Creek and raw water from Kettle Creek was used in the gas production processes. The raw oil was piped from Port Stanley harbor to produce natural gas which was then supplied to the main gas line near Highway 3. The George Street Drain directed excess water from the wetlands and springs to the east along George Street to Kettle Creek flowing across the historic oil gasification complex. The relative location of facilities to Kettle Creek and the George Street Drain in the study area can be seen in Figure 3.5



Figure 3.5 The relative location of facilities to Kettle Creek and the George Street Drain (MOEE, 1996)

The main waste products generated from oil and coal gasification include heavy metals and polycyclic aromatic hydrocarbons (PAHs) which are commonly referred to as “oil tar” (Warith et al., 1992; Griffiths and Smith, 2010). Feed oil contains sulfides and oxides of vanadium (V), nickel (Ni), and iron (Fe), which are the main ash components in soot (Higman and van der Burgt, 2003; Loehr et al., 1993). Other potential contaminants from oil gasification process include copper (Cu), zinc (Zn), and chromium (Cr) (Warith et al., 1992; Loehr et al., 1993; Higman and van der Burgt, 2003). Similarly, coal feeds as well as gasification products and wastes may contain arsenic (As), cadmium (Cd), selenium (Se), lead (Pb), zinc (Zn), vanadium (V), and antimony (Sb) (Higman and van der Burgt, 2003; Diaz-Somoano et al., 2006). In the following discussion, the wastes from oil and/or coal gasification will simply be denoted as “oil tar” which is more likely to be present. However, contaminants from coal gasification were also included and investigated.

The oil tar from the Port Stanley gasification complex was mainly stored in lagoons for disposal (Griffiths and Smith, 2010). Oil tar is mainly comprised of benzene, toluene, xylene (BTX), cyanide, heavy metals, PAHs and phenols as well as sulphur or nitrogen-containing compounds (Warith et al., 1992). It is reported that metal concentrations in Kettle Creek sediments are most likely caused by this oil tar source because there are no other identified industrial sites in the study area with metal wastes (CH2MHILL, 2009a). The major environmental concern in the study area is the presence of PAH contaminants which have typical concentrations ranging from 300 to 400 mg/kg in soil samples (Warith et al., 1992). In 1970, the oil tar storage lagoons were capped with sediments dredged from Kettle Creek and Port Stanley Harbor, resulting in expansion of the site contamination beyond the initial boundaries (Hyzy and Schepart, 1995). Also, acid spills and acid seepage have been reported to have been discharged into the creek, making assessment of contamination conditions more complicated (Thompson, 2008).

In the mid-1980s, PAH contamination was found on the historic oil/coal gasification complex land and in Kettle Creek sediments downstream of the confluence of the new outlet of the George Street Drain and the creek (Riggs Engineering Ltd, 2007; Griffiths and Smith, 2010). The PAH contaminants detected in 1987 include acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b,c)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorine, ideno(1,2,3-c,d)pyrene, naphthalene, phenanthrene, and pyrene. The contamination in Kettle Creek sediments was predominantly caused by leakage of contaminants (e.g. PAHs and heavy metals) into Kettle Creek via the George Street Drain. As well, the contaminants within the oil tar deposits could have been absorbed and/or adsorbed by sediments and finally washed into Kettle Creek due to agricultural practices, urban development, and bank erosion. The large seasonal changes in flow rate are likely responsible for transport and redistribution of sediments plume to some extent (Acres and Associated, 2001). On the gasification site, the oil tar contaminated soil covered an area of approximately 11,000 m² and the total estimated volume was approximately 38,000 m³ (Warith et al., 1992). The contaminants were found from 1 to 5 m depth (average = 3.5 m) below ground level (Warith et al., 1992).

Remediation has been conducted by the Ontario MOE on the Shamrock Chemicals property and by Ultramar Canada on their own property. The soil had to be excavated and an ex-situ landfarm bioaugmentation technology was successfully applied to remediate contaminated soil (Hyzy and Schepart, 1995). The total PAHs (TPAH) were reduced from initial concentrations of 1,000 ppm to < 100 ppm TPAH (Hyzy and Schepart, 1995). By the mid-1990s, the source of oil tar in Kettle Creek had been essentially eliminated and hence the discharge of PAHs to Kettle Creek had stopped. However, the oil tar contaminated sediments remain in Kettle Creek and are being transported downstream.

According to historical records, the potential contaminants from on-site gasification wastes are summarized in Table 3.2. Those potential contaminants can be generally classified as heavy metals, inorganics, and organics in nature. Polycyclic aromatic hydrocarbons (PAHs) are listed separately from organic contaminants due to their complexity of composition.

Table 3.2 Potential contaminants originating from the oil tar contamination site

| Type | Contaminant |
|---------------------|---|
| Heavy metals | Antimony; arsenic; cadmium; chromium; copper; iron; lead; nickel; selenium; vanadium; zinc |
| Organics | Benzene, toluene, xylene, phenols |
| PAHs | Acenaphthene; anthracene; benzo(a)anthracene; benzo(a)pyrene; benzo(b,c)fluoranthene; benzo(g,h,i)perylene; chrysene; dibenzo(a,h)anthracene; fluoroanthene; fluorene; ideno(1,2,3-cd)pyrene; naphthalene; phenanthrene; pyrene |
| Inorganics | Cyanide |

3.2 Identification of Oil Tar Contaminants

To evaluate the impacts of oil tar contaminants on downstream sites and drinking water intake protection zones, various compartments, including surface water, groundwater, creek/lake sediments and soil sediment, were investigated through reviewing historical sampling data sets. There are various fates (F1 – F3) determining migration and distribution of those contaminants in various compartments (Figure 3.6). The sediment/water parameters can be considered as direct or indirect indicators of potential contamination risk. Therefore, any sediment or water parameter of the contaminants listed in Table 3.2 that exceeds

guideline/regulation requirements in any compartment will be considered as having originated from an oil tar source and listed as a potential risk to intake protection zones.

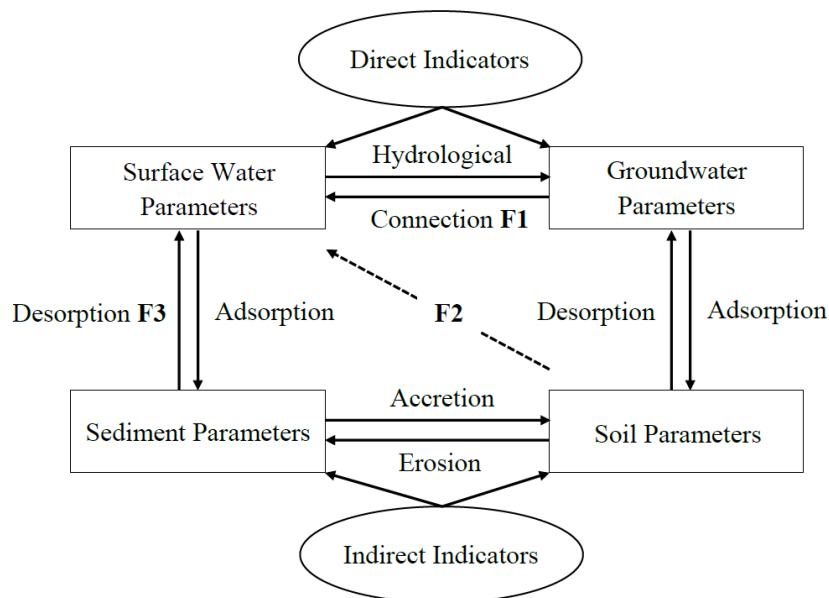


Figure 3.6 Contamination indicators in various compartments

3.2.1 Sediment Analysis

Due to the ability of contaminants (e.g. heavy metals, PAHs) to adsorb and/or absorb onto or within sediment particles, sediment quality of the lakebed and tributaries can directly impact the quality of raw water. To identify the potential contamination risk within the scope of vulnerable areas including IPZ-1 and IPZ-2, sediment analysis was done by comparing available sediment data to appropriate provincial standards. Analytical results for sediment data are compared with the MOE guidelines for the protection and Management of Aquatic Sediment Quality in Ontario Lowest Effect Level (LEL) and Severe Effect Level (SEL), and the Fill Quality Guidelines (FQG) for lake filling in Ontario and sediment standards in Table 1 of the Ontario MOE Soil, Groundwater and Sediment Standards (Ontario MOE, 2007). The MOE standards were selected as they have a wider range of contaminants than does the federal guideline issued by the Canadian Council of Ministers of the Environment (CCME) Canadian Environmental Quality Guidelines (CEQG) – Interim Freshwater Sediment Quality

Guidelines (ISQG) (CCME, 2007). However, the CCME ISQG has more stringent requirements for PAHs and was used to evaluate sediment data.

3.2.1.1 Sources of Sediment Data

To investigate and assess the potential environmental risk within the Elgin Area WTP intake protection zones, the Regional Water Supply and Conservation Authority conducted a series of sediment samplings from 2001 to 2008. The detailed distribution of sediment sampling locations is illustrated in Appendix A. The sediment sampling locations include the drinking water intake pipe and Kettle Creek, which directly discharges into the Elgin Area WTP IPZ-2 vulnerable area (Figure A.1 – 2). The sediment data were acquired from consultant reports (Stantec Consulting Ltd., 2008; 2009a; CH2MHILL, 2009).

Due to the prevailing west to east littoral drift in Lake Erie, oil tar contaminated fine silt and clayey materials from the Kettle Creek have been carried to the intake. The erosion of the Lake Erie bluffs also contributes to sediment accumulation. Sediments have settled out along the intake since plant was commissioned. Riggs Engineering Ltd and Delcan (2004) have reported that the sediment layer accumulated reaches 10 to 45 cm deep in the near shore zone and 50 – 60 cm deep in the offshore zone. It is also reported that sediment movement is most prevalent during spring runoff conditions in Lake Erie, especially at intake depth, where small wave-driven suspension of sediments readily occurs (Stantec Consulting Ltd., 2009c). This study involved sediment deposition and was not specifically designed to determine if PAH and heavy metal concentrations have been changing over time. All the available sediment data were summarized by Riggs Engineering Ltd and Delcan (2004).

Data were examined from a worst-case scenario by comparing maximum heavy metal and PAH concentrations of subsamples for each sampling site from Kettle Creek and water intake to MOE standards. Parameter exceedances in Kettle Creek and water intake sediments are compared to MOE standards and summarized in Tables 3.3 – 3.5.

Table 3.3 Summary of maximum sediment sample heavy metal concentrations which exceed MOE Soil, Groundwater and Sediment Standards ($\mu\text{g/g}$) (Ontario MOE, 2007)

| Heavy metals | MOE Standards ($\mu\text{g/g}$) | Sediment maximum heavy metal concentration ($\mu\text{g/g}$) | | | | | | | | | | |
|--------------|-----------------------------------|--|----|----|----|----|-----|-----|-----|-----|-----|-----|
| | | C3 | S5 | S6 | R5 | R9 | R10 | MS1 | MS2 | MS3 | MS5 | MS6 |
| Copper | 16 | 18 | 18 | 19 | 20 | 20 | 18 | 27 | 26 | 41 | 24 | 25 |
| Nickel | 16 | | | | 17 | | | | | | | |

Table 3.4 Summary of parameter exceedances for PAHs relative to the CCME Interim Freshwater Sediment Guidelines (CCME, 2007)

| PAHs | ISQG ($\mu\text{g/g}$) | Sediment maximum PAH concentration ($\mu\text{g/g}$) | | | | | | | | | | | | | |
|--------------------|--------------------------|--|------|------|------|------|------|------|------|------|------|------|------|------|------|
| | | C1 | C2 | C3 | C4 | R5 | R6 | R10 | S1 | S2 | S3 | S4 | S5 | S6 | S9 |
| Anthracene | 0.0469 | | | | | | | | | | 0.06 | | | 0.07 | |
| Benzo(a)anthracene | 0.0317 | 0.18 | 0.09 | 0.09 | 0.08 | | | 0.06 | 0.07 | 0.06 | 0.18 | 0.07 | 0.06 | 0.06 | 0.12 |
| Benzo(a)pyrene | 0.0319 | 0.15 | 0.08 | 0.08 | 0.08 | | | 0.06 | 0.06 | 0.06 | 0.13 | 0.05 | 0.05 | 0.05 | 0.11 |
| Chrysene | 0.0571 | 0.20 | 0.13 | 0.12 | 0.10 | 0.06 | | 0.11 | 0.10 | 0.08 | 0.18 | 0.09 | 0.09 | 0.08 | 0.14 |
| Fluoroanthene | 0.111 | 0.35 | 0.19 | 0.19 | 0.17 | | | 0.17 | 0.15 | 0.13 | 0.35 | 0.17 | 0.14 | 0.14 | 0.22 |
| Phenanthrene | 0.0419 | 0.09 | 0.09 | 0.11 | 0.08 | 0.05 | | 0.07 | 0.08 | 0.08 | 0.20 | 0.08 | 0.07 | 0.07 | 0.12 |
| Pyrene | 0.053 | 0.31 | 0.17 | 0.17 | 0.16 | 0.08 | 0.06 | 0.15 | 0.13 | 0.11 | 0.30 | 0.14 | 0.12 | 0.12 | 0.25 |

Table 3.5 Summary of parameter exceedances for PAHs relative to CCME Interim Freshwater Sediment Guidelines (intake sediments)

| PAHs | ISQG ($\mu\text{g/g}$) | Sediment maximum PAH concentration ($\mu\text{g/g}$) | | |
|--------------------|--------------------------|--|------|------|
| | | MS2 | MS3 | MS6 |
| Benzo(a)anthracene | 0.0317 | | | 0.05 |
| Naphthalene | 0.0348 | 0.09 | | |
| Pyrene | 0.053 | | 0.06 | |

3.2.1.2 Sediment Analysis Results for Heavy Metals

According to Table 3.3, parameter exceedances for the sediment samples in Kettle Creek include nickel and copper. The sediment analysis results of intake samples indicate that levels exceeding the MOE standards for copper and mercury were observed (Stantec Consulting Ltd., 2009a). However, mercury exceedances may be attributed to the bioaccumulation of mercury by zebra mussels rather than oil tar contaminated sediments (Stantec Consulting Ltd., 2009a). All the other samples have heavy metal concentrations that are below MOE Soil, Groundwater, and Sediment standards.

3.2.1.3 Sediment Analysis Results for PAHs

PAHs were detected at sample sites C1 – C4, S1 – S6, S8, S9, R5, R6, R8, R9, and R10. Sample sites are identified and discussed in detail in Chapter 4. Trace levels of PAHs, which may have originated from Kettle Creek contaminated sediments, were detected at intake sample sites MS2, MS3, and MS6 (Delcan, 2004). All sediment samples in Kettle Creek and the water intake had PAH concentrations that were below MOE Soil, Groundwater, and Sediment standards but above CCME ISQW (Table 3.4 – 3.5) except for R8, R9, S8, and pyrene at MS2, which were also below the CCME ISQW.

3.2.2 Soil Analysis

Dredged contaminated sediments have been used as infill materials to create and expand the East Headland over the course of three decades. The last expansion was recorded in 1978 (CH2MHILL, 2009a). Even though East Headland is somewhat removed from the oil tar contamination site, it could still reflect the impacts of contaminated sediments. Therefore, a soil analysis was conducted by collecting test-pit and borehole samples from the East Headland study area to investigate impacts of oil tar contaminated sediments (Figure A3.1.2). The soil parameters were compared with MOE Soil, Groundwater, and Sediment standards (Full Depth Background Site Condition Standards) which have better parameter availability.

3.2.2.1 Sources of Soil Data

All the available soil and sediment data have been summarized in Stantec Consulting Ltd (2008, 2009a) and CH2MHILL (2009). Similarly, the comparison with criteria was done

assuming the worst-case scenario by using maximum contaminant concentrations of subsamples for each sampling site from East Headland. All the sediment parameter exceedances for East Headland compared to MOE standards are summarized in Table 3.6.

Table 3.6 Summary of parameter exceedances for soil samples

| Contaminants | MOE Standards (µg/g) | Soil maximum concentration (µg/g) | | | | |
|-----------------------|----------------------|-----------------------------------|----------|----------|----------|---------|
| | | TP 08-3A | TP 08-3B | TP 08-4A | TP 08-4B | BH 08-2 |
| Heavy metals | | | | | | |
| Arsenic | 18.00 | | | 41.00 | | |
| Selenium | 1.20 | 2.00 | | 2.00 | | |
| PAHs | | | | | | |
| Acenaphthene | 0.07 | 0.16 | 0.08 | | | |
| Anthracene | 0.16 | 1.17 | 0.43 | | | |
| Benzo(a)anthracene | 0.70 | 1.73 | | | | |
| Benzo(a)pyrene | 0.30 | 0.94 | | | | |
| Benzo(b)fluoranthene | 0.47 | 0.96 | | | | |
| Benzo(g,h,i)perylene | 0.68 | 0.77 | | | | |
| Benzo(k)fluorathene | 0.48 | 0.71 | | | | |
| Chrysene | 0.94 | 2.03 | | | | |
| Dibenzo(ah)anthracene | 0.16 | 0.18 | | | | |
| Fluoroanthene | 1.10 | 2.24 | | | | |
| Fluorene | 0.12 | 0.49 | 0.30 | | | |
| Ideno(1,2,3-cd)pyrene | 0.38 | 0.49 | | | | |
| Naphthalene | 0.09 | 3.23 | 1.41 | 0.29 | 0.76 | 0.13 |
| Phenanthrene | 0.42 | 5.10 | 2.11 | 0.89 | | |
| Pyrene | 1.00 | 3.48 | | | | |

3.2.2.2 Soil Analysis Results for Heavy Metals

All eight borehole (BH) samples had heavy metal concentrations that were below MOE Soil, Groundwater, and Sediment standards. As per Table 3.6, parameter exceedances for the test-pit (TP) samples in East Headland include arsenic and selenium at two locations (TP08-3 and TP08-4). All surface soil (SS) heavy metal concentrations were below MOE standards.

3.2.2.3 Soil Analysis Results for PAHs

Parameter exceedances of PAHs for soil samples in East Headland include acenaphthene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b,c)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoroanthene, fluorine, ideno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene (Table 3.6). However, it should be noted that TP08-3 and TP08-4 are located at a coal fill area which may be the cause of high PAH concentrations. All surface soil PAH concentrations were below MOE standards. However, PAH contaminants were detected at SS08-2 and SS08-4.

3.2.2.4 Soil Analysis Results for Xylenes

Xylenes were detected at TP08-2 and BH08-4. However, detected concentrations were observed below the MOE standards.

3.2.3 Groundwater Quality Analysis

Groundwater samples data collected on the East Headland and along West and East Piers are available. West Pier (BH1, BH3, BH8, and BH10) and East Pier (BH08-5, BH08-6, BH08-7, and BH08-8) are hydrologically connected to Kettle Creek and the groundwater quality was impacted by oil tar contamination. Therefore, samples from these two sites were also analyzed. CH2MHILL (2009a) indicates that groundwater flows radially out from the center of the East Headland. To better understand the impacts of oil tar contaminants on the East Headland, groundwater parameters were compared with MOE standards.

3.2.3.1 Sources of Groundwater Data

All available groundwater data were summarized in CH2MHILL (2009a). The groundwater parameter exceedances for East Headland compared to MOE standards are summarized in Tables 3.7 and 3.8.

Table 3.7 Summary of groundwater standard maximum exceedances for heavy metals and organics

| Contaminant | MOE Standards (µg/L) | Groundwater maximum concentration (µg/L) | | | | | | | | | |
|---------------------|----------------------|--|---------|---------|---------|---------|---------|---------|---------|---------|----------|
| | | BH 08-1 | BH 08-2 | BH 08-3 | BH 08-4 | BH 08-5 | BH 08-6 | BH 08-7 | BH 08-8 | BH 08-9 | BH 08-10 |
| Heavy metals | | | | | | | | | | | |
| Antimony | 1 | | | | | | | | | | |
| Arsenic | 4.7 | | 6 | 6 | | | | | | | 7 |
| Cadmium | 0.13 | 569 | 112 | 156 | 196 | | | | | | |
| Chromium | 15 | 20 | | | | | | | | | |
| Copper | 8.6 | | | | 10 | | | | | | |
| Lead | 0.72 | | | | | | | | | | |
| Nickel | 4.8 | 30 | 8 | 6 | 17 | | 8 | 8 | 9 | 5 | |
| Selenium | 9.6 | | | | | | | | | | |
| Vanadium | 2.3 | | 9 | 6 | 12 | | 6 | 6 | 8 | 18 | |
| Zinc | 42 | | | | | | | | | | |
| Organics | | | | | | | | | | | |
| Benzene | 0.05 | | | | 0.5 | 0.5 | | | | | |
| Phenols (4AAP) | 5 | | | | 13 | | | | | | |
| Toluene | 0.05 | | | | | 0.9 | | | | < 3 | |

Table 3.7 Summary of groundwater standard maximum exceedances for heavy metals and organics (continued)

| Contaminant | MOE Standards (µg/L) | Groundwater maximum concentration (µg/L) | | | | | | | | |
|---------------------|----------------------|--|------|-----|-----|---------|--------|--------|--------|--------|
| | | BH1 | BH10 | BH3 | BH8 | MW 06-1 | MW 2-R | MW 3-R | MW 5-R | MW 9-R |
| Heavy metals | | | | | | | | | | |
| Antimony | 1 | | | | | | | | | |
| Arsenic | 4.7 | | | | 9 | | 5 | | | |
| Cadmium | 0.13 | | | | | | | | | |
| Chromium | 15 | | | | | | | 30 | | |
| Copper | 8.6 | | | | | | | | | |
| Lead | 0.72 | | | | | | | | | |
| Nickel | 4.8 | 8 | 11 | 8 | 12 | 11 | 23 | 30 | 11 | 7 |
| Selenium | 9.6 | | | | | | | | | |
| Vanadium | 2.3 | 7 | 8 | 7 | 5 | 4 | 20 | | 3 | 5 |
| Zinc | 42 | | | | | | | | | 113 |
| Organics | | | | | | | | | | |
| Benzene | 0.05 | | 0.7 | | | | | | | |
| Phenols (4AAP) | 5 | | | | | 9 | | | 6 | |
| Toluene | 0.05 | | | | | | | | | |

Table 3.8 Summary of groundwater standard maximum exceedances for PAHs

| Contaminant | MOE Standards (µg/L) | Groundwater maximum PAH concentration (µg/L) | | | | | | | | | |
|-----------------------|----------------------|--|---------|---------|---------|---------|---------|---------|---------|---------|----------|
| | | BH 08-1 | BH 08-2 | BH 08-3 | BH 08-4 | BH 08-5 | BH 08-6 | BH 08-7 | BH 08-8 | BH 08-9 | BH 08-10 |
| PAHs | | | | | | | | | | | |
| Anthracene | 0.01 | | | | | 0.05 | 2.3 | 0.03 | 0.05 | 6 | 0.3 |
| Benzo(a)anthracene | 0.02 | | | | | | 1.26 | | | 0.31 | 0.05 |
| Benzo(a)pyrene | 0.005 | | | 0.007 | 0.007 | | 0.805 | 0.007 | | 0.052 | 0.045 |
| Benzo(b)fluoranthene | 0.01 | | | | | | 0.33 | | | 0.05 | 0.05 |
| Benzo(g,h,i)perylene | 0.02 | | | | | | 0.19 | | | 0.02 | 0.04 |
| Benzo(k)fluorathene | 0.01 | | | | | | 0.24 | | | | 0.02 |
| Chrysene | 0.01 | | | | | | 1.33 | | | 0.78 | 0.07 |
| Dibenzo(ah)anthracene | 0.02 | | | | | | 0.03 | | | | |
| Fluoroanthene | 0.01 | | | | 0.04 | 0.1 | 4.95 | 0.05 | 0.09 | | |
| Fluorene | 29 | | | | | 0.04 | 1.48 | 0.12 | 0.04 | 64 | |
| Ideno(1,2,3-cd)pyrene | 0.02 | | | | | | 0.2 | | | | 0.04 |
| Naphthalene | 7 | | | | | | | | | 7 | |
| Phenanthrene | 0.01 | | | 0.04 | 0.32 | 0.21 | 3.08 | 0.32 | 0.22 | 135 | |
| Pyrene | 0.01 | | | 0.02 | 0.04 | 0.15 | 8.66 | 0.04 | 0.14 | 3 | 0.2 |

Table 3.8 Summary of groundwater standard maximum exceedances for PAHs (continued)

| Contaminants | MOE Standards (µg/L) | Groundwater maximum PAH concentration (µg/L) | | | | | | | | |
|-----------------------|----------------------|--|-------|-----|-----|---------|--------|--------|--------|--------|
| | | BH1 | BH10 | BH3 | BH8 | MW 06-1 | MW 2-R | MW 3-R | MW 5-R | MW 9-R |
| PAHs | | | | | | | | | | |
| Anthracene | 0.01 | | 0.07 | | | | | | | |
| Benzo(a)anthracene | 0.02 | | | | | | | | | |
| Benzo(a)pyrene | 0.005 | 0.009 | 0.023 | | | | | | | |
| Benzo(b)fluoranthene | 0.01 | | | | | | | | | |
| Benzo(g,h,i)perylene | 0.02 | | 0.05 | | | | | | | |
| Benzo(k)fluorathene | 0.01 | | | | | | | | | |
| Chrysene | 0.01 | 0.05 | 0.04 | | | | | | | |
| Dibenzo(ah)anthracene | 0.02 | | | | | | | | | |
| Fluoroanthene | 0.01 | | 0.04 | | | | | | | |
| Fluorene | 29 | 9 | | 1.3 | | | | | | |
| Ideno(1,2,3-cd)pyrene | 0.02 | | | | | | | | | |
| Naphthalene | 7 | | | | | | | | | |
| Phenanthrene | 0.01 | 8 | | 1.1 | | | 0.08 | | | |
| Pyrene | 0.01 | | 0.12 | | | | 0.02 | | | |

3.2.3.2 Groundwater Quality Analysis Results for Heavy Metals

As per Table 3.7, groundwater standard exceedances for heavy metals include antimony, arsenic, cadmium, cobalt, copper, lead, nickel, selenium, vanadium, and zinc compared to MOE. Those exceedances were distributed widely on the West and East Piers, and on the East Headland.

3.2.3.3 Groundwater Quality Analysis Results for PAHs

PAH contaminants were detected in all samples located on the West and East Piers as well as most of samples on the East Headland. Many detected concentrations of PAH contaminants exceed MOE standards. According to flow direction of groundwater in the study areas, these PAHs will flow into Kettle Creek and Lake Erie, increasing the quantity of oil tar contaminated sediments.

3.2.3.4 Groundwater Quality Analysis Results for Organics

Phenols were detected at sample sites BH08-4, MW06-1 and MWR-5. Those detected concentrations of phenols were observed above the MOE standards. Parameter exceedances of benzene were also found at BH08-4, BH08-5, and BH10. One concentration exceedance of toluene was found at BH08-5.

3.2.4 Surface Water Quality Analysis

3.2.4.1 Sources of Surface Water Data

In terms of raw water parameters including heavy metals, pesticides and volatile organics, the Ontario MOE's Drinking Water Surveillance Program (DWSP) is the most comprehensive database available. All the parameter exceedances of DWSP data using annual maximum for the Elgin Area WTP intake for the sampling period from 1990 to 2008 are summarized in Table 3.9.

To investigate the contamination risk of PAH contaminants detected from sediment analysis of Kettle Creek, Riggs Engineering Ltd. and Delcan Corporation conducted a single water sampling event in 2003 and the same PAHs detected in the sediment analysis were monitored. All the available data were summarized in Riggs Engineering Ltd. and Delcan (2004).

Stantec Consulting Ltd. (2008) also reviewed and summarized the available data from the Provincial Water Quality Monitoring Network (PWQMN), the Great Lakes Surveillance Program, beach sampling, and annual reports from regional municipalities. The results from this study are also included in the following discussion.

Table 3.9 Summary of parameter exceedances for DWSP data

| <i>Heavy metal</i> | <i>ODWQS</i> ($\mu\text{g/L}$) | <i>Surface water maximum concentration ($\mu\text{g/L}$)</i> | | | | | | | |
|--------------------|-------------------------------------|---|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | | 1990 | 1991 | 1992 | 1993 | 1994 | 1995 | 1997 | 1998 |
| Iron | 300 | 1800 | 1100 | 560 | 3000 | 1470 | 1230 | | 948 |

| <i>Heavy metal</i> | <i>ODWQS</i> ($\mu\text{g/L}$) | <i>Surface water maximum concentration ($\mu\text{g/L}$)</i> | | | | | | |
|--------------------|-------------------------------------|---|-------------|-------------|-------------|-------------|-------------|-------------|
| | | 1999 | 2000 | 2002 | 2004 | 2005 | 2007 | 2008 |
| Iron | 300 | 411 | 742 | | | 1610 | 900 | 267 |

3.2.4.2 Surface Water Quality Analysis Results for Heavy Metals

All the available data were compared to Ontario Drinking Water Quality Standards (ODWQS). According to Table 3.9, iron in raw water regularly exceeded ODWQS aesthetic objective for sampling period 1990 – 2008. The same findings have been reported by Stantec Consulting Ltd. (2008). Treated drinking water concentrations for iron were always lower than its aesthetic guideline values.

3.2.4.3 Surface Water Quality Analysis Results for PAHs

PAH contaminants including chrysene, fluoranthene, naphthalene, pyrene, 1-methylnaphthalene were detected in water at the sampling location which was situated in Kettle Creek across the deepest point in the channel where oil tar contaminated sediment has reached. However, none of them exceeded the ODWQS criteria (Stantec Consulting Ltd., 2008).

3.2.5 Contaminant List (Guidelines and Regulations)

Based on the above analysis, all the potential contaminants which originated from oil tar contamination site (Table 3.2) and exceed any of the various regulatory criteria that exist for groundwater, surface water, soil, and sediment, have been identified as contaminants of

concern for Elgin area intake protection zones and are summarized in Table 3.10. Also, the drinking water guidelines/standards for these contaminants have been included.

Table 3.10 List of possible contaminants and drinking water guidelines/standards if any

| Contaminant | Ontario MOE^a MAC or IMAC | Health Canada^b MAC (mg/L) | USEPA^c MCL or TT (mg/L) | WHO^d (mg/L) |
|----------------------------|--|---|---|-----------------------------------|
| <i>Heavy Metals</i> | | | | |
| Antimony | 0.006(IMAC) | 0.006 | 0.006 | 0.02 |
| Arsenic | 0.025(IMAC) | 0.010 | 0.010 | 0.01 (P)* |
| Cadmium | 0.005 | 0.005 | 0.005 | 0.003 |
| Chromium | 0.05 | 0.05 | 0.1 | 0.05 (P)* |
| Copper | 1.0 ^e | ≤ 1.0 ^e | TT5; AL = 1.3 | 2 |
| Iron | 0.3 ^e | ≤ 0.3 ^e | 0.3 ^e | 0.3 ^e |
| Lead | 0.01 | 0.01 | TT5; AL = 0.015 | 0.01 |
| Nickel | N/A | N/A | 0.1 | 0.07 |
| Selenium | 0.01 | 0.01 | 0.05 | 0.01 |
| Vanadium | N/A | N/A | N/A | N/A |
| Zinc | 5.0 ^e | ≤ 5.0 ^e | 5 ^e | 5 ^e |
| <i>Organic</i> | | | | |
| Benzene | 0.005 | 0.005 | 0.005 | 0.01 |
| Toluene | 0.024 | ≤0.024 ^e | 1.0 | 0.70(C)* |
| Phenols | N/A | N/A | N/A | N/A |
| <i>PAHs</i> | | | | |
| Acenaphthene | N/A | N/A | N/A | N/A |
| Anthracene | N/A | N/A | N/A | N/A |
| Benzo(a)anthracene | N/A | N/A | 0.0001(P)* | N/A |
| Benzo(a)pyrene | 0.00001 | 0.00001 | 0.0002(P)* | 0.0007 |
| Benzo(b)fluoranthene | N/A | N/A | 0.0002(P)* | N/A |
| Benzo(g,h,i)perylene | N/A | N/A | N/A | N/A |
| Benzo(k)fluorathene | N/A | N/A | 0.0002(P)* | N/A |
| Chrysene | N/A | N/A | 0.0002(P)* | N/A |
| Dibenzo(a,h)anthracene | N/A | N/A | 0.0003(P)* | N/A |
| Fluoroanthene | N/A | N/A | N/A | N/A |
| Fluorene | N/A | N/A | N/A | N/A |
| Ideno(1,2,3-cd)pyrene | N/A | N/A | 0.0004(P)* | N/A |
| Naphthalene | N/A | N/A | N/A | N/A |
| Phenanthrene | N/A | N/A | N/A | N/A |
| Pyrene | N/A | N/A | N/A | N/A |

N/A: No standard or guideline

AL = Action Level

^aOntario MOE, 2006a. Technical Support Document for Ontario Drinking Water Standards, Objectives and Guidelines. MAC is maximum acceptable concentration and IMAC is the interim maximum acceptable concentration (Ontario MOE, 2006a)

^bFPT Committee on Drinking Water (2008), Guidelines for Canadian Drinking Water Quality – Summary Table. MAC is maximum acceptable concentration (FPT Committee on Drinking Water, 2008).

^cFrom USEPA (2009), National Primary Drinking Water Regulations.

^dWorld Health Organization (WHO) (2008), Guidelines for Drinking Water Quality, third edition

^eAesthetic objectives (AO) and Operational Guidance (OG) values (FPT Committee on Drinking Water, 2008).

(P)* = provisional guideline value because there is evidence of a hazard but the available information on health effects is limited.

(C)* = concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, resulting in consumer complaints.

According to the sources used to compile Table 3.10, there are no guidelines or standards value specified for vanadium, phenol, and some of the PAHs, including acenaphthene, anthracene, benzo(g,h,i)perylene, fluoroanthene, fluorine, naphthalene, phenanthrene, and pyrene. These contaminants in Table 3.10 could potentially impact the water intake for the Elgin Area WTP. Fortunately, water quality sampling results have confirmed that treated water quality has not been impacted in years for which data are available.

3.3 Existing Treatment Units at Water Treatment Plant

The Elgin Area Primary Water Supply System (EAPWSS) is owned by the EAPWSS Joint Board of Management which is administered by the City of London. The supply system was constructed in 1969 with a series of expansions and improvements in the following decades, including capacity expansion and installation of a zebra mussel control system, fluoridation system and baffle curtains (in clear well) (EAPWSS, 2008).

The EAPWSS is classified as a large municipal residential water system and supports two distinct groups of users including the City of London and area municipalities (Stantec Consulting Ltd., 2008). Approximately 94,400 people are supplied with drinking water from Elgin Area WTP and the raw water is solely obtained from Lake Erie (EAPWSS, 2008). The type A (Great Lakes) intake is situated 7.9 m below low water datum for Lake Erie and is

located 1200 m offshore (Stantec Consulting Ltd., 2009b).The capacity and flow data for EAPWSS are summarized in Table 3.11.

Table 3.11 Capacity and flow data for the EAPWSS

| Parameter | m³/d |
|--------------------------|------------------------|
| Design capacity | 91,000 |
| Average day treated flow | 47,162 |
| Average day raw flow | 49,356 |
| Maximum day treated flow | 59,589 |
| Maximum day raw flow | 63,571 |

The major components of the EAPWSS include the raw water intake, low lift pumps, raw water pipeline, rapid mix and flocculation tanks, sedimentation tanks, dual media filters, UV disinfection system, clearwell, highlift pumps, backup power, plant drain, Supervisory Control and Data Acquisition (SCADA) system, storage reservoir, and a booster pumping station. The low lift pumping station, which is situated on the shore of Lake Erie, is located approximately 1.1 km south of the WTP (EAPWSS, 2008). A concrete pressure pipe with 1500 mm diameter extends from the low lift pumping station approximately 1.3 km into Lake Erie to draw raw water from the lake (EAPWSS, 2008). The raw water is transferred from the low lift pumping station to the pre-treatment process of the WTP via a raw water pipeline approximately 1.4 km long. The plant drain, which can be temporarily used as an alternate intake and supply line under emergency conditions, is a 300 m steel and concrete pipe with a diameter of 900 mm (EAPWSS, 2008). The detailed capacity and flow data for waterworks in EAPWSS are summarized Table 3.12.

The Elgin Area WTP is a conventional Class IV water treatment plant. The treatment processes in the WTP include pre-chlorination, screening, powdered activated carbon addition (as required), coagulation-flocculation, sedimentation, filtration, UV disinfection (as required), post-chlorination and fluoridation (Figure 3.7).

Table 3.12 Capacity and flow data for the Elgin Area Water Treatment Plant

| Parameter | m ³ /d |
|------------------------------------|-------------------|
| Raw water intake | 182,000 |
| Low lift pumps | 91,000 |
| Raw water pipeline | 91,000 |
| Rapid mixing tanks | 91,000 |
| Flocculation tanks | 91,000 |
| Sedimentation tanks | 91,000 |
| Dual media filters | 91,000 |
| UV disinfection system | 91,000 |
| Clearwell | 91,000 |
| Highlift pumps | 91,000 |
| St. Thomas storage reservoir | 27,000 |
| St. Thomas booster pumping station | 45,000 |

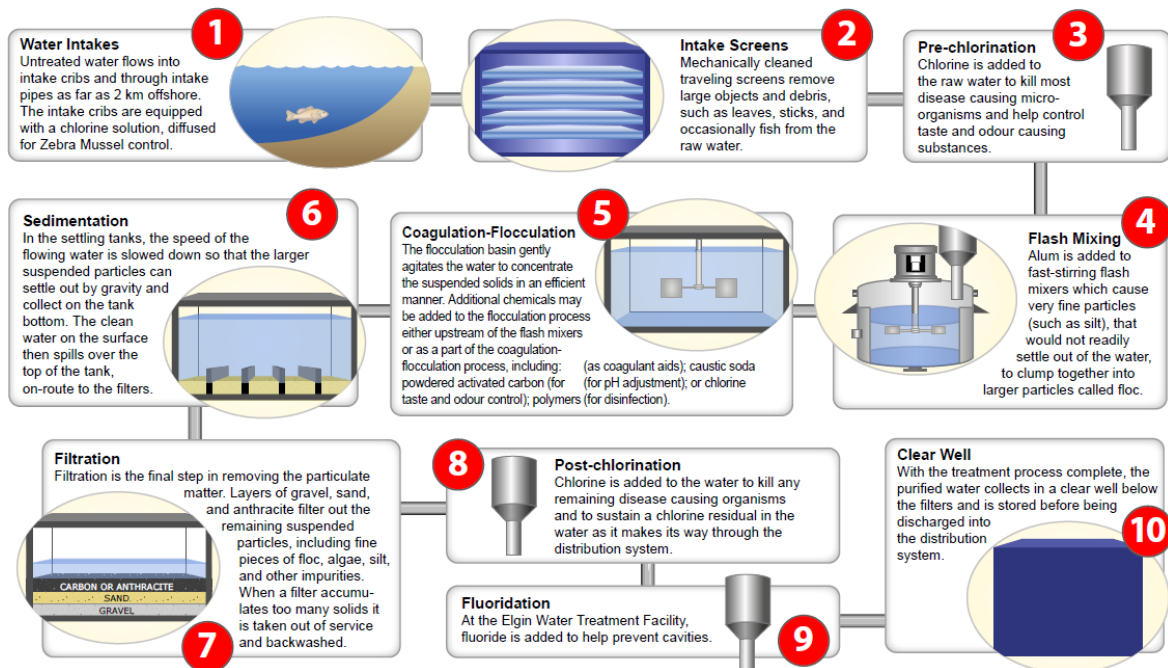


Figure 3.7 Treatment Processes in the Elgin Area WTP (Lake Huron and EAWSS, 2009)

3.3.1 Pre-chlorination

Chlorine, which can kill most potential pathogens and provide some taste and odor control, is utilized as the main disinfectant and is provided on a continual basis. Prior to injection, liquefied chlorine gas stored at the chlorine facility is converted to hypochlorous acid and then added at the settled water conduit through a 38mm diffuser.

3.3.2 Coagulation

The primary coagulant is acidified aluminum sulfate (alum). The coagulation process utilizes 4 concrete flash mixing tanks with 2 tanks per pre-treatment module. The design parameters for the flash mixing tank are summarized as follows:

Table 3.13 Design parameters for flash mixing tank (EAPWSS)

| Design Parameter | Value |
|---------------------------|--------------|
| Number of stages | 2 |
| Length | 2.4 m |
| Width | 2.4 m |
| Surface water depth (SWD) | 3.0 m |

3.3.3 Flocculation

There are 4 concrete flocculation tanks with 2 tanks per pre-treatment module. The design parameters of each mixing tank are summarized as follows:

Table 3.14 Design parameters for mixing tank (EAPWSS, 2008)

| Design Parameter | Value |
|-------------------------|--------------|
| Number of stages | 2 |
| Length | 7.8 m |
| Width | 6.1 m |
| SWD | 3.0 m |

3.3.4 Sedimentation

There are 2 concrete sedimentation tanks which are manually cleaned. Those sedimentation tanks can help remove the flocculated solids through settling process prior to filtration. All the sludge from sedimentation tank is conveyed to the plant drain. The design parameters of each tank are summarized as follows:

Table 3.15 Design parameters for each sedimentation tank (EAPWSS, 2008)

| Design Parameter | Value |
|-------------------------|------------------------|
| Length | 60.96 m |
| Width | 16 m |
| Area | 4.1 m ² |
| Capacity | 45.4 m ³ /d |

3.3.5 Filtration

The plant has 4 dual media rapid rate filters. The media consists of anthracite over sand and has a clay block underdrain. The design parameters of each filter are summarized as follows:

Table 3.16 Design parameters for each rapid rate filter (EAPWSS, 2008)

| Design Parameter | Value |
|-------------------------|-------------------|
| Length | 15.9 m |
| Width | 6.1 m |
| Area | 97 m ² |
| Sand media depth | 150 – 230 mm |
| Anthracite media depth | 740 mm |

3.3.6 Post-chlorination

Aqueous chlorine is utilized as the primary disinfectant and a free chlorine residual in the distribution system is maintained between 1.0 and 1.5 mg/L (EAPWSS, 2008). UV disinfection is only applied as required to meet CT (product of concentration and time) requirements. The design parameters for the clearwell are summarized as follows:

Table 3.17 Design parameters for clearwell (EAPWSS, 2008)

| Design Parameter | Value |
|-------------------------|--------------------|
| Length | 28.6 m |
| Width | 26.7 m |
| SWD | 3.65 m |
| Capacity | 2.7 m ³ |

Chapter 4

Source Identification and Pathway Delineation of Oil Tar Contaminated Sediments Using FALCON Analysis

4.1 Introduction

Between 1920 and 1950 an oil/coal gasification plant operated on a property adjacent to Kettle Creek about 1 km from the mouth of Port Stanley harbour on Lake Erie in Ontario, Canada (Figure 4.1). Oil tar wastes from the gasification plant were stored on the site until it was abandoned in 1987. At that time the Ontario Ministry of the Environment (MOE) determined that the site was contaminated with heavy metals and polycyclic aromatic hydrocarbons (PAHs) and that some of this waste had been flowing into Kettle Creek through the George Street drain in the town of Port Stanley for an undetermined period of time. The site was completely remediated in 1995 and the flow of contaminated water from the drain into the creek ceased. However, sediment sampling revealed the presence of heavy metals and PAHs in Kettle Creek at the point of contaminant input, downstream in both an inner and outer harbour, and in Lake Erie where the creek discharges. From a source protection perspective, there was an interest in assessing contaminated sediment transport within the Elgin Area Drinking Water Treatment Plant intake protection zones (IPZs). This water treatment plant provides water to about 94,400 consumers in part of the City of London (Ontario) and some surrounding municipalities.

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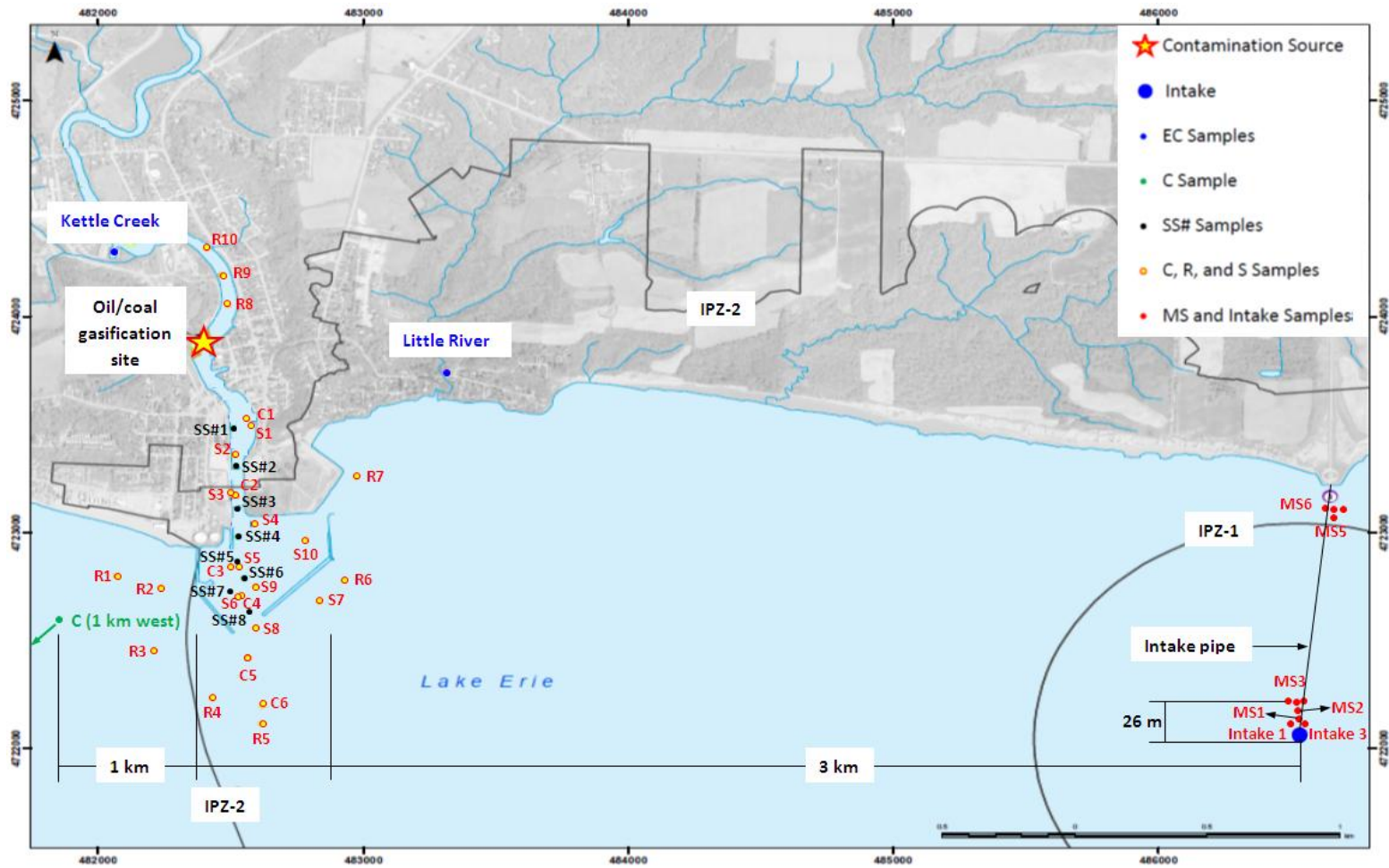


Figure 4.1 Sample sites within the Port Stanley study area including the drinking water intake in Lake Erie (excluding those used for the source fingerprint shown in Figure 4.2). Differing sample designations represent different sample campaigns (Adapted from

Stantec Consulting Ltd., 2009a)

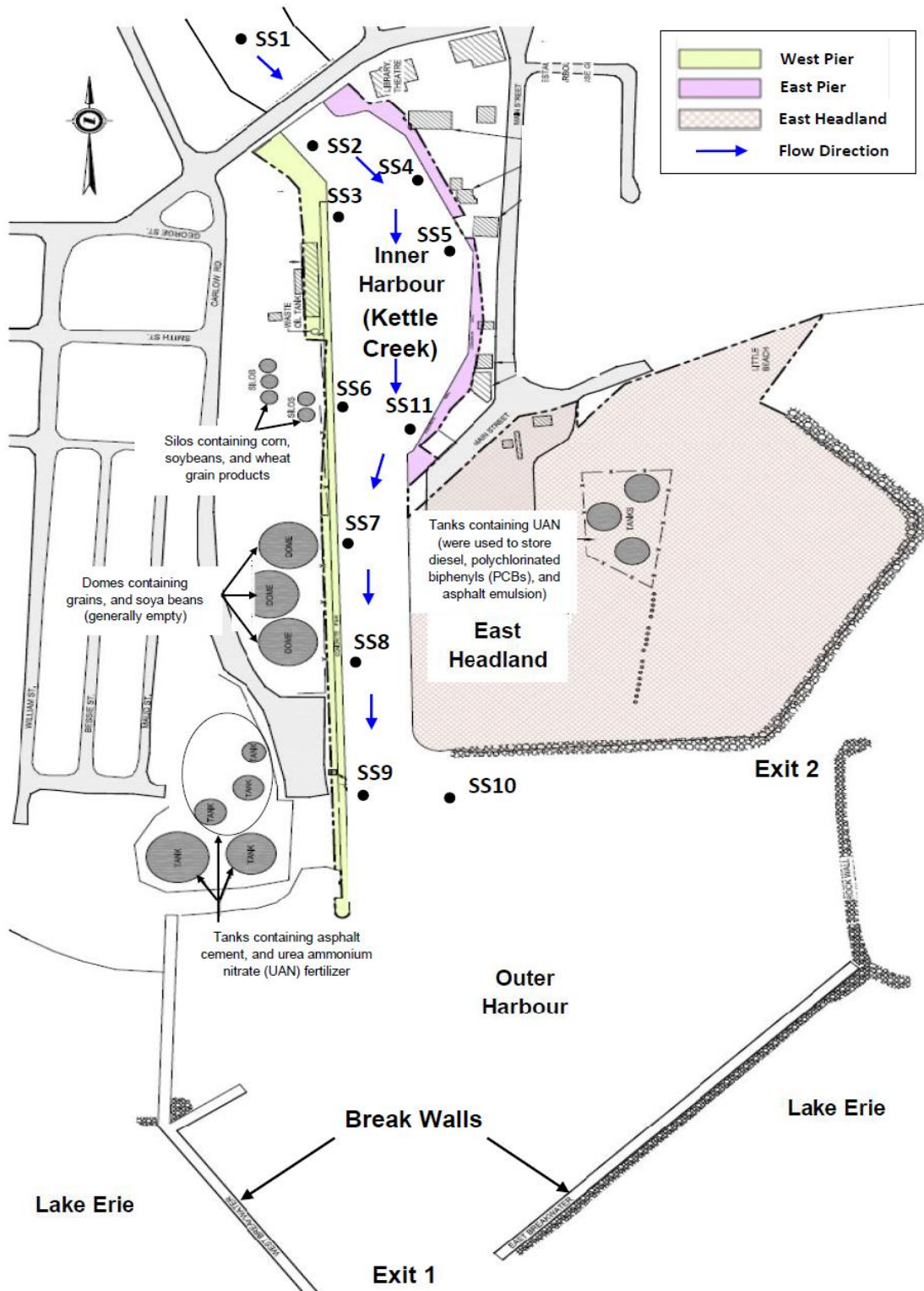


Figure 4.2 Port Stanley area showing Kettle Creek, inner and outer harbours, break walls, and Lake Erie with the source fingerprint sample sites (SS1-SS11)

Port Stanley is situated on the north bank of Lake Erie and is frequently exposed to westerly and south-westerly winds, with occasionally strong but less frequent winds from the south through east. The wave height distributions are generally consistent with wind distributions (Stantec Consulting Ltd., 2009b). The outer harbour structure at Port Stanley is the predominant feature of the local shoreline and is protected by two break walls, one to the west and the other to the east (Figures 4.1 and 4.2). The flow from Kettle Creek can enter Lake Erie through one of two exits in the break walls. Along with the hydrodynamic patterns in Lake Erie and Kettle Creek, the harbour structure substantially influences local currents in the near shore region and sedimentation patterns in the study area.

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals represent two highly persistent groups of organic and inorganic contaminants in the natural environment. Because of their wide distribution and potential toxicity in humans and ecosystems, they have received considerable attention. In many cases, heavy metals coexist with PAHs due to common sources such as automobile exhaust and oil/coal gasification (Wang et al., 2004; Morillo et al., 2008). The coexistence of these two groups of contaminants may amplify the potency of the contamination and increase the complexity of remediation efforts. At sufficiently high concentrations or in certain forms or combinations, heavy metals may inhibit or even prevent the biodegradation of PAHs by naturally-occurring microorganisms (Wang et al., 2004; Thavamani, et al., 2011). For example, Wild et al. (1991) reported that PAHs were more resistant to biochemical degradation in soil amended with nickel-rich sludge.

Due to their low aqueous solubility and high hydrophobicity, PAHs in aquatic environments are typically rapidly bound to particles and deposit as sediments. These particle-associated PAHs are readily mixed within surficial sediment through various physical and biological processes, including sediment resuspension, biogeochemical activities, and bioturbation which play an important role in determining the migration and fate of PAHs (Yang et al., 2008; Orecchio et al., 2010). Sediment resuspension, through hydrodynamic processes (e.g. wave action, tides, and currents) and anthropogenic activities (e.g. dredging, boating), can facilitate the release of PAHs from entrained sediments into the water phase increasing their bioavailability.

When introduced into the aquatic environment, heavy metals can be bound to different constituents within sediments in various ways, including adsorption on sediment, clogging in amorphous materials, complexation with organic matter, and bioaccumulation in benthic organisms (Tessler et al., 1979; Jain and Sharma, 2001; Yu et al., 2001; Singh et al., 2005). Therefore, sediments can act either as carriers or sinks for heavy metals (Singh et al., 2005). Compared to PAHs, heavy metals cannot be degraded or destroyed through natural processes and hence tend to be enriched in sediment by organisms and/or other compartments (Peng et al., 2009). It is reported that under some conditions more than 99% of heavy metals introduced into a river can be retained in river sediments in various compartments (Salomons and Stigliani, 1995). As in the case of PAHs, sediments will change from a sink to a source of heavy metals through diffusion between water-sediment interfaces (van den Berg et al., 2001) and the various processes discussed above.

Fingerprint analysis of leachate contaminants (FALCON), which was developed by the USEPA, is an empirical multivariate statistical method that can be applied to combine sampling data from several measurements for different contaminants to identify the distinctive multi-parameter chemical signature of a point source or contaminant plume (Plumb, 2004). In this technique, the relative abundance of selected constituents, rather than the actual concentrations of individual contaminants, is considered as a chemical signature specific to the point source or contaminant plume. This chemical signature is analogous to a human fingerprint and can help characterize a contaminant plume or point source and distinguish the contaminant plume from the background environment. The migration of a contaminant plume can also be monitored by comparing with fingerprints of downstream samples. Five brief case studies are provided as examples in Plumb (2004) and references for reports and conference presentations are provided. Interestingly, despite the utility of this technique it has not been widely addressed in peer-reviewed scientific literature.

In the Province of Ontario, Canada, legislation known as the Clean Water Act (Bill 43; Government of Ontario, 2006) stipulates that drinking water providers must submit source protection plans to the Ontario Ministry of the Environment. This includes the identification of vulnerable areas within each watershed and drinking water threats associated

with those vulnerable areas. Such information eventually leads to the creation of up to three types of intake protection zones (IPZs), two of which applied in the study area. An IPZ-1 includes the primary area immediately adjacent to the intake and is circular with a 1 km radius around the intake (Ontario MOE, 2009). Due to geographic proximity to the intake, contaminants of concern entering IPZ-1 are considered to undergo little to no dilution or sequestration before reaching the intake. An IPZ-2 is a secondary protective zone that extends upstream from an IPZ-1, and in the case of lakes, taking into account currents. Large quantities of contaminants discharged within an IPZ-2 may not be sufficiently diluted or sequestered before reaching the intake. An IPZ-2 includes either water courses or inland water bodies that may contribute water to an intake within a travel time determined based on the minimal response time required by water treatment plant operators to respond to a contamination event. The minimum time of travel is 2 hours or greater (Ontario MOE, 2009).

The purpose of this study was to employ the FALCON analysis in a surface water application to characterize contaminated sediments in a creek near an on-shore point source and to assess transport of the sediments within the vicinity of a drinking water intake protection zone. The suitability of using a combination of inorganic (i.e. heavy metals) and organic (i.e. PAHs) contaminants as FALCON constituents was investigated and is discussed for the first time. The potential for the FALCON analysis to assist with the delineation of drinking water intake protection zones is also addressed.

4.2 Approach

4.2.1 Data Acquisition and Site Description

Creek and lake sediment studies in the Port Stanley area were commissioned by various governmental agencies and were summarized in 10 reports published from 2001 to 2009. Relevant reports are identified when data are presented. Sediment sampling conditions may have varied between sampling agencies but this is not addressed in this chapter. This to some extent makes a priori assumption that sample sites which are close to each other but sampled by different agencies are similar. It will be shown later in this chapter that most samples were well correlated with the source fingerprint, indicating that variation of sampling conditions

among agencies was relatively unimportant. While this may be true for the relatively inert PAHs and heavy metals investigated here it may not be so for all contaminants.

Figure 4.2 shows the layout of a portion of the village of Port Stanley including Kettle Creek (flowing from north to south into Lake Erie), the inner and outer harbours, break walls, and Lake Erie. The points designated ‘SS’ for “source sediment” are those which were used to characterize contaminated sediments along Kettle Creek by generating a ‘source’ fingerprint; data were extracted from CH2MHILL (2006a). The samples were collected in 2004 from a zone in between 5 and 10 cm deep in the sediment and include samples designated SS1 through SS11. This data set was selected for three reasons including (1) its proximity to the target point source, (2) it was the earliest data set for which inner harbour data were available, and (3) it was a relatively large and complete set with 11 points. Samples SS3 and SS3(S) were drilled side-by-side for quality assurance/quality control. Another set of inner-harbour sediment samples denoted as ‘SS#_’ was collected 2 years later in 2006 (shown in Figure 4.1). Although some of these sample sites were also in the inner harbour, most were in the outer harbour so these data were not used to generate the ‘source’ fingerprint. This SS#_ data set was extracted from Stantec Consulting Ltd. (2008). Water can only pass from the outer harbour into Lake Erie through Exit 1 to the south and Exit 2 to the east.

Figure 4.1 was extracted and adapted from (Stantec Consulting Ltd., 2009a) Kettle Creek can be seen flowing from north to south into the inner harbour, the outer harbour (with break walls), and ultimately into Lake Erie. The source of contamination is now gone but the former coal/oil tar gasification site was just to the west of the point at which most of the contaminants entered the creek and is marked with a large yellow star. The inner harbour is the area in which samples S1 to S3, SS#1-SS#3, and C1 and C2 were collected. The outer harbour is the area contained between the inner harbour and the break walls (samples C3-C4 and S4, S5, S6, S9, and S10; SS#4-SS#8; C3-C4). The curved line in the lake to the west extending onto dry land around the intake is the intake protection zone 2 (IPZ-2) for the drinking water intake shown on the east side of the figure (large blue dot). The circle around the intake, designated IPZ-1, is the first level intake protection zone, 1 km in diameter. The

samples designated 'MS#_ ' and Intake 1 & 3 are sediment samples taken from within an intake pipe which runs along the lake bed for just over 1 km before it reaches the shore. The distance from Kettle Creek to the intake is about 3 km. Little River, another tributary entering into IPZ-2, is shown to the east of Kettle Creek with a small blue dot.

In 2001, one sediment sample located 1 km to the west in Lake Erie from Port Stanley harbour was collected as a control ('C') sample to investigate the dispersion of PAH contaminants (Riggs and Delcan, 2004). In 2002, an investigation of sediment quality in Lake Erie tributaries was conducted by Environment Canada (Dove et al., 2002). A number of sub samples were combined as one 'EC' sample to represent the overall conditions within Kettle Creek immediately upstream from the contaminant source and a second, also designated as 'EC', in the nearby Little River to the east. Raw data were published in Stantec Consulting Ltd. (2008). The locations of the C sample and the EC samples in Kettle Creek and Little River are illustrated in Figure 4.1.

Sediment data for comparison with the source fingerprint, including 81 sediment samples in Kettle Creek and Lake Erie, were collected in 2006 (SS#1 to SS#8) while the remainder of the samples were collected in the period from September 17 – 20th, 2008 (CH2MHILL, 2009b) (Table 4.1). All sample locations are shown in Figure 4.1. For the sediment samples in Kettle Creek and Lake Erie, shallow sediment samples were collected from 10 reference locations in triplicate or quadruplicate and were averaged and are denoted with an 'R' for "Reference." All reference locations were outside the outer harbour. Shallow sediment samples were collected from 10 additional areas in triplicate or quadruplicate (and averaged) and are denoted with an 'S' for "Site." All but one 'S' sample were collected in the inner and outer harbours. Six deep cores were also sampled along Kettle Creek (without replicates) and samples are denoted with a 'C' for "Core." The shallow core samples were taken at a maximum depth of 10 cm or less and the deep core samples were taken at a minimum depth of 50 cm and a maximum depth of 70 cm. No distinction between the shallow and deeper cores was made in this study as it was assumed that PAHs with more than three rings and heavy metals were essentially recalcitrant. Given that Lake Erie is a very large body of water, it was also assumed that there would be substantial mixing at most of the

depths sampled. Finally, the FALCON analysis is performed based on the relative abundance of selected constituents rather than their actual concentrations. Therefore, if there were differences at various depths these should be readily observed when the analysis was conducted. Shallow and deeper samples, in close proximity to one another were closely correlated to the source fingerprint as will be shown later.

The data sets characterizing sediment in the drinking water intake pipe within intake protection zone 1 (IPZ-1) and the near shore zone in the lake were collected during the period from 2001 to 2003 and were extracted from Riggs and Delcan (2004). All samples which are denoted with an ‘MS’ for “Monitoring Station” and ‘intake’ samples were grab samples collected from within the intake pipe by a diver entering the pipe through an on-shore wet well. The distribution of all ‘MS’ samples is illustrated to the east on Figure 4.1.

The year in which various samples were collected is summarized in Table 4.1.

Table 4.1 Year of sediment sample collection

| Year | Sampling Sites |
|-------------|--|
| 2001 | C (1 km west of Kettle Creek in Lake Erie), EC (Kettle Creek), EC (Little River), and intake samples: MS1(I), MS3(I), MS5(I), MS6(I), Intake 1 & 3 |
| 2002 | Intake: MS2(II), MS3(II), MS6(II) |
| 2003 | Intake: MS3(III), MS6(III) |
| 2004 | SS1 – 10 |
| 2006 | SS#1 – 8 |
| 2008 | C1 – 6, S1 – 10, R1 – 10 |

4.2.2 Selection of FALCON Constituents

Contaminants which are non-biodegradable, photo-insensitive, and chemically non-degradable in the natural environment, make the best choices for FALCON analysis as these can better retain the original characteristics (chemical identity) of the contaminated sediments as they migrate away from the source. As the main components of the oil/coal tar contaminated sediments along Kettle Creek, heavy metals and PAHs, which are relatively persistent in the natural environment, were chosen as FALCON constituents to characterize

contaminated sediment in proximity to the point source and assess transport of these sediments.

A recent study which systematically investigated the co-occurrence of PAHs with heavy metals at a former manufactured gas plant site demonstrated the importance of metal speciation and bioavailability on site characterization (Thavamani et al., 2011). While those authors employed a fingerprinting technique, it differed from that which was employed in this study. Their work does, however, support the selection of both PAHs and heavy metals as constituents to characterize contaminated sediments from gasworks sites.

Six higher molecular weight PAHs (containing more than 3 rings), which are more refractory to photodegradation and biodegradation (Lors et al., 2010), were selected as fingerprint constituents for this study. They included benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), chrysene (Chrys), fluoroanthene (FluoA), ideno(1,2,3-c,d)pyrene (IcdPyr), and pyrene (Pyr). In addition, four typical heavy metal gasification wastes, including arsenic (As), chromium (Cr), lead (Pb), and nickel (Ni), were selected to develop the fingerprint pattern of the contaminated sediments in Kettle Creek due to their inert nature and availability of good quality data. For some heavy metal-only fingerprint investigations described later, the four metals listed above, in addition to copper (Cu) and Zinc (Zn) were utilized (Table 4.2).

4.2.3 Development of the Source Fingerprint

The FALCON analysis is clearly described in a step by step fashion in Plumb (2004). The analysis was performed exactly as outlined and the steps are summarized in Figure 4.3.

Heavy metal and PAH concentrations in the Kettle Creek sediment used to generate the source fingerprint are summarized in Table 4.2 (samples SS1-SS11). Two variations of the source fingerprint were prepared (6 PAHs and 4 heavy metals; and 6 heavy metals). Table 4.3 summarizes similar data for heavy metal and PAH concentrations in sediment collected in the drinking water intake pipe.

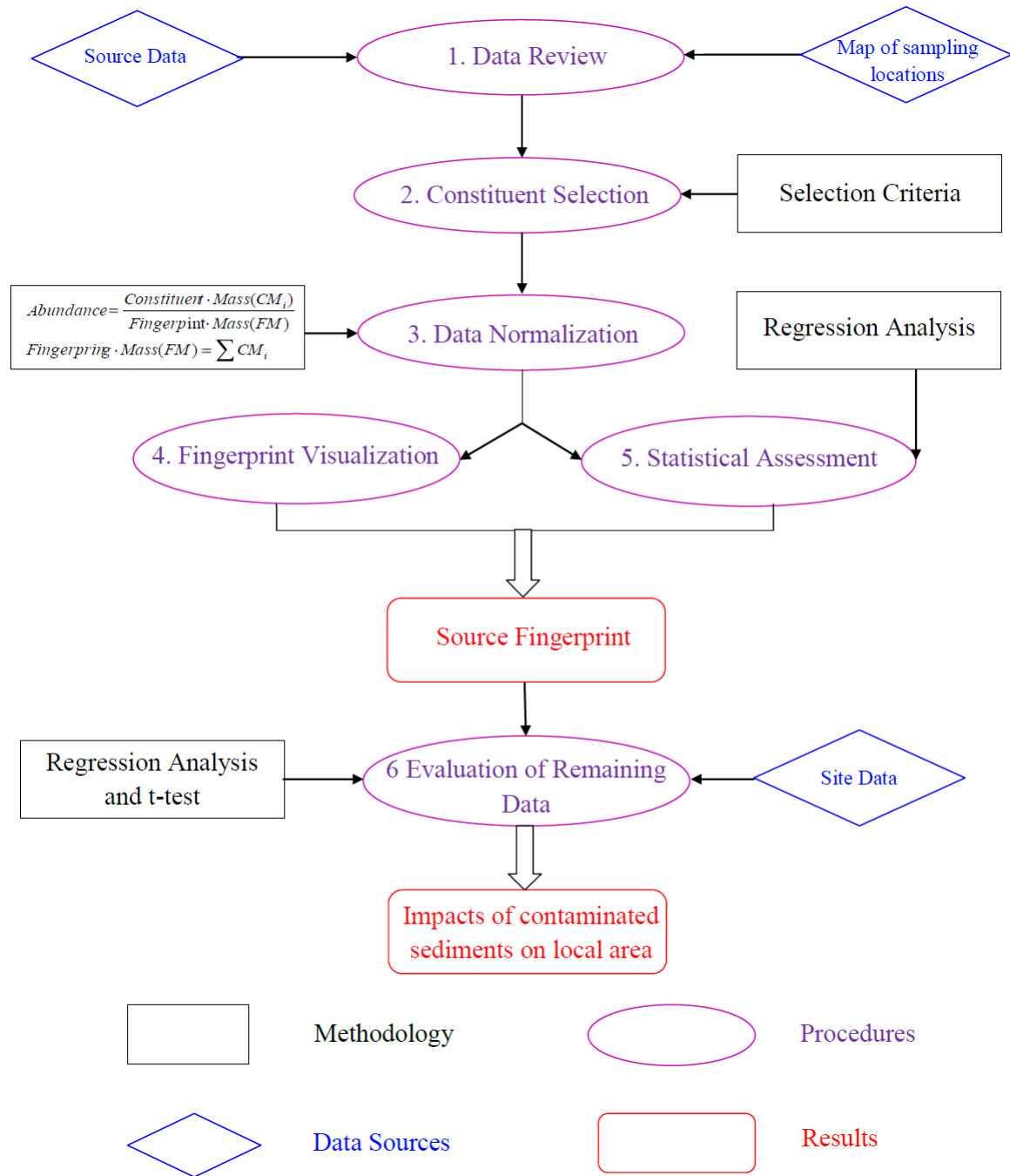


Figure 4.3 Description of FALCON procedure

Table 4.2 Heavy metal and PAH concentrations in Kettle Creek sediment samples used to create the source fingerprint (mg/kg)^a

| | SS1 | SS2 | SS3 | SS3(S) ^b | SS4 | SS5 | SS6 | SS7 | SS8 | SS9 | SS10 | SS11 |
|-----------------------|------|------|------|---------------------|------|------|------|------|------|------|------|------|
| As | 5 | 4 | 4 | 4 | 3 | 3 | 5 | 4 | 5 | 5 | 4 | 5 |
| Cr | 23 | 18 | 20 | 23 | 13 | 13 | 30 | 28 | 25 | 24 | 17 | 26 |
| Cu^c | 30 | 24 | 25 | 28 | 16 | 15 | 38 | 31 | 28 | 28 | 20 | 30 |
| Pb | 18 | 16 | 14 | 17 | 13 | 9 | 19 | 17 | 17 | 16 | 12 | 18 |
| Ni | 22 | 17 | 20 | 23 | 13 | 13 | 28 | 25 | 25 | 26 | 18 | 26 |
| Zn^c | 92 | 81 | 78 | 87 | 51 | 48 | 104 | 94 | 90 | 88 | 63 | 96 |
| BaP | 0.09 | 0.12 | 0.06 | 0.07 | 0.03 | 0.08 | 0.08 | 0.05 | 0.04 | 0.04 | 0.05 | 0.05 |
| BbF | 0.11 | 0.13 | 0.08 | 0.06 | 0.03 | 0.08 | 0.09 | 0.06 | 0.05 | 0.03 | 0.05 | 0.07 |
| Chrys | 0.13 | 0.24 | 0.06 | 0.08 | 0.03 | 0.08 | 0.10 | 0.06 | 0.05 | 0.05 | 0.06 | 0.07 |
| FluoA | 0.19 | 0.20 | 0.13 | 0.15 | 0.06 | 0.20 | 0.18 | 0.10 | 0.05 | 0.08 | 0.11 | 0.12 |
| IcdPyr | 0.12 | 0.14 | 0.09 | 0.10 | 0.03 | 0.08 | 0.11 | 0.07 | 0.06 | 0.05 | 0.05 | 0.07 |
| Pyr | 0.16 | 0.25 | 0.12 | 0.14 | 0.05 | 0.16 | 0.14 | 0.08 | 0.07 | 0.07 | 0.10 | 0.10 |

^aData from CH2MHILL (2006)

^bDuplicate sediment sample for SS3

^cCopper and zinc were not used to generate the PAH/heavy metal fingerprint

Notes: Non detect values have been replaced with numerical values (detection limit/2) and are in italics

Table 4.3 Heavy metal and PAH concentrations in drinking water intake sediment (mg/kg)^a

| | MS 1(I) | MS 2(II) | MS 3(I) | MS 3(II) | MS 3(III) | MS 5(I) | MS 6(I) | MS 6(II) | MS 6(III) | INT 1 | INT 3 |
|-----------------------|------------|-------------|------------|-------------|--------------|------------|------------|-------------|--------------|----------|----------|
| As | 5.3 | 5.4 | 5.2 | 5.7 | 4.9 | 3.7 | 3.7 | 3.4 | 3.4 | 4.2 | 5.0 |
| Cr | 22 | 22 | 25 | 19 | 9 | 18 | 19 | 20 | 24 | 23 | 20 |
| Cu^b | 27 | 26 | 41 | 23 | 9 | 24 | 25 | 25 | 27 | 22 | 22 |
| Pb | 14 | 13 | 21 | 16 | 6 | 13 | 13 | 12 | 8 | 13 | 15 |
| Ni | 26 | 26 | 29 | 26 | 12 | 22 | 24 | 26 | 29 | 27 | 24 |
| Zn^b | 72 | 70 | 79 | 67 | 32 | 62 | 66 | 69 | 78 | 65 | 60 |
| BaP | NA | 0.03 | NA | 0.03 | 0.03 | NA | NA | 0.03 | 0.03 | NA | NA |
| BbF | NA | 0.03 | NA | 0.03 | 0.05 | NA | NA | 0.03 | 0.03 | NA | NA |
| Chrys | NA | 0.03 | NA | 0.03 | 0.03 | NA | NA | 0.03 | 0.03 | NA | NA |
| FluoA | NA | 0.03 | NA | 0.03 | 0.29 | NA | NA | 0.03 | 0.03 | NA | NA |
| IcdPyr | NA | 0.03 | NA | 0.03 | 0.05 | NA | NA | 0.03 | 0.03 | NA | NA |
| Pyr | NA | 0.05 | NA | 0.05 | 0.27 | NA | NA | 0.03 | 0.03 | NA | NA |

^aData from Riggs and Delcan (2004)

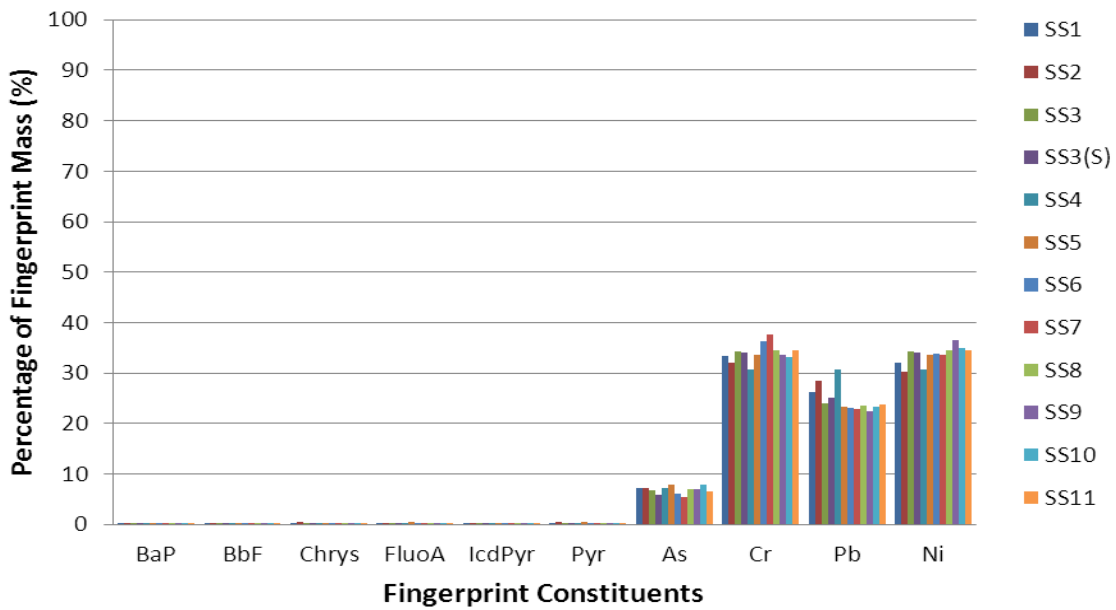
^bCopper and zinc were not used to generate the PAH/heavy metal fingerprint

NA – Data not available

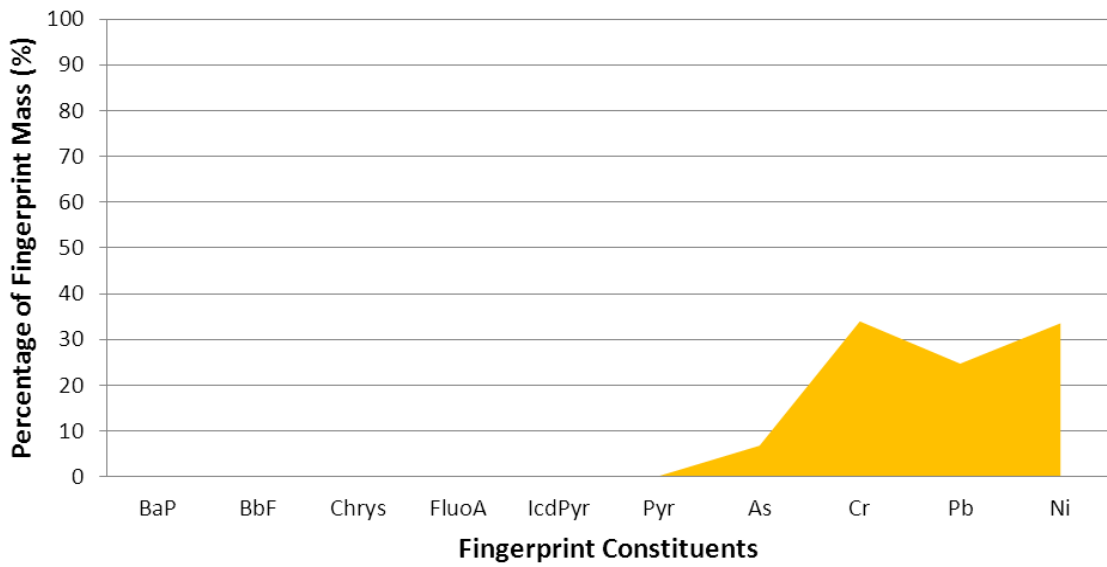
Notes: Non detect values have been replaced with numerical values (detection limit/2) and are in italics

Sediment data were normalized to the total concentration of all target contaminants in one sampling location (fingerprint mass) and each contaminant concentration is expressed as percentage of the total calculated fingerprint mass. Unlike heavy metals, individual PAHs were detected at levels very close to or below their detection limits. For the purpose of this fingerprint analysis, non detect (ND) data designations were replaced by values which are equal to one-half of the detection limit for the particular contaminant (as per Plumb, 2004). This transformation process allowed for individual data sets to be visualized relative to a common y-axis and to help conduct a better statistical analysis.

The normalized data for all sampling locations has been plotted as a series of histograms as illustrated in Figure 4.4(a). The fingerprint pattern of the contaminated sediment is also presented as an area plot using the average value of the relative abundance of each constituent from all sites as illustrated in Figure 4.4(b). The visualization of the source fingerprint can help to better interpret its characteristics and more easily distinguish locations impacted by the contaminated sediments from those locations that are not impacted. The y-axis represents the relative abundance of different constituents expressed as percentage of the calculated fingerprint mass and hence the y-axis ranges from 0% to 100%. A visual inspection of Figure 4.4(b) shows that the 6 PAHs and 4 heavy metals define a distinct fingerprint pattern characterized by approximately 34.0% Cr, 33.6% Ni, 24.7% Pb, 6.80% As, and less than 1% of various PAH contaminants (based on means). Fig. 4.5 provides additional detail, showing the average relative abundance of the PAHs in the range of 0-1%. The average relative abundances for the individual PAHs were 0.11% BaP, 0.11% BbF, 0.14% Chrys, 0.22% FluoA, 0.13% IcdPyr, and 0.20% Pyr.



(a)



(b)

Figure 4.4 Oil tar source heavy metal/PAH-based fingerprint as a (a) histogram plot and (b) an area plot

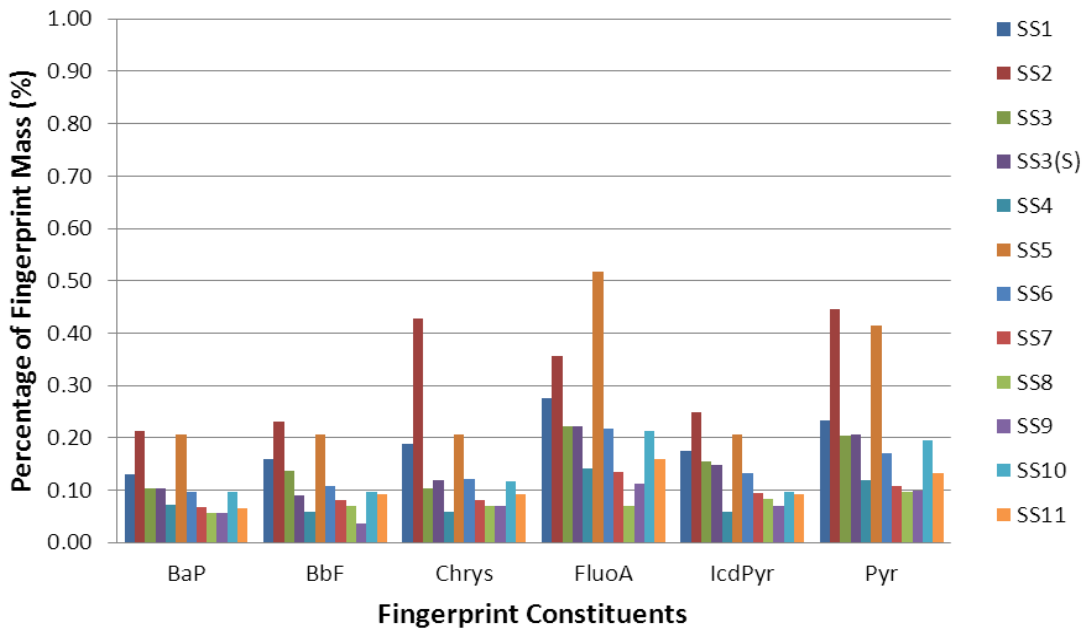


Figure 4.5 Average relative abundances for each PAH at source fingerprint sample sites

As per the FALCON procedure, regression analysis was also applied to statistically estimate the comparability or reproducibility of each histogram (fingerprint pattern) by individually comparing each histogram with the remaining histograms to calculate regression coefficient squared (R^2) values. As shown in Table 4.4, 66 histogram comparisons were produced and R^2 values ranged from 0.943 to 1.000. The average estimated reproducibility of the heavy-metal/PAH fingerprints shown in Fig. 4.4 is 0.987. Despite the magnitude of sample concentration variability for the two different groups of contaminants along Kettle Creek due to impacts of hydrogeological factors and other potential contaminant sources, a distinctive and reproducible chemical signature characterizing the oil/coal tar source was successfully identified through the application of the FALCON process. The high correlation among sampling locations indicates that all these locations were contaminated by a single predominant source.

Table 4.4 Regression analysis comparison of individual sample sites used to generate the source fingerprint to one another (heavy metal/PAHs)

| | SS2 | SS3 | SS3(S) | SS4 | SS5 | SS6 | SS7 | SS8 | SS9 | SS10 | SS11 |
|---------------|------------|------------|---------------|------------|------------|------------|------------|------------|------------|-------------|-------------|
| SS1 | 0.995 | 0.995 | 0.997 | 0.984 | 0.994 | 0.990 | 0.985 | 0.993 | 0.984 | 0.991 | 0.994 |
| SS2 | | 0.980 | 0.986 | 0.996 | 0.978 | 0.971 | 0.966 | 0.976 | 0.962 | 0.974 | 0.978 |
| SS3 | | | 0.999 | 0.964 | 1.000 | 0.997 | 0.994 | 1.000 | 0.996 | 0.998 | 1.000 |
| SS3(S) | | | | 0.973 | 0.997 | 0.995 | 0.992 | 0.998 | 0.993 | 0.996 | 0.999 |
| SS4 | | | | | 0.961 | 0.950 | 0.943 | 0.959 | 0.945 | 0.959 | 0.962 |
| SS5 | | | | | | 0.996 | 0.992 | 1.000 | 0.997 | 0.999 | 0.999 |
| SS6 | | | | | | | 0.999 | 0.998 | 0.993 | 0.993 | 0.998 |
| SS7 | | | | | | | | 0.994 | 0.987 | 0.987 | 0.994 |
| SS8 | | | | | | | | | 0.997 | 0.999 | 1.000 |
| SS9 | | | | | | | | | | 0.999 | 0.997 |
| SS10 | | | | | | | | | | | 0.998 |

The contaminated sediments can be further differentiated from the background environment and transport of contaminated sediments can be verified by comparing the geochemical pattern at each downstream sampling location with the source fingerprint through regression analysis. If the location has been impacted by the contaminant sediments from the inner harbour, it would be expected to have a geochemical fingerprint that closely resembles the fingerprint illustrated in Figure 4.4(b).

To assess the probability that calculated correlation coefficients are not related, a t-test was used (Myers, 1990):

$$t = R \sqrt{\frac{N-2}{1-R^2}}; df = N - 2$$

where R is the calculated correlation coefficient and N is the number of fingerprint constituents (usually 6 PAHs and 4 heavy metals, N = 10)

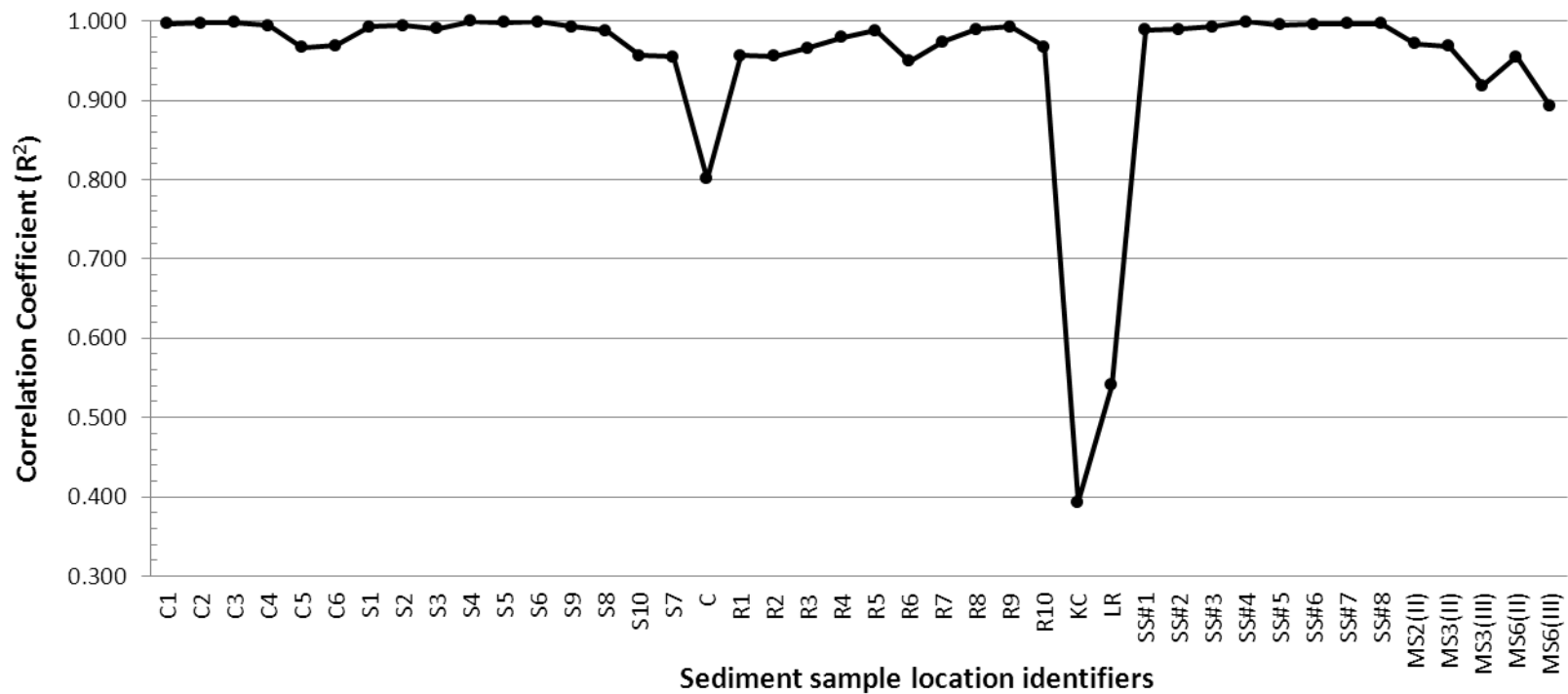


Figure 4.6 Summary of heavy metal/PAH FALCON analysis correlation coefficients for creek, lake, and intake sediments (compared to the source fingerprint). Sites are not in any specific order

Table 4.5 Summary of t-test results of heavy metal/PAH-based FALCON analysis results for each sampling site relative to three potential sources (critical t-value = 3.355 at $\alpha = 0.01^*$)

| Source | Sampling Sites | | | | | | | | |
|-----------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | | C1 | C2 | C3 | C4 | C5 | C6 | S1 | S2 |
| Oil Tar** | R ² | 0.997 | 0.997 | 0.998 | 0.995 | 0.967 | 0.969 | 0.993 | 0.995 |
| | t | <i>51.575</i> | <i>55.355</i> | <i>64.571</i> | <i>37.978</i> | <i>15.300</i> | <i>15.822</i> | <i>33.754</i> | <i>38.281</i> |
| Kettle Creek*** | R ² | 0.399 | 0.410 | 0.372 | 0.376 | 0.357 | 0.386 | 0.453 | 0.415 |
| | t | 2.306 | 2.359 | 2.178 | 2.195 | 2.108 | 2.241 | 2.576 | 2.384 |
| Little River | R ² | 0.551 | 0.558 | 0.515 | 0.518 | 0.470 | 0.508 | 0.602 | 0.560 |
| | t | 3.134 | 3.179 | 2.912 | 2.932 | 2.664 | 2.874 | 3.481 | 3.194 |

| Source | Sampling Sites | | | | | | | | |
|-----------------|----------------|---------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 |
| Oil Tar** | R ² | 0.990 | 1.000 | 0.998 | 0.999 | 0.955 | 0.988 | 0.993 | 0.957 |
| | t | <i>28.370</i> | <i>139.706</i> | <i>61.231</i> | <i>79.244</i> | <i>12.978</i> | <i>25.756</i> | <i>32.660</i> | <i>13.305</i> |
| Kettle Creek*** | R ² | 0.402 | 0.377 | 0.399 | 0.379 | 0.468 | 0.341 | 0.433 | 0.437 |
| | t | 2.318 | 2.200 | 2.304 | 2.210 | 2.653 | 2.032 | 2.473 | 2.492 |
| Little River | R ² | 0.544 | 0.523 | 0.545 | 0.523 | 0.574 | 0.469 | 0.588 | 0.539 |
| | t | 3.086 | 2.963 | 3.095 | 2.962 | 3.286 | 2.658 | 3.378 | 3.061 |

| Source | Sampling Sites | | | | | | | | |
|-----------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | | R1 | R2 | R3 | R4 | R5 | R6 | R7 | R8 |
| Oil Tar** | R ² | 0.957 | 0.956 | 0.966 | 0.979 | 0.988 | 0.949 | 0.973 | 0.990 |
| | t | <i>13.305</i> | <i>13.168</i> | <i>15.060</i> | <i>19.388</i> | <i>25.730</i> | <i>12.197</i> | <i>17.113</i> | <i>27.586</i> |
| Kettle Creek*** | R ² | 0.437 | 0.433 | 0.378 | 0.388 | 0.363 | 0.382 | 0.492 | 0.350 |
| | t | 2.492 | 2.472 | 2.205 | 2.253 | 2.133 | 2.223 | 2.783 | 2.076 |
| Little River | R ² | 0.539 | 0.535 | 0.488 | 0.507 | 0.502 | 0.500 | 0.618 | 0.492 |
| | t | 3.061 | 3.032 | 2.759 | 2.867 | 2.840 | 2.828 | 3.600 | 2.785 |

| Source | Sampling Sites | | | | | | | | |
|-----------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | | R9 | R10 | SS#1 | SS#2 | SS#3 | SS#4 | SS#5 | SS#6 |
| Oil Tar** | R ² | 0.993 | 0.967 | 0.989 | 0.990 | 0.992 | 0.999 | 0.995 | 0.996 |
| | t | <i>32.599</i> | <i>15.377</i> | <i>26.585</i> | <i>27.957</i> | <i>32.295</i> | <i>79.140</i> | <i>40.216</i> | <i>42.948</i> |
| Kettle Creek*** | R ² | 0.408 | 0.526 | 0.443 | 0.363 | 0.382 | 0.492 | 0.351 | 0.398 |
| | t | 2.348 | 2.982 | 2.521 | 2.133 | 2.223 | 2.783 | 2.079 | 2.301 |
| Little River | R ² | 0.555 | 0.683 | 0.592 | 0.563 | 0.568 | 0.547 | 0.491 | 0.542 |
| | t | 3.160 | <i>4.147</i> | <i>3.405</i> | 3.211 | 3.246 | 3.108 | 2.779 | 3.075 |

| Source | Sampling Sites | | | | | | | | |
|-----------------|----------------|---------------|---------------|--------------|---------------|---------------|--------------|---------------|--------------|
| | | SS#7 | SS#8 | C | MS2(II) | MS3(II) | MS3(III) | MS6(II) | MS6(III) |
| Oil Tar** | R ² | 0.997 | 0.997 | 0.801 | 0.971 | 0.968 | 0.919 | 0.955 | 0.892 |
| | t | <i>50.155</i> | <i>48.144</i> | <i>5.682</i> | <i>16.452</i> | <i>15.579</i> | <i>9.495</i> | <i>13.037</i> | <i>8.138</i> |
| Kettle Creek*** | R ² | 0.375 | 0.390 | 0.065 | 0.271 | 0.358 | 0.316 | 0.234 | 0.125 |
| | t | 2.193 | 2.262 | 0.743 | 1.726 | 2.110 | 1.922 | 1.561 | 1.068 |
| Little River | R ² | 0.514 | 0.538 | 0.136 | 0.405 | 0.506 | 0.425 | 0.373 | 0.233 |
| | t | 2.907 | 3.052 | 1.124 | 2.334 | 2.860 | 2.431 | 2.180 | 1.558 |

* Italicized values exceed critical t-value

- ** Upstream from PAH/heavy metal point source
- *** Oil tar refers to sediment collected in Kettle Creek downstream from oil/coal gasification site contaminant input; sample designated Kettle Creek is collected upstream from input from oil/coal gasification site; and Little River is a Lake Erie tributary to the east of Kettle Creek-closer to drinking water treatment plant intake

4.3 Results and Discussion

4.3.1 Heavy Metal/PAH-based FALCON Analysis

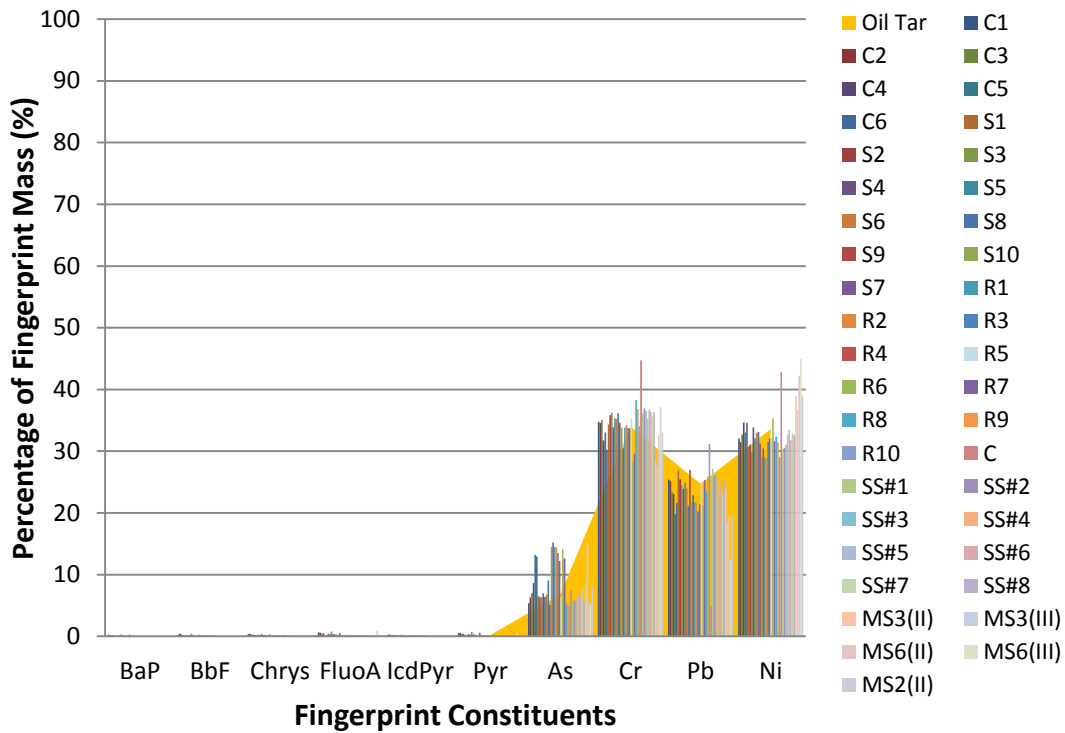
According to Figure 4.6 and Table 4.5, all sampling sites except for sites upstream from the source input in Kettle Creek (KC, blue dot on Figure 4.1), the Little River site (LR, also a blue dot on Figure 4.1) and a control site in Lake Erie (C, green dot on Figure 4.1), have correlation coefficients higher than 0.89. Correlation t-test results indicate that all those sites are significantly correlated with the oil/coal tar source fingerprint generated from sample data at sites SS1 to SS11 at $p < 0.01$ (fingerprint shown in Figure 4.3). The small t-value of the C sample indicates a weak correlation, which is believed to be attributable to wind and wave directions generally pushing Kettle Creek sediments away in the opposite direction from this sample site. Both KC and LR sites have t-values (2.276 and 3.070, respectively) smaller than the critical t-value (3.355), indicating they are significantly different from oil/coal tar source fingerprint in the inner harbour. This confirms that a distinctive oil tar source fingerprint has been produced and that it differed from ‘background’ upstream samples in Kettle Creek, an adjacent tributary to the east (Little River), and in Lake Erie to the west.

The samples for Kettle Creek and Little River discussed above are combined samples using different sub samples and represent the overall conditions within the Kettle Creek and Little River. In their own right, fingerprints generated at these sites are source fingerprints representing areas unimpacted by the point source of concern in this study. To evaluate impacts of these supposedly uncontaminated sources on downstream sampling sites, the FALCON procedure was repeated to test all available samples using KC and LR data as new ‘source’ fingerprints, respectively. Upstream sample sites in Kettle Creek were not responsible for downstream contamination as evidenced by the small t-values for all

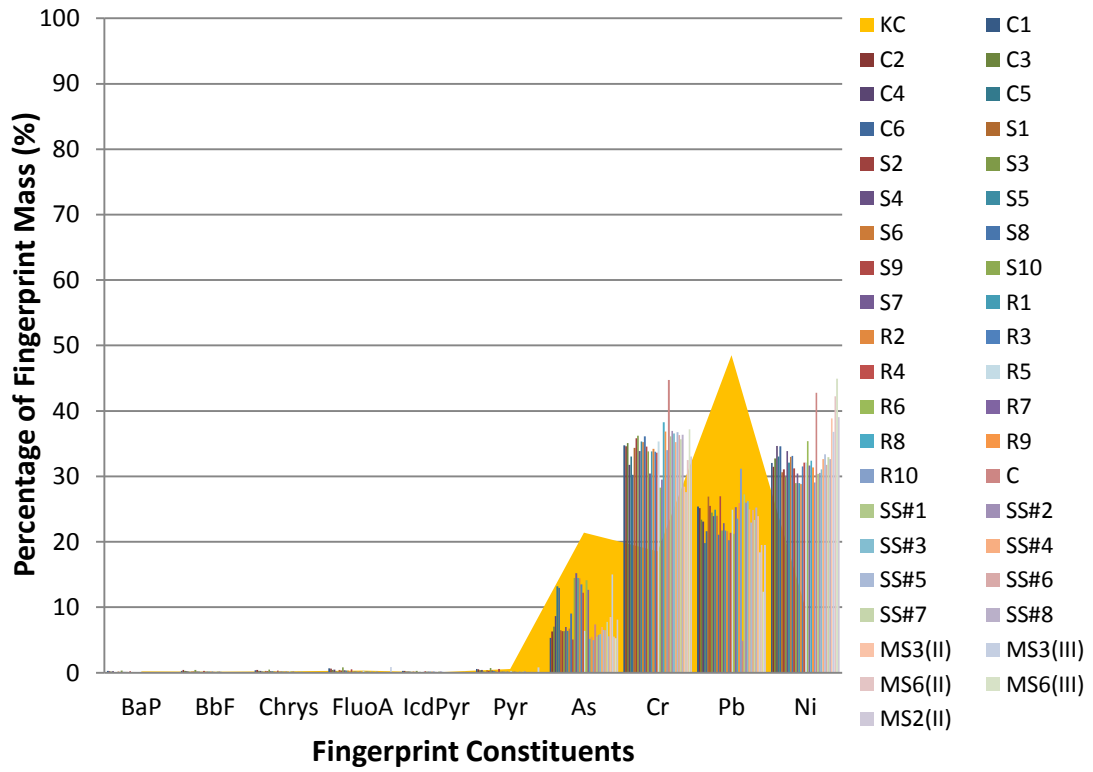
sampling sites (C1-C6; S1-S10; R1- R10; SS#1- SS#8; C; MS2(II), MS3(II), MS3(III), MS6(II); MS6(III) (Table 4.5). For the analysis relative to Little River sites, four samples, including S9, R7, R10, and SS#1, have t-values very close to the critical value indicating a very weak correlation with Little River sites. All other samples were not correlated with the source fingerprint of the Little River sites. Therefore, it can be concluded that the oil/coal tar source in the Kettle Creek inner harbour is the controlling source for the contaminants investigated in more distant sites. Another feature shown in Figure 4.6 is that, with the exception of sample site S10, the inner and outer harbour sampling sites (C1-C4, S1-S6, S9, SS#1-SS#8, and transitional point S8) are more closely correlated with the oil tar source fingerprint than the sampling sites outside the break walls (C5-C6, S7, R1-R7), especially in the case of the intake sediment samples (MS1-MS3, MS5-MS6, Intake 1 & 2). As can be seen, and to some extent be expected, the inner and outer harbour sediment samples are more closely correlated to the point source fingerprint due to their geographic proximity to the samples used to generate the source fingerprint.

To visualize the results for differentiating locations which were impacted versus those which were not, the source fingerprint pattern is presented as an area plot using the average value of relative abundance of each constituent from all source (SS) samples and the sediment fingerprints of downstream sampling locations are plotted as a series of histograms and compared to the source area plot. Figure 4.7(a) illustrates that most chemical signatures of the sampling sites fit very well with the oil/coal tar source fingerprint (23 of 40 correlation coefficients exceed 0.98). The poor fit of sampling sites relative to KC and LR sources was confirmed as illustrated in Figure 4.7(b) and 4.7(c) (correlation coefficients of 0.39 and 0.54, respectively). Compared to the oil/coal tar source sediments, the KC and LR sources have higher abundances of lead and arsenic but lower abundances of chromium and nickel. The C sample (correlation coefficient = 0.80), which is representative of upstream (upwind) sites about 1 km away from the mouth of the creek in Lake Erie, has a relatively high abundance of chromium (Cr) and nickel (Ni) but low abundance of lead (Pb). Also, slightly less correlated samples (correlation coefficients between 0.94 and 0.98) including R1 – R4, R6 – R7, R10, C5, C6, S7, and S10, which all have a high abundance of As but lower abundance

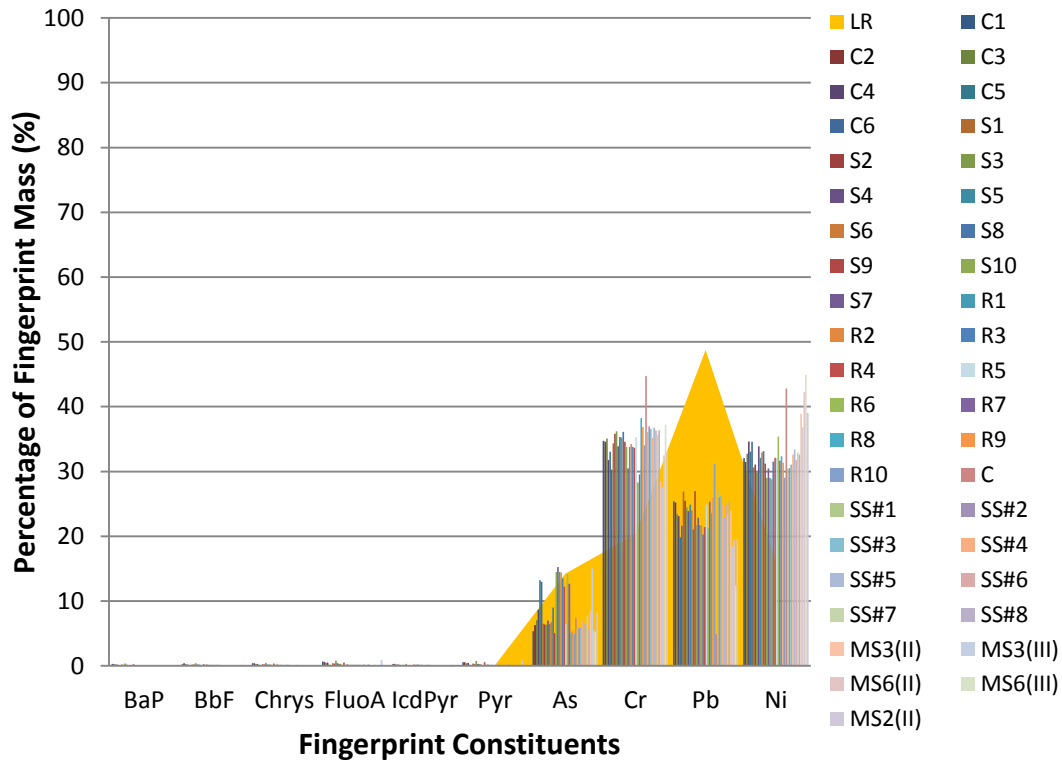
of Pb compared to the oil/coal tar source fingerprint, are all located in Lake Erie beyond the break walls (except R10 which is just at the upstream edge of contaminated sediment from the point source and S10 which is within the inner harbour but is affected by mixing of lake and creek currents). This indicates that the lower correlations of Lake Erie samples with oil tar source fingerprint are a result of less sediment migration to some sample sites and/or interaction with lake sediments.



(a)



(b)



(c)

Figure 4.7 Fingerprint plot of creek, lake, and intake sediments relative to (a) the oil tar source fingerprint; and (b) upstream Kettle Creek [KC] and (c) Little River [LR]

The good correlation of intake sediment samples with the Kettle Creek inner harbour source fingerprint indicates that the oil/coal tar contaminated sediments have been transported through IPZ-2 to IPZ-1 and deposited within the drinking water intake pipe. This has also been confirmed by the presence of trace concentrations of PAHs in the sediments in the water intake pipe.

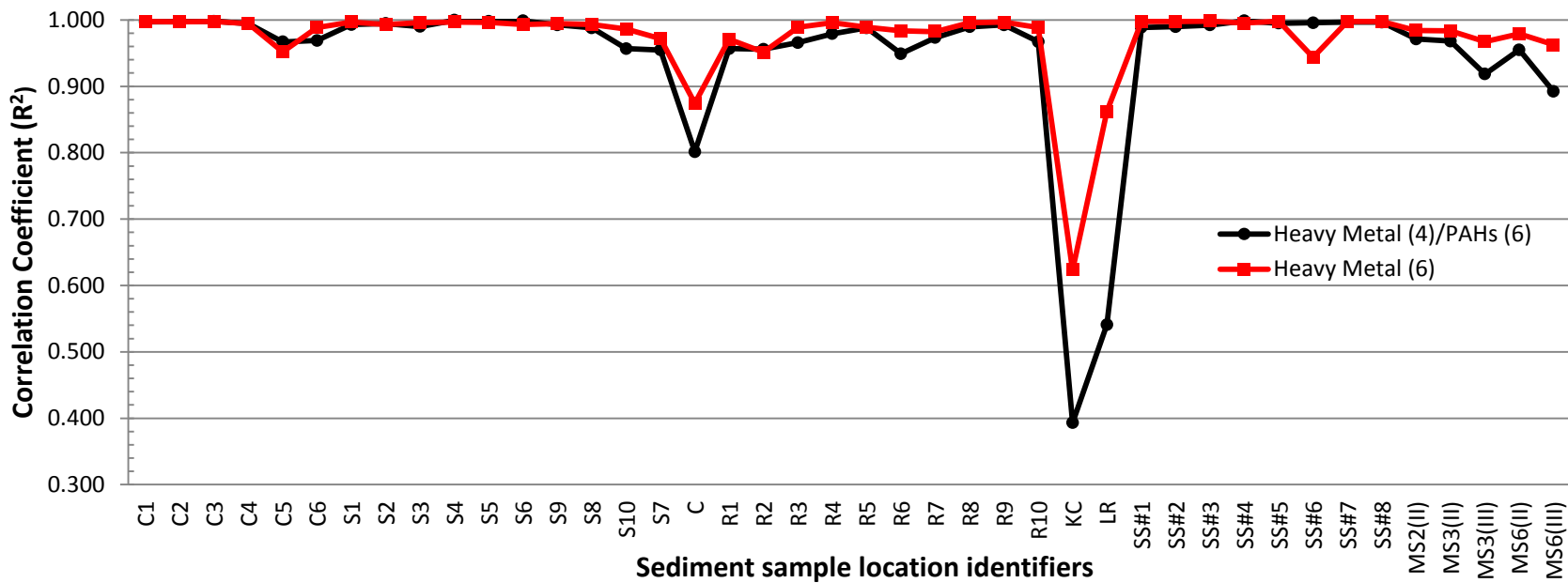


Figure 4.8 Comparison of heavy metal only to heavy metal/PAH fingerprint correlation coefficients for creek, lake, and intake sediment constituent mass distributions.

4.3.2 Heavy Metal-based FALCON Analysis

For the drinking water intake sediment samples, only 5 data sets containing both PAHs and heavy metals were available. However, 6 additional sites had heavy metal data only. In order to increase the number of samples for the FALCON analysis the two sets were combined to provide 11 sediment samples with heavy metal data in the intake pipe.

Instead of using only 4 heavy metals (as was the case with the heavy metal/PAH-based fingerprints), it was decided to use 6 heavy metals as FALCON constituents by incorporating two more potential gasification waste products, copper (Cu) and zinc (Zn). The average reproducibility of the heavy metal-based fingerprints was 0.996. The six heavy metals have a distinct fingerprint pattern characterized by approximately 47% Zn, 15% Cu, 13% Cr and Ni, 9.0% Pb, and 3.0% As (based on means). To validate the heavy metal-based fingerprints, correlation coefficients obtained using the heavy metal-based fingerprints were compared with the results based on heavy metal/PAH-based fingerprints.

As can be seen in Figure 4.8, the heavy metal-based fingerprint generated a similar trend of correlation coefficients compared to the heavy metal/PAH-based fingerprint, especially since the two types of fingerprints obtained very similar correlation coefficients for the inner and outer harbour samples. Comparatively though, the heavy metal-based fingerprint was less sensitive than the heavy metal/PAH-based fingerprint when it came to distinguishing the oil tar source from other contamination sources. When fingerprints are not well correlated, the heavy metal/PAH-based fingerprint is less well correlated than the heavy metal-based fingerprint making it easier to distinguish. Therefore, it can be concluded that at least in this case, the heavy metal/PAH-based fingerprint may be more sensitive and hence more appropriate for the characterization of the oil/coal tar source, confirming the importance of the PAHs even though concentrations and the relative percentage of fingerprint mass of the PAHs were very low. t-test results of the heavy metal-based FALCON analysis indicate that the upstream site (KC) in Kettle Creek (t-value = 2.57) is significantly different from the oil/coal tar source fingerprint at $p < 0.01$ (critical t-value = 4.604). Sample C (t-value = 5.27) and the Little River sites (t-value = 5.00) were only very weakly correlated with the source fingerprint. These results suggest that the heavy metal-

based fingerprint can still successfully predict the correlation trend for all sampling sites as well as distinguish the oil tar source from other potential sources.

Table 4.6 Summary of t-test results of heavy metal-based FALCON analysis* for intake samples relative to three potential contaminant sources

(critical t-value = 4.604 at $\alpha = 0.01^{**}$)

| Source | | Sampling Sites in Intake | | | | | |
|---------------------|----------------------|--------------------------|---------------|--------------|---------------|---------------|---------------|
| | | MS1(I) | MS2(II) | MS3(I) | MS3(II) | MS3(III) | MS5(I) |
| Oil | R² | 0.988 | 0.984 | 0.953 | 0.984 | 0.967 | 0.988 |
| Tar*** | t | <i>18.023</i> | <i>15.766</i> | <i>8.952</i> | <i>15.553</i> | <i>10.883</i> | <i>18.172</i> |
| Kettle Creek | R² | 0.524 | 0.507 | 0.502 | 0.566 | 0.559 | 0.539 |
| | t | 2.096 | 2.027 | 2.008 | 2.286 | 2.252 | 2.161 |
| Little River | R² | 0.788 | 0.773 | 0.760 | 0.820 | 0.806 | 0.800 |
| | t | 3.851 | 3.694 | 3.563 | 4.268 | 4.078 | 3.999 |

| Source | | Sampling Sites in Intake | | | | |
|---------------------|----------------------|--------------------------|---------------|---------------|---------------|---------------|
| | | MS6(I) | MS6(II) | MS6(III) | Intake 1 | Intake 3 |
| Oil | R² | 0.985 | 0.979 | 0.963 | 0.966 | 0.983 |
| Tar*** | t | <i>16.304</i> | <i>13.618</i> | <i>10.150</i> | <i>10.682</i> | <i>15.318</i> |
| Kettle Creek | R² | 0.524 | 0.497 | 0.437 | 0.480 | 0.542 |
| | t | 2.097 | 1.990 | 1.760 | 1.921 | 2.174 |
| Little River | R² | 0.788 | 0.766 | 0.711 | 0.744 | 0.799 |
| | t | 3.857 | 3.616 | 3.135 | 3.412 | 3.986 |

* PAHs not included in this analysis (6 heavy metals)

** Italicized values exceed critical t-value

*** Oil tar refers to sediment collected in Kettle Creek downstream from oil/coal gasification site contaminant input; sample designated Kettle Creek is collected upstream from input from oil/coal gasification site; and Little River is a Lake Erie tributary to the east of Kettle Creek-closer to drinking water treatment plant intake

As per data summarized in Table 4.6, upstream sites in Kettle Creek and the Little River source fingerprints were shown to not be correlated with drinking water intake sediment samples. However, it is clear that the intake sediment samples significantly correlate with the oil/coal tar source fingerprint from Kettle Creek, indicating that oil tar contaminated sediments have reached water intake. While the relatively high correlation represents a link to the original contaminant source it is beyond the capability of this analysis

to assess risk. However, monitoring results from the Ontario Ministry of the Environment's Drinking Water Surveillance Program and other sampling activities reported only trace concentrations of PAHs (0.05 to 0.09 µg/g, detection limit = 0.05 µg/g) were present in the intake sediments, if at all, and no PAHs were detected in treated water samples (Riggs and Delcan, 2004; CH2MHILL, 2009).

4.3.3 Contaminated Sediment Pathway Identification

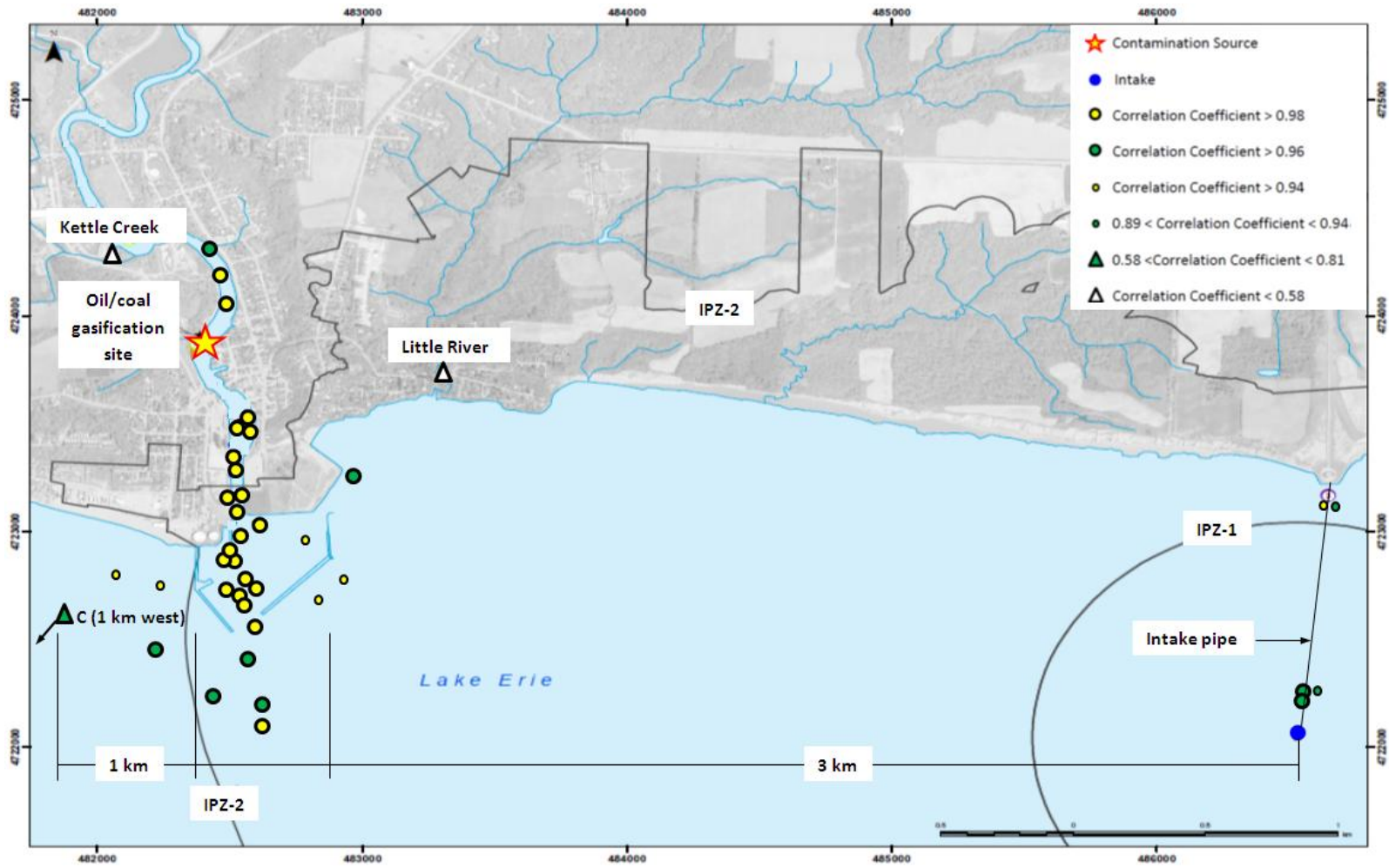
Because the contaminants of interest in this study are relatively recalcitrant, the proportions of each should remain constant as they are transported downstream and into Lake Erie, and as such the FALCON fingerprint can be used as an internal tracer of the oil/coal tar contaminated sediments. By comparing the source fingerprint with downstream sampling location fingerprints, areas that have been impacted by the contaminated sediments can be mapped.

To better visualize/interpret the FALCON analysis results, the correlation coefficients of all sampling sites were plotted using colour coding in Figure 4.9(a) (heavy metal/PAHs) and 4.9(b) (heavy metals only). The high correlation of R8 – R10 (upstream sites in Kettle Creek, Figures 4.1 and 4.9a) with the source fingerprint indicates those three points have somehow been impacted by gasification wastes suggesting undocumented groundwater infiltration or run-off from the site other than through the George Street drain. A third possibility may be the prior existence of an uncharted route for the George Street drain as it is referred to on some maps as the 'new' George Street drain. R1 – R3 to the west in Lake Erie have relatively high correlation coefficients but nonetheless are less well correlated than samples closer to Exit 1 (R4 and R5) (Figure 4.1 and 4.9a). The higher correlation coefficient indicates R1 – R3 are also somewhat impacted by the oil/coal tar contaminated sediments despite being 'upstream' (upwind) of the Kettle Creek discharge point into Lake Erie (as it relates to general lake currents). This is believed to be caused by local hydrodynamic conditions and wave dispersion. Contaminated sediments around Exit 1 can be distributed by wave movement from east to west (less frequent) and/or anthropogenic activities. Another observation of note is the decreasing correlation trend to the west (R5 – R4 – R3 – R2 – R1 –

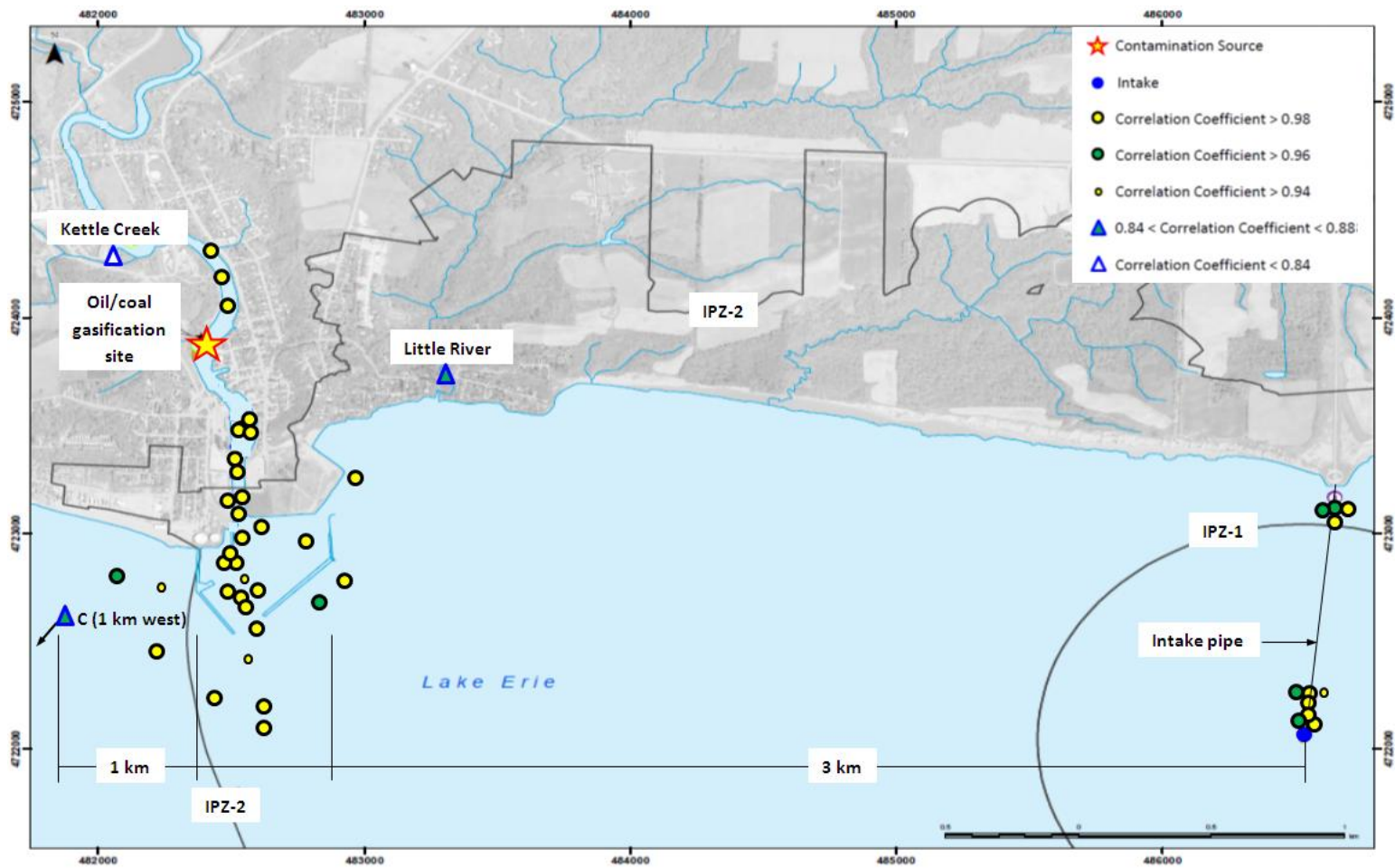
C), indicating that contaminated sediments are dispersing as would be expected based on distance from the source (Figure 4.9a and Table 4.5).

According to Figure 4.9(a), correlation coefficients decrease from the inner/outer harbour sites (C1-C4, S1-S6, S9, SS#1-SS#8, and transitional point S8) to sites in Lake Erie (C5, C6, S7, R6, and R7). It was also noted that R7 has a higher correlation coefficient compared to S7 and R6, which is somewhat expected given that the oil/coal tar contaminated sediments passing through Exit 2 had an unimpeded route to the sample point (and is consistent with general wind and wave patterns). As can be seen when comparing Figure 4.9(a) and 4.9(b), the difference between correlation coefficients is more pronounced between the inner/outer harbour sites and those in Lake Erie when using the heavy metal/PAH-based fingerprint. As indicated previously, this makes the heavy metal only fingerprint slightly less sensitive than the PAH/heavy metal combination.

Figure 4.9(a) shows that the oil/coal tar contaminated sediments have made their way down Kettle Creek to the Port Stanley outer harbour and into Lake Erie, beyond the break walls. There are two potential pathways for migration from the outer harbour into Lake Erie (Exits 1 and 2) but there is insufficient data beyond the outer harbour break walls to accurately predict which may be the predominant route. However, with some careful planning and sampling, the preferred route could be determined in a future study using the FALCON analysis. Hydrodynamic conditions suggested that the contaminated sediments could move in the direction of the Elgin Area WTP IPZ-1 (intake) through the prevailing Lake Erie littoral drift (Stantec Consulting Ltd., 2008) but until now it was not possible to definitively confirm this. The high correlation of the intake pipe sediments with the source fingerprint confirm that sediments from the inner harbour have been transported to the intake area. This would be consistent with an observation made by Riggs and Delcan (2004) that the fine silt and clayey materials which predominate in the intake sediment originated from the Kettle Creek outfall plume and erosion of the nearby Lake Erie bluffs.



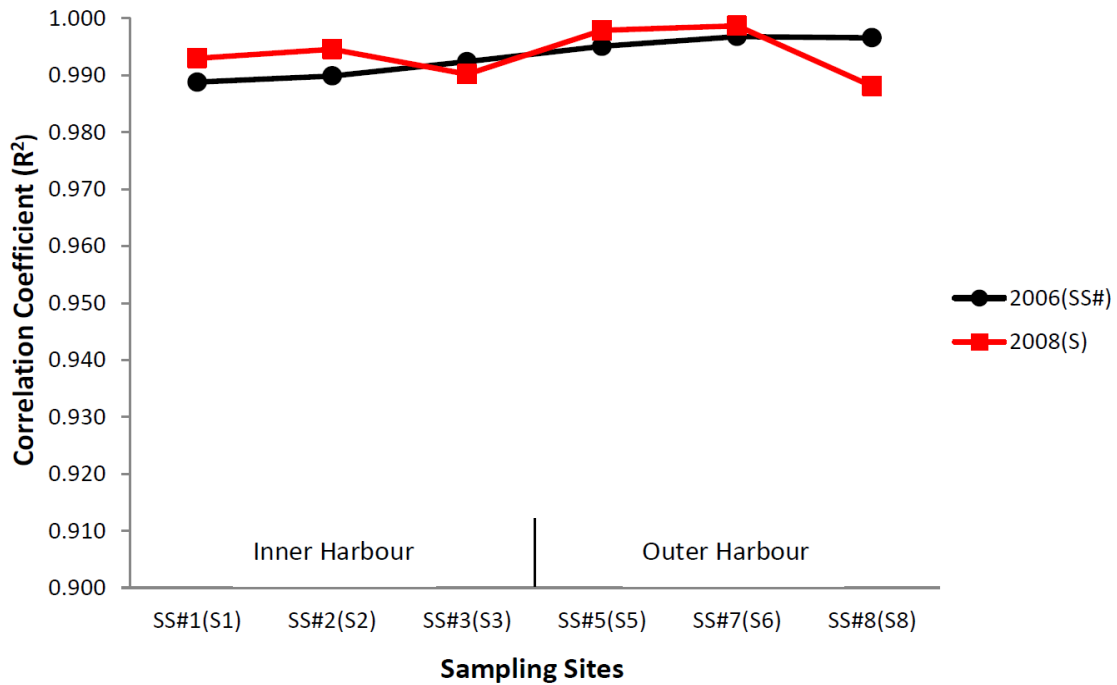
(a)



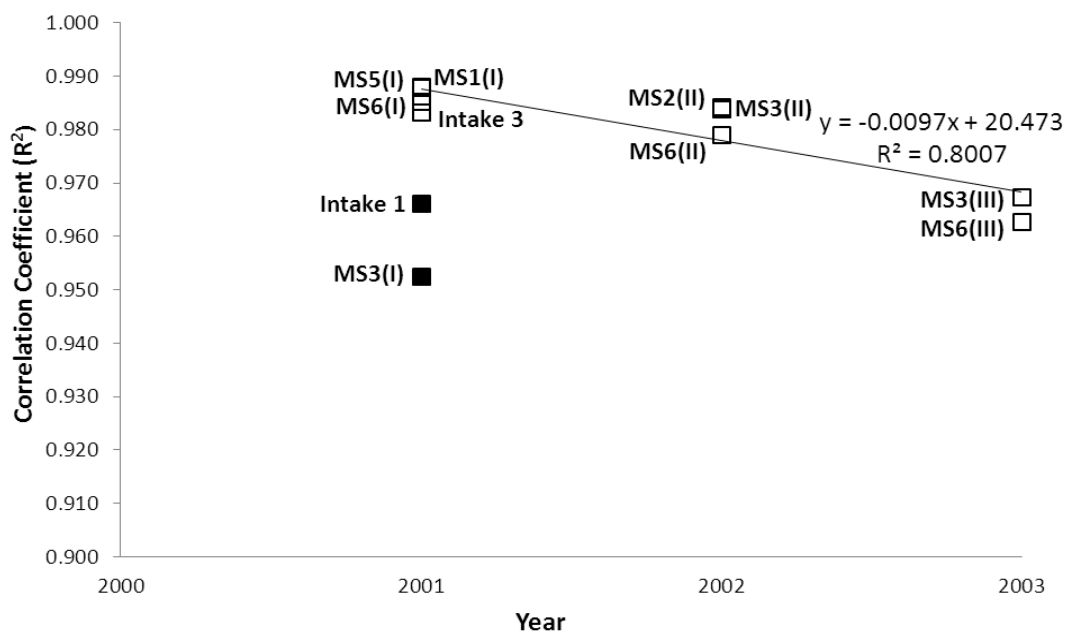
(b)

Figure 4.9 Summary of sediment sample degrees of correlation with source fingerprint using
 (a) heavy metal and PAHs and (b) heavy metals only

Interestingly, correlation coefficients have remained similar over the years in the inner and outer harbour sampling sites, presumably due to their geographical proximity to the point source input from the gasification site (Figure 4.10a) but have been decreasing over the years for which data are available at intake sampling sites (Figure 4.10b). [Two of the 11 sample points were treated as outliers for the preparation of the trend line. This was not based on a statistical test but instead by visual observation based on expected variation in real world sampling situations.] This suggests that any potential for impact of the oil/coal tar source on the water intake is decreasing due to effective site remediation (or at the very least is not increasing). (Note that heavy metal fingerprints were used to generate Figure 4.10b due to the better availability of data and number of sample points.)



(a)



(b)

Figure 4.10 Temporal correlation coefficient changes in (a) inner and outer-harbour sediment samples [heavy metals and PAHs]; (b) intake sediment samples [heavy metals only]. Intake 1 and MS3(I) treated as outliers and are not included in trend line

Intake protection zone vulnerability assessments take into account several considerations which may be obvious (such as existing chemical storage tanks) or intuitive (former industrial sites handling or producing toxic wastes). In cases where contaminants have been transported to a surface water source and have become associated with sediments it may be difficult to track the contaminated sediments back to their source. This could result in an intake protection zone delineation that is overly conservative or perhaps not conservative enough which has economic and even political implications. On the other hand, the contaminant source could be improperly attributed, resulting in inadequate intake protection zone delineation. A FALCON analysis can be used to avoid such problems by providing a definitive method for source attribution (assuming contaminants are sufficiently conserved). Once a source is identified it can be difficult to determine if the risk/threat of the target contaminant(s) is increasing or decreasing. This too has an impact on intake protection zone

delineation. However, if temporal contaminant data are available then FALCON-derived correlation coefficient trends can be plotted or calculated to predict whether the risk of a threat is increasing or decreasing. It should be noted that dispersion at this study site occurred over decades. Sites with less lengthy histories of exposure will have less widespread areas of influence and increased opportunities for this tool to be put to good use.

4.4 Conclusions

Drinking water regulators are beginning to integrate source protection initiatives into more comprehensive strategies and guidance for utilities. Within this context, the fingerprint analysis of leachate contaminants (FALCON) was employed in a surface water setting to assess its appropriateness as a tool to assist with understanding contaminated sediment transport in a drinking water intake protection zone. This study demonstrates for the first time that application of the FALCON method can be applied using a combination of PAHs and heavy metals to assess and potentially assist with the delineation of intake protection zones in which coal/oil gasification activities have occurred. The following conclusions can be drawn based on using a combination of heavy metals and PAHs or with heavy metals alone as the primary sediment contaminants:

- FALCON provided valuable information regarding contaminant characterization, source attribution, and transport within a surface water context without the need for knowledge of local hydrodynamic conditions, potentially reducing reliance on complicated hydrodynamic analysis (e.g. modelling and simulation).
- Heavy metals and PAHs (containing more than 3 rings) are sufficiently conserved in surface water sediments to be used in this analysis.
- The heavy metal fingerprint was slightly less sensitive than the heavy metal/PAH fingerprint but was shown to be a reasonable alternative for oil/coal gasification contaminated sediment characterization and transport in this instance. This observation may hold true in general but would have to be demonstrated at other sites before being conclusively accepted.

- Temporal comparisons of correlation coefficients (degree of correlation) between the fingerprint generated in close proximity to the contaminant source (the source fingerprint) and fingerprints at more distant locations can provide valuable information regarding contaminated sediment deposition trends (increasing, remaining steady, or decreasing).
- In addition to being able to calculate correlation coefficients between the source and more distant fingerprints, it is also possible to statistically assess the probability of various potential point sources being responsible for fingerprints at a given point (in this case a drinking water intake).
- In situations where exposure to a contaminant source has been long (on the order of decades), correlations between the source fingerprint and more distant fingerprints can be quite high. In this case, the sediment fingerprints within a drinking water intake in excess of 3 km from the point source were between 89 and 97% correlated.
- This fingerprint analysis could potentially be used to help delineate drinking water intake protection zones, not only for the contaminants discussed herein but for others which are resistant to chemical and microbial degradation. It may also be possible under some circumstances to use common water constituents (e.g. chloride, sulfate, calcium, sodium, nitrate, etc.) which may be present in different ratios in intersecting water courses as opposed to the contaminants of concern if data are lacking for those.

Site-specific conclusions include the observations that:

- The fingerprint of the oil/coal tar contaminated sediment was distinguishable from those from other potential contamination sources including an upstream Kettle Creek site, an upwind/up current site to the west in Lake Erie, and the Little River site to the east.
- Sediment from the identified point source was responsible for local PAH and heavy metal contamination inside and outside Port Stanley Harbour.
- Harbour structure and hydrodynamic factors influenced the distribution and migration of oil tar contaminated sediments.

- While contaminated sediments are generally dispersing in intake protection zone-2, they appear to be moving to the east and south through the prevailing Lake Erie littoral drift and mixing of sediment.
- The high correlation between sediment fingerprints collected in the drinking water intake and the point source fingerprint indicates that some contaminated sediments have reached the drinking water intake. However, the correlation has been decreasing in intake sediments since the contaminated site remediation. Drinking Water Surveillance Program data indicate that heavy metals and PAHs have not been detected above any existing Ontario regulatory Maximum Acceptable Concentrations in treated drinking water from this source.

Chapter 5

Treatment of Oil Tar Contaminants

Previous chapters have demonstrated that oil tar contaminated sediments with varying degrees of potential health impact have migrated into intake protection zone (IPZ) I of the Elgin area water treatment plant (WTP). Typically, heavy metals and PAHs tend to adsorb onto or become otherwise associated with sediment particles, which in turn can be effectively removed through coagulation-flocculation-sedimentation and potentially filtration. However, a certain portion remains in dissolved form in raw water. While they are not anticipated to reach levels in influent water requiring treatment, it was felt that it would be prudent to assess the capability of the current WTP configuration for the removal of PAHs and heavy metals in dissolved form. In this chapter, treatment alternatives for these dissolved species are identified and discussed. However, those contaminants with low toxicity and exposure probability were excluded from the final contaminant list as described in the next section, and are not further discussed thereafter.

Published studies include mainly bench-scale experiments, some pilot-scale investigations, and relatively few full-scale applications of water treatment processes. On the basis of a review of published information, the efficiency of the existing conventional treatment processes at the Elgin Area WTP were assessed. Oil tar contaminants which are less likely to be effectively removed through the current water treatment processes are identified. Potential treatment alternatives were evaluated and ranked based on their technical complexity, cost, and efficiency. The most cost-effective treatment technology for each contaminant is recommended for the eventuality that treatment might be required.

5.1 Condensation of Contaminant List

Chapter 3 identified various oil tar contaminants with potential impacts on intake protection zones of the Elgin Area WTP (Table 3.10). The contaminants were further classified according to their varying degree of impacts on human health. As per Table 2.5, copper, iron, selenium, zinc, and phenol have minimum impacts on human health. Iron and zinc only have aesthetic objectives (AO) values which are not established based on operational

considerations. Phenols do not have a guideline value due to their extremely low raw water concentration in natural environment. Therefore, iron, zinc, and phenol were excluded from the contaminant list and are not discussed in this chapter. The Ontario MOE and Health Canada have only proposed an AO value for copper. However, the USEPA regulates copper by a Treatment Technique (TT) that requires systems to control the corrosiveness of their water and is also health-based. Moreover, the WHO has proposed a provisional health-based guideline value of 2 mg/L. Similarly, selenium, which is another essential element for human nutrition, is also regulated by the WHO on the basis of human health. Therefore, copper and selenium are included in the following discussion.

Table 5.1 List of possible contaminants and drinking water guidelines/standards for each

| Contaminant | Ontario MOE^a MAC or IMAC | Health Canada^b MAC (mg/L) | USEPA^c MCL or TT (mg/L) | WHO^d (mg/L) |
|----------------------------|--|---|---|-----------------------------------|
| <i>Heavy Metals</i> | | | | |
| Antimony | 0.006(IMAC) | 0.006 | 0.006 | 0.02 |
| Arsenic | 0.025(IMAC) | 0.010 | 0.010 | 0.01 (P)* |
| Cadmium | 0.005 | 0.005 | 0.005 | 0.003 |
| Chromium | 0.05 | 0.05 | 0.1 | 0.05 (P)* |
| Copper | 1.0 ^e | ≤ 1.0 ^e | TT; AL = 1.3 | 2 |
| Lead | 0.01 | 0.01 | TT; AL = 0.015 | 0.01 |
| Nickel | N/A | N/A | 0.1 | 0.07 |
| Selenium | 0.01 | 0.01 | 0.05 | 0.01 |
| <i>Organic</i> | | | | |
| Benzene | 0.005 | 0.005 | 0.005 | 0.01 |
| Toluene | 0.024 | ≤0.024 ^e | 1.0 | 0.70(C)* |
| PAHs | | N/A | 0.0002 | 0.0002 |

AL = Action Level

^aOntario MOE, 2006a. Technical Support Document for Ontario Drinking Water Standards, Objectives and Guidelines. MAC is maximum acceptable concentration and IMAC is the interim maximum acceptable concentration (Ontario MOE, 2006a).

^bFPT Committee on Drinking Water (2008), Guidelines for Canadian Drinking Water Quality – Summary Table. MAC is maximum acceptable concentration (FPT Committee on Drinking Water, 2008).

^cFrom USEPA (2009), National Primary Drinking Water Regulations.

^dWorld Health Organization (WHO) (2008), Guidelines for Drinking Water Quality, third edition.

^cAesthetic objectives (AO) and Operational Guidance (OG) values (FPT Committee on Drinking Water, 2008).

(P)* = provisional guideline value because there is evidence of a hazard but the available information on health effects is limited.

(C)* = concentrations of the substance at or below the health-based guideline value may affect the appearance and taste or odour of the water, resulting in consumer complaints.

According to Table 3.7, vanadium and some PAH contaminants, including acenaphthene, anthracene, benzo(g,h,i)perylene, fluoroanthene, fluorine, naphthalene, phenanthrene, and pyrene, do not have guideline values due to their extremely low raw water concentrations and exposure probability in the natural environment. These contaminants were also excluded from the final contaminant list. Furthermore, various PAH species were therefore monitored and reported as total PAHs. For convenience, total PAHs are used in the final contaminant list as opposed to including individual PAH species as there are no data for individual PAHs from 1993 to 2008. The final contaminant list with drinking water guidelines/standards for each contaminant is provided in Table 5.1.

A discussion of existing and potential treatment techniques for each of the contaminants listed in Table 5.1 follows. Section 5.2.12 provides a detailed summary table of treatment alternatives currently available in the existing WTP and other potential techniques.

5.2 Treatment Alternative Summary for Oil Tar Contaminants

5.2.1 Antimony (Sb)

Studies indicate that conventional coagulation with either polyaluminum chloride or ferric chloride is not sufficiently effective to remove antimony to meet drinking water standards (Kang et al., 2003; WHO, 2008). However, a recent bench-scale investigation of coagulation using ferric chloride for antimony (V) removal reported removal efficiencies of approximately 90 – 98% independent of initial antimony concentration ranging from 50 to 500 µg/L (Guo et al., 2009). An average of 90% removal of antimony (III) was achieved over a broad pH range from 4.0 to 10.0 (Guo et al., 2009). Comparatively, coagulation with aluminum sulfate had a very low removal efficiency for both Sb(III) and Sb(V), indicating that ferric coagulant may be more effective than alum (Guo et al., 2009). It was also reported

that Sb(V) is more refractory to coagulation compared to As(V) but Sb(III) removal was better than As(III) and Sb(V) over a broad pH range (Guo et al., 2009).

A bench-scale application of reverse osmosis conducted by Kang et al. (2000) reported constant removal efficiencies between 85% and 95% over all investigated pH levels ranging from 3 to 10. Full-scale application of ferric hydroxide adsorptive media seems to be a promising technique, which in at least one study was shown to successfully control antimony to meet the USEPA MCL of 6 µg/L in pH operating range of 5.5 to 8.5 (Cumming et al., 2009).

5.2.2 Arsenic (As)

Coagulation with iron- or aluminum-based compounds is recommended as a cost-effective process for As(V) removal from drinking water (Fields et al, 2000; Gregor, 2001; USEPA, 2002b; WHO, 2008; Chen et al., 2010). If As(III) is present in raw water, however, preoxidation of As(III) to As(V) prior to coagulation is required to ensure the effectiveness of As(III) removal (Kang et al., 2003; Chen et al., 2010). Previous studies have also reported that the removal efficiency of coagulation depends on coagulant type as well as dosage. Typically, ferric sulfate has been reported to be slightly better than alum for arsenic removal (Fields et al., 2000).

Other full-scale treatment alternatives include lime softening, iron/manganese oxidation, ultrafiltration (UF), and nanofiltration (NF) (Sato et al., 2002; WHO, 2008; Malik et al., 2009; Pguna et al., 2008). In small and domestic systems, ion exchange, manganese green-sand filtration, and activated alumina adsorption have also been applied for arsenic removal (WHO, 2008; Malik et al., 2009). Some innovative technologies, including reverse osmosis, permeable reactive barriers, biological treatment, phytoremediation and electrokinetic treatment, appear to be effective for arsenic removal (Kang et al., 2000; Malik et al., 2009). However, these technologies remain to be incorporated into full-scale practice, for this purpose, and must be further validated (WHO, 2008; Malik et al., 2009). As(III) rejection ranging from 9.9% to 50% was reported by a variety of pilot-scale studies on ultrafiltration (Brandhuber and Amy, 1998). Five treatment alternatives including lime softening, activated

aluminum adsorption, ion exchange, iron oxide adsorption, reverse osmosis, and nanofiltration have been demonstrated to be sufficiently effective to control arsenic to below USEPA MCL of 10 µg/L (Brandhuber and Amy, 1998; Wang et al., 2007; Moore et al., 2008; WHO, 2008; Pgana et al., 2008; Cumming et al., 2009; Malik et al., 2009; Lipps et al., 2010; Wang et al., 2010). The efficiency of nanofiltration for As(V) removal is in the range of 95% but is only approximately 75% for As(III), indicating that pre-oxidation may be necessary to convert As(III) to As(V) if removals in the range of 75% are not sufficient to get below regulated levels (Sato et al., 2002).

5.2.3 Cadmium (Cd)

Coagulation is recommended as a promising technology to eliminate cadmium to meet drinking water standards in conventional treatment plant (WHO, 2008). Terashima et al. (1986) reported essentially complete removal of cadmium by coagulation-flocculation-sedimentation using ferric chloride under optimal conditions.

Bench-scale ion exchange has demonstrated selective and effective elimination of trace levels of cadmium from raw waters used for drinking water treatment (Zhao et al., 2002). The cadmium concentration was well controlled to below 5 µg/L when the initial concentration was 100 µg/L. Precipitation softening is widely used to remove cadmium in industrial wastewater treatment (Zhao et al., 2002), and although not widely used in drinking water treatment, the WHO (2008) recommends this technology as an effective alternative for drinking water applications. Previous studies have also demonstrated that membrane filtration is effective for cadmium removal (Zhao et al., 2002; Qdais and Moussa, 2004; WHO, 2008). Qdais and Moussa (2004) reported reverse osmosis has an average removal efficiency of 98.5% while nanofiltration removal efficiencies ranged from 82% and 97% over a broad range of initial Cd concentration between 25 ppm and 200 ppm.

5.2.4 Chromium (Cr)

The WHO (2008) also suggests that coagulation is a promising conventional treatment process for chromium removal. In a bench-scale investigation, 79 – 99% of chromium was removed from a wastewater solution with an initial concentration of 12 mg/L at the optimal

pH of 7.5 (Song et al., 2004). Both aluminum sulfate and ferric chloride were excellent for chromium removal.

Adsorption using granular activated carbon has also been proven to be an effective alternative to remove chromium from drinking water (Zhao et al., 2005; Yue et al., 2009). Chemical modification of activated carbon surfaces by increasing the number of oxygen groups can significantly improve adsorption and maximum chromium removal efficiency can reach 95% under optimum conditions (Zhao et al., 2005). A bench-scale nanofiltration study reported that the optimum removal efficiency of chromium can range from 90% – 100% at pHs > 7.5 (Lazaridis et al., 2004). Ultrafiltration may also be a promising alternative to remove Cr(III) to below the USEPA MCL of 0.1 mg/L (Pgana et al., 2008). Mousavi Rad et al. (2009) reported that reverse osmosis can achieve rejections exceeding 99% over a broad range of initial feed concentration ranging from 5 to 100 mg/L. Activated alumina adsorption of chromium (III) can achieve an optimal removal efficiency of more than 80% according to a bench-scale study by Mahmoud et al. (2010).

5.2.5 Copper (Cu)

Copper cannot be removed through conventional treatment processes (WHO, 2008). As an essential element in human nutrition, copper is not always considered as a raw water contaminant due to its low toxicity. However, the USEPA regulates copper using a treatment technique regulation. The action level is 1.3 mg/L. A point-of-use (POU) application of granular activated carbon exhibited a good performance to remove copper in drinking water, providing an alternative to remove excess copper (Ahmedna et al., 2004). Another bench-scale GAC application reported a removal efficiency of 65.5% and an enhanced performance with an efficiency of 89.0% using tannic acid immobilized activated carbon (Üçer et al., 2006). Mahmoud et al. (2010) reported that activated alumina adsorption can achieve a maximum removal efficiency of 95%. A bench-scale study of reverse osmosis has reported an average removal efficiency of 97%, while nanofiltration removal efficiencies for copper ions ranged from 84% to 96% at initial Cu concentrations of 25 ppm and 200 ppm, respectively (Qdais and Moussa, 2004). A bench-top ion exchange system, which is

comprised of a weakly acidic resin and GAC containing silver, was reported to have average removal efficiencies of more than 80% for copper in tap water (Gulson et al., 1997). Also, pH adjustment is theoretically possible but not likely feasible.

5.2.6 Lead (Pb)

Bench-scale application of powdered activated carbon (PAC) has been reported to have a maximum lead (II) removal efficiency of 97.95% in dilute aqueous solutions (< 40 mg/L) at pH = 6.5, indicating that lead can be potentially removed by conventional treatment (Singh et al., 2008).

Adsorption by granular activated carbon has been shown to be a promising technique to remove Pb(II) from drinking water according to some bench-scale studies (Goel et al., 2005; Sreejalekshmi et al., 2009). At an initial concentration of 0.5 mmol/L, the maximum removal efficiency reported by Sreejalekshmi et al. (2009) was 88.6% at pH = 6.5. Activated alumina adsorption also performed well for removing Pb(II) from drinking tap water with a removal efficiency of more than 90% reported in a bench-scale study conducted by Mahmoud et al. (2010). Gupta et al. (2001) also demonstrated that metal oxide adsorption can eliminate 95% of lead at pH = 6. Bench-scale ion exchange system performance is variable with respect to lead removal depending on initial lead levels and chemical composition of the water but it is reported that lead concentrations can be successfully controlled by ion exchange to within the WHO guideline of 10 µg/L (Gulson et al., 1997). Johnston (1975) reported that reverse osmosis can remove 97.6% of lead under optimum conditions.

5.2.7 Nickel (Ni)

Conventional drinking water treatment, e.g. coagulation, can effectively remove nickel in the raw water (WHO, 2008). A bench-scale adsorption study with powdered activated carbon (PAC) reported a maximum removal efficiency of 60% (Abdel-Shafy et al, 1998), while it appears that some modified PAC (using 10% H₂SO₄ and carbon dioxide gas) can achieve Ni (II) removals of up to 97.8% at an initial concentration of 25 mg/L (Hasar, 2003).

Abdel-Shafy et al. (1998) reported that maximum nickel removal efficiency of granular activated carbon (GAC) can reach 80% under optimum conditions. The WHO (2008) also recommends ion exchange as a promising technology for the removal of naturally occurring nickel. Both adsorption and ion exchange are mainly applied to eliminate nickel in groundwater sources (WHO, 2008). Ozaki et al. (2002) reported that reverse osmosis can achieve rejections exceeding 98.5% over a wide range of pH (from 3 to 9).

5.2.8 Selenium (Se)

Selenium (IV) is more toxic than selenium (VI) and hence is more frequently studied for its removal. Conventional treatment processes such as coagulation, flocculation, and sedimentation are also promising alternatives for selenium (IV) removal to meet drinking water guidelines (WHO, 2008). Merrill et al. (1987) demonstrated that a pilot-scale chemical coagulation system can remove 80% of selenium under optimal conditions. They also noted that Se (IV) is more readily removed through coagulation than Se (VI).

Adsorption of Se by metal oxides and iron-coated GAC has been reported as an efficient technique for selenium (IV) removal over a wide range of pH with the optimal removal efficiency achieved being 97.3% (Zhang et al., 2008). Reverse osmosis has also been demonstrated to be effective for Se removal with the efficiency exceeding 99.94% under optimal conditions (Mariñas et al., 1992). Bench-scale nanofiltration has been demonstrated to be capable of removing more than 95% of selenium (total) (Kharaka et al., 1996).

5.2.9 Benzene

Conventional treatment processes are not well suited to organic contaminant removal. Activated carbon is suggested as an effective treatment alternative for benzene in drinking water (WHO, 2008). A pilot-scale application of a jet flocculator with powdered activated carbon adsorption exhibited an excellent performance for benzene removal with an efficiency of 95% using an influent containing 100 µg/L of benzene (Jose et al., 1997). Similar results were reported by Gray (2008).

A bench-scale study with granular activated carbon reported an average removal efficiency of 84% at an initial concentration of 100 µg/L (Bansode et al., 2003). Other promising alternatives include air stripping and ozonation (WHO, 2008). Benzene can be also removed by advanced oxidation processes (UV-A photo-Fenton processes) with efficiencies exceeding 99% (Tiburtius et al., 2005).

5.2.10 Toluene

Activated carbon is also reported as an effective treatment alternative for the removal of toluene to meet drinking water regulations (WHO, 2008). Addition of PAC during coagulation can significantly improve the removal of trace level of organic contaminants, indicating the potential of conventional treatment processes to remove toluene from raw water (Gray, 2008). Tierney et al. (2005) reported that powdered activated carbon adsorption can completely remove vapor-phase toluene under optimal conditions (temperature 25°C and 20g/m³ PAC), indicating the high adsorption tendency of toluene onto PAC media.

Other effective treatment alternatives recommended by WHO (2008) include aeration, ozonation, and AOPs. Tiburtius et al. (2005) conducted a bench-scale investigation of advanced oxidation processes (Tiburtius et al., 2005) on benzene, toluene, and xylenes (BTX) removal and reported that BTX can be almost completely degraded in approximately 30 mins.

5.2.11 Polycyclic Aromatic Hydrocarbons (PAHs)

The presence of PAHs in drinking water sources is not common and hence most studies have focused on wastewater treatment. However, WHO (2008) suggests that coagulation/flocculation/sedimentation is a potential alternative for the control of PAHs as 65% to 76% of the PAH contaminants in surface water are attached to particulate matter (WHO, 2008).

Effective removal of PAH contaminants can be achieved by GAC treatment and optimal efficiencies often exceed 95% (Snoeyink and Chen, 1985). Bench-scale investigation of PAH removal efficiency using ozone has been reported in various publications and it has been demonstrated to be a promising treatment alternative (Trapido et al., 1995; Tran et al.,

2009). An advanced oxidation process known as effective electrochemical oxidation technology using Ti/RuO₂ anode has been investigated and the average PAH removal efficiency was reported to be 80.1% (Tran et al., 2009).

5.2.12 Summary of Treatment Alternatives

Promising treatment alternatives with important experimental conditions and reported efficiencies are summarized in Table 5.2 for each oil tar contaminant.

5.3 Qualitative Evaluation of Treatment Achievability of Oil Tar Contaminants in Elgin Area WTP

Many of the previously-described studies were conducted at bench-scale and the actual performance of alternatives in full-scale application significantly depends on the scale of application, initial concentration in the source water, co-existence of other contaminants, and plant-specific process configuration and operational aspects. Attainable removal efficiencies need to be determined by testing actual waters to be treated.

Treatment processes in the Elgin Area WTP include pre-chlorination, coagulation, flocculation, sedimentation, rapid dual-media filtration, and powdered activated carbon (seasonally on an as-required basis). PAC is added when required and settles out quickly in the flocculation and sedimentation basins. Comparatively, GAC is used as a filter media and can be reused after backwashing but it is susceptible to prior loading by competitive species of contaminants and organic carbon. PAC is expected to be efficient because PAC is always fresh when added (no prior adsorption of NOM). Therefore, powdered activated carbon is considered to be a potentially effective treatment alternative for oil tar contaminants which can be removed by adsorption. However, PAC is affected by simultaneous competition from total organic carbon (TOC) and other contaminants, and there is a practical limit to the dosage that can be applied. In addition, the actual removal efficiency cannot be determined at this plant due to lack of contaminant-specific data.

Table 5.2 Summary of treatment alternatives for oil tar contaminants

| Contaminant | Alternatives | Influent Conc. ($\mu\text{g/L}$)* | pH | %Removal | Reference |
|--------------------|-----------------------|---|-----------|-------------------------|--------------------------|
| Antimony | C (FeCl_2) | 50 – 500 | 4.5 – 5.5 | 90 – 98% | Guo et al., 2009 |
| | MO | 15.8 – 18 | 7.4 – 7.5 | < 6 $\mu\text{g/L}^a$ | Cumming et al., 2009 |
| | RO | 10 | 3 – 10 | 85 – 95% | Kang et al., 2000 |
| Arsenic | C | 27.3 – 43.3 | 8.3 | < 10 $\mu\text{g/L}^a$ | Chen et al., 2010 |
| | AA | 34.6 – 50.2 | 8.5 – 8.6 | < 10 $\mu\text{g/L}^a$ | Lipps et al., 2010 |
| | IX | 33.6 – 60.8 | 7.3 – 7.9 | < 10 $\mu\text{g/L}^a$ | Wang et al., 2007 |
| | MO | 87.9 – 93 | 7.4 – 7.5 | < 10 $\mu\text{g/L}^a$ | Cumming et al., 2009 |
| | NF(PO) | 50 | 6.8 | > 95% | Sato et al., 2002 |
| | PS | NS | NS | > 80% | WHO, 2008 |
| | RO(PO) | 15 – 30 | 6 – 7 | > 95% | Brandhuber and Amy, 1998 |
| | UF(PO) | 15 – 30 | 6 – 7 | > 95% | Brandhuber and Amy, 1998 |
| Cadmium | C | 20 mg/L | 9.5 – 10 | > 99% | Terashima et al., 1986 |
| | IX | 100 | 7.4 – 8.7 | < 5 $\mu\text{g/L}^a$ | Zhao et al., 2002 |
| | NF | 25 – 200 ppm | 2.5 - 11 | 82 – 97% | Qdais and Moussa, 2004 |
| | PS | NS | NS | > 80% | WHO, 2008 |
| | RO | 25 – 200 ppm | 4 – 11 | > 93% | Qdais and Moussa, 2004 |
| Chromium | C | 2 – 12 mg/L | 7.5 – 10 | 79 – 99% | Song et al., 2004 |
| | AA | 1 – 2 mg/L | 5 – 7 | > 80% | Mahmoud et al., 2010 |
| | GAC | 100 mg/L | 3 – 5 | 83 – 95% | Zhao et al., 2005 |
| | NF | 1 – 10 mg/L | 7.5 – 9.3 | 90 – 100% | Lazaridis et al., 2004 |
| | RO | 5 – 100 mg/L | NS | 99.5 – 99.8% | Mousavi Rad et al., 2009 |
| | UF | 500 | 7 | < 0.1 mg/L ^a | Pgana et al., 2008 |

Table 5.2 Summary of treatment alternatives for oil tar contaminants (continued)

| Contaminant | Alternatives | Influent Conc. ($\mu\text{g/L}$)* | pH | %Removal | Reference |
|-----------------|--------------|-------------------------------------|------------|------------------------|----------------------------|
| Copper | AA | 1 mg/L | 5 – 7 | 91 – 95% | Mahmoud et al., 2010 |
| | GAC | 1 – 10 mg/L | 5.4 | 89% | Üçer et al., 2006 |
| | IX | 100 – 1250 | Tap water | > 80% | Gulson et al., 1997 |
| | NF | 25 – 200 ppm | 2.5 – 11 | 84 – 96% | Qdais and Moussa, 2004 |
| | RO | 25 – 200 ppm | 4 – 11 | 97% | Qdais and Moussa, 2004 |
| Lead | PAC | 10 – 40 mg/L | 6.5 | 94 – 97.95% | Singh et al., 2008 |
| | AA | 1 – 4.8 | 5 – 7 | 92 – 99% | Mahmoud et al., 2010 |
| | GAC | 0.5 mmol/L | 5 – 8 | 80 – 88.6% | Sreejalekshmi et al., 2009 |
| | IX | 4 – 39 | Tap water | < 10 $\mu\text{g/L}^b$ | Gulson et al., 1997 |
| | MO | 0.48 – 4.83 mM | 2 – 6 | 85 – 95% | Gupta et al., 2001 |
| | NF | 10 ppm | 5.17 | 85.5 – 97.6% | Johnston, 1975 |
| Nickel | C | NS | NS | > 80% | WHO, 2008 |
| | PAC | 25 – 100 mg/L | 5 | 85 – 97.8% | Hasar, 2003 |
| | GAC | 2 mg/L | NS | 80% (max.) | Abdel-Shafy et al, 1998 |
| | IX | NS | NS | > 80% | WHO, 2008 |
| | NF | 50 mg/L | 3 – 9 | 98.9 – 99.9% | Ozaki et al., 2002 |
| Selenium | C | 120 | ≤ 6.2 | 75 – 80% | Merrill et al., 19870 |
| | GAC | 1 mg/L | 2 – 8 | 85 – 97.4% | Zhang et al., 2008 |
| | IX | NS | NS | < 10 $\mu\text{g/L}^b$ | Zhang et al., 2008 |
| | NF | < 1000 | 4.4 – 8.5 | > 95% | Kharaka et al., 1996 |
| | RO | 30 – 90 mg/L | 5.5 | > 99.94 % | Mariñas et al., 1992 |

Table 5.2 Summary of treatment alternatives for oil tar contaminants (continued)

| Contaminant | Alternatives | Influent Conc. ($\mu\text{g/L}$)* | pH | %Removal | Reference |
|----------------|----------------|--|------------|--------------------------------------|-------------------------|
| Benzene | C(PAC) | 100 | 6.8 – 7.2 | 85 – 95% | Jose et al., 1997 |
| | A | – | – | > 80% | WHO, 2008 |
| | AOPs | 411.339 | 3 | > 99% | Tiburtius et al., 2005 |
| | GAC | 100 | 5.2 – 10.2 | 75.8 – 91.5% | Bansode et al., 2003 |
| | O ₃ | – | – | > 80% | WHO, 2008 |
| Toluene | PAC | 15 Pa (P _{Partial}) ^c | – | 80 – 99% | Tierney et al., 2005 |
| | A | – | – | > 80% | WHO, 2008 |
| | AOPs | 305.367 | 3 | > 99% | Tiburtius et al., 2005 |
| | O ₃ | – | – | > 80% | WHO, 2008 |
| PAHs | C | – | – | < 0.2 $\mu\text{g/L}$ ^{a,b} | WHO, 2008 |
| | GAC | – | – | > 95% | Snoeyink and Chen, 1985 |
| | AOPs | 513 mg/L | 4 – 9 | 75.7 – 83.6% | Tran et al., 2009 |

^aUSEPA MCL; ^bWHO guideline; ^cP_{Partial}: partial pressure of toluene; *Unless specified otherwise

A: aeration; AA: activated alumina; AOPs: advanced oxidation processes; C: coagulation; GAC: granular activated carbon; MO: metal oxides; IX: ion exchange; NF: nanofiltration; O₃: ozonation; PAC: powdered activated carbon; PO: pre-oxidation; PS: precipitation softening; RO: reverse osmosis; UF: ultrafiltration; NS: not specified

A summary of available treatment alternatives at the Elgin Area WTP for effective removal of oil tar contaminants is provided in Table 5.3. The percentage removal cut-offs were extracted from Table 5.2.

Table 5.3 Summary of current treatment processes at the Elgin Area WTP for target contaminants

| Contaminant | Process | | |
|-------------|--|-----------------------------|---------------------------|
| | Coagulation-Flocculation-Sedimentation | Rapid Dual-Media Filtration | Powdered Activated Carbon |
| Antimony | ● | | ? |
| Arsenic | ● | | |
| Cadmium | ● | | |
| Chromium | ● | | ? |
| Copper | | | ? |
| Lead | | | ● |
| Nickel | ● | | ○ |
| Selenium | ● | | ? |
| Benzene | ● | | ● |
| Toluene | | | ● |
| PAHs | ● | | |

Symbols are as follows:

- 80% or more removal (to below most or all regulated values)
- 50% or more removal
- ? Undetermined removal efficiency
- No entry: no data available

According to Table 5.3, it can be seen that most of the potential contaminants can be removed through the conventional drinking water treatment processes currently available in the Elgin Area WTP. The coagulation/flocculation/sedimentation process can effectively remove most dissolved and particle-associated heavy metals and PAHs. However, this technology has a limited effect on the removal of volatile organic contaminants such as benzene and toluene. PAC addition during coagulation has been demonstrated to be an effective method for removing trace concentrations of organic compounds and in some cases can also help to provide additional removal of heavy metals which cannot be completely removed by coagulation (Jose et al., 1997; Gray, 2008). However, PAC is only seasonally

applied at this plant. As would be expected, rapid dual-media filtration is of limited value for the removal of most dissolved oil tar contaminants.

It should also be noted that the conventional treatment processes in the Elgin Area WTP likely cannot effectively remove copper. However, according to Table 2.5, copper is classified into Group III due to its low toxicity and status as an essential element in human nutrition. The risk of copper exceedance and its potential impacts are evaluated and discussed in the following sections.

5.4 DWSP Monitoring Results of Treated Water

According to Ontario MOE's Drinking Water Surveillance Program (DWSP) monitoring results of treated samples from 1987 to 2010 for Elgin Area WTP, the concentrations of oil tar contaminants in treated water were all below the MOE regulated concentrations, suggesting that the current Elgin Area WTP configuration is sufficiently effective to ensure the safety of drinking water at raw water concentrations encountered to-date. Even though Table 5.3 indicates copper is more refractory to current conventional treatment processes available within Elgin Area WTP, copper is being removed in the WTP suggesting that it is predominantly sediment-bound and has been removed through the coagulation/flocculation/sedimentation process.

5.5 Quantitative Evaluation of Treatment Achievability of Oil Tar Contaminants in Elgin Area WTP

5.5.1 Critical Raw Water Concentration (CRWC)

For the Elgin Area WTP, the functionality of the treatment train can be defined as the overall removal efficiency for each predetermined oil tar contaminant. The removal efficiency of each treatment unit for a specified contaminant can initially be described by a local transfer function. Then the overall transfer function (T_o) of the whole system can be calculated by integrating local transfer functions for each treatment unit. In this way, effluent concentrations can be expressed as a function of the influent concentrations for specific oil tar contaminants.

Ideally, the overall transfer function should be determined for both the normal operating (nominal) modes and possible failure modes of the treatment plant. Full and non-optimal removal efficiencies for each treatment unit have to be determined for nominal and failure modes, respectively. Then, the critical concentration (Cr_{ij}) of contaminant j in raw water that must not be exceeded to comply with drinking water guidelines/standards in the nominal ($i = 0$) and failure modes ($i > 0$) can be expressed as follows (adapted from Hokstad et al., 2009):

$$Cr_{ij}(M_{ij}) = \frac{Cg_j}{To_{ij}};$$

$$To_{ij} = \prod_{k=0}^m (1 - R_{ijk}) = 1 - Ro_{ij}$$

Where M_{ij} is mode i for contaminant j ; Cg_j is the guideline/regulated value for the specific contaminant; R_{ijk} is the local removal factor for treatment process k for contaminant j in mode i . Ro_{ij} is overall removal factor for contaminant j in mode i . To_{ij} is the overall transfer factor for treatment process k for contaminant j in mode i . m is the total number of treatment processes.

The major purpose of this study was to investigate potential adverse impacts of distribution and transport of oil tar contaminants on drinking water quality on the Elgin Area WTP. Therefore, the Elgin Area WTP was assumed to be in the nominal mode and the possible extreme concentration of each oil tar contaminant in raw water that exceeds its critical concentration in the nominal mode was considered as the single important cause of low quality drinking water production. Therefore, the critical raw water concentration of contaminant j in the nominal mode ($i = 0$) can then be simplified as follows:

$$Cr_{0j}(M_{0j}) = \frac{Cg_j}{To_{0j}};$$

$$To_{0j} = \prod_{k=0}^m (1 - R_{0jk}) = 1 - Ro_{0j}$$

5.5.2 Determination of CRWC for Oil Tar Contaminants

The maximum allowable concentrations (MACs) mandated by the Ontario MOE were selected as guideline values (C_g). For those contaminants which are not included in the MOE guidelines, USEPA maximum contaminant level (MCL) values were instead used to calculate C_r . Overall removal factors were then determined using Ontario MOE Drinking Water Surveillance Program (DWSP) data and literature review results. It was noted that the raw water concentrations were much lower than the C_g values for each contaminant according to DWSP influent data. DWSP data include both influent (C_{in}) and treated water concentrations (C_t), and overall removal efficiencies (R_o) can be calculated as follows:

$$R_o\% = \frac{C_t - C_{in}}{C_{in}} \times 100\%$$

Treatment efficiencies calculated based on DWSP data take into account the impacts of inherent redundancy within the treatment system and competition among various contaminants. Therefore, the average DWSP treatment efficiencies through the years 1987 to 2010 were preferentially used to calculate C_r . However, it should be noted that overall removal efficiencies for the Elgin Area WTP reported by the DWSP data may not reflect optimal performance due to the consistently low influent concentrations (and therefore no need to optimize). For those contaminants which were not included in the DWSP database, average literature review removal efficiencies were substituted. The local removal efficiencies for the three existing treatment processes ($m = 3$), including coagulation/flocculation/sedimentation (CFS), rapid anthracite/sand filtration (RF), and powdered activated carbon (PAC), are summarized in Table 5.3. Overall removal efficiencies can then be calculated using the three local removal rates. In this calculation, it was assumed that the removal rates reported in Table 5.3 are not affected by prior removal in an upstream treatment process recognizing that they may have been.

Elgin Area DWSP data sets for raw and treated water oil tar contaminants through the years 1987 to 2010 are summarized in Appendices F and G. Table 5.4 provides summary data for this period. The critical raw water concentrations (CRWC) of oil tar contaminants

for the Elgin Area WTP in nominal mode (under normal operating conditions) were calculated and are summarized in Table 5.5.

Table 5.4 Summary of Elgin Area DWSP data for raw and treated water

| Contaminant | Raw water (µg/L) | | | Treated Water (µg/L) | | |
|-------------|------------------|---------|---------|----------------------|---------|---------|
| | Sample Size | Average | Maximum | Sample Size | Average | Maximum |
| Antimony | 78 | 0.463 | 0.990 | 75 | 0.526 | 0.960 |
| Arsenic | 88 | 1.066 | 2.400 | 85 | 0.464 | 1.300 |
| Cadmium | 84 | 0.087 | 0.450 | 85 | 0.073 | 0.300 |
| Chromium | 88 | 2.301 | 13.600 | 85 | 1.511 | 11.00 |
| Copper | 88 | 16.95 | 160.00 | 85 | 2.138 | 38.20 |
| Lead | 87 | 1.681 | 30.96 | 85 | 0.492 | 6.000 |
| Nickel | 88 | 1.634 | 4.200 | 85 | 0.982 | 2.800 |
| Selenium | 75 | 0.973 | 6.800 | 85 | 1.223 | 9.000 |
| Benzene | 22 | 0.050 | 0.050 | 21 | 0.050 | 0.050 |
| Toluene | 22 | 0.052 | 0.100 | 21 | 0.052 | 0.100 |

Table 5.5 Critical raw water concentrations for oil tar contaminants under normal operating conditions

| Contaminant | Regulated concentration (mg/L) ^a | Removal efficiency (Ro) | Transfer Factor (To) | CRWC (mg/L) |
|-------------|---|-------------------------|----------------------|-------------|
| Antimony | 0.006 | 95.0% ^c | 0.050 | 0.120 |
| Arsenic | 0.010 | 62.8% | 0.372 | 0.027 |
| Cadmium | 0.005 | 53.0% | 0.470 | 0.011 |
| Chromium | 0.05 | 41.2% | 0.588 | 0.085 |
| Copper | 1.0 | 59.0% | 0.410 | 2.437 |
| Lead | 0.01 | 86.4% | 0.136 | 0.074 |
| Nickel | 0.1 ^b | 49.9% | 0.501 | 0.199 |
| Selenium | 0.01 | 77.5% ^c | 0.225 | 0.044 |
| Benzene | 0.005 | 90.0% ^c | 0.100 | 0.050 |
| Toluene | 0.024 | 90.0% ^c | 0.100 | 0.240 |
| PAHs | 0.0002 ^b | 70.0% ^c | 0.300 | 0.001 |

^aOntario MOE MAC; ^bUSEPA MCL; ^cLiterature review results; ^dOntario MOE's DWSP

5.5.3 Quantitative Evaluation of Exceedance Probabilities of Oil Tar Contaminants

In order to better understand the risk of target contaminants, the probability of exceedance relative to CRWC was estimated for each contaminant. The first step was to select the probability distribution model for each oil tar contaminant. Numerical parameters of a statistical distribution were then estimated from a sample with method-of-moments estimators (USWRC, 1981; U.S. Army Corps of Engineers, 1994). Moments of a sample of the parent population include mean of the sample, variance, and the sample skewness (G). The skewness measures the asymmetry of the probability distribution and the skewness for a normal distribution is zero. Chow (1951) demonstrated that for many types of frequency analysis, the extreme measurement Y_p could be written in the general form as follows:

$$Y_p = \bar{Y} + k_p S$$

Where Y_p is the quantile with specified exceedance probability p ; \bar{Y} is the mean of the sample; k_p is the frequency factor which is dependent on the distribution selected, exceedance probability (P), and sometimes on skewness (G); S is the standard deviation of the data.

Normal and lognormal distributions have been widely applied to describe raw data distribution in various applications. Central tendency or normality is not typical for sample data sets which have dominating legitimate outliers. A logarithmic transformation can suppress the impacts of outliers and can better illustrate the central tendency of the data distribution. However, the lognormal distribution has limited flexibility to fit the data due to fixed skewness by two moments, i.e. the mean and standard deviation (McBean and Rovers, 1992). The t-values can be used as frequency factors for inverse normal and lognormal distributions when sample size is small.

The Log Pearson Type III (LP) distribution has been extensively used in flood frequency analysis (e.g. Rao, 1980; U.S. Army Corps of Engineers, 1994). The advantage of using the LP distribution is additional flexibility in fitting the monitoring data because the LP model incorporates the third moment of skewness (McBean and Rovers, 1992). The inverse Log Pearson type III distribution can be written as follows:

$$X_p = \bar{X} + k_p S; \quad \bar{X} = \frac{\sum X}{N}; \quad S = \left[\frac{\sum (X - \bar{X})^2}{N-1} \right]^{0.5}; \quad G = \frac{N \sum (X - \bar{X})^3}{(N-1)(N-2)S^3}$$

Where X_p is the log-transformed extreme measurement which has the potential to be equaled or exceeded with an exceedance probability P ; \bar{X} is the mean of the log-transformed data (X); G is the skewness of the log-transformed data; S is the standard deviation of the log-transformed data; N is the sample size; k_p is the Pearson frequency factor.

It is noted that the Pearson frequency factor is a function of the specified exceedance probability and the skewness of the logarithms of the sample (USWRC, 1981). In the present research, when the selected distribution model was parameterized using DWSP data sets, the frequency factor k_p could then be calculated using fixed X_p (log-transformed extreme measurement or CRWC) and the other two moments (standard deviation and mean) that were estimated from the fitted probability distribution based on DWSP data. The LP frequency factors for selected values of skewness and exceedance probability were tabulated in Bulletin 17B of the hydrology subcommittee (USWRC, 1981). The table can be used directly to estimate the exceedance probability when skewness (G) and the value of the LP frequency factor (k_p) are both fixed. The exceedance probability can be also estimated from approximating functions when necessary. For G values other than zero, the following equations can be used (U.S. Army Corps of Engineers, 1994):

$$p = \left[\frac{1}{e^{w^2}} \right]^{\frac{1}{2}}; \quad z = w - \frac{2.515517 + 0.802853w + 0.010328w^2}{1 + 1.432788w + 0.189269w^2 + 0.001308w^3}$$

$$K_T = z + z^2 k + (z^3 - 6z) \frac{k^2}{3} - (z^2 - 1)k^3 + zk^4 + \frac{k^5}{3}; \quad k = \frac{G}{6}$$

The exceedance probabilities of the raw water concentration for the target oil tar contaminants relative to their CRWCs are summarized in Table 5.6. Benzene, toluene, and the PAHs have been removed from this analysis as their concentrations are too close to their detection limits to be meaningful (or are below their detection limits).

Table 5.6 Exceedance probabilities of raw water concentration for oil tar contaminants

| Contaminant | Sample Size | Mean | Standard Deviation | Skewness | Frequency factor | Exceedance probability |
|-------------|-------------|----------|--------------------|----------|------------------|------------------------|
| Antimony | 78 | -0.37046 | 0.18246 | -0.3 | 13.42540 | <0.0001 |
| Arsenic | 88 | -0.00366 | 0.19448 | -3.3 | 7.36980 | <0.0001 |
| Cadmium | 84 | -1.20285 | 0.36692 | 0.3 | 6.07660 | <0.0001 |
| Chromium | 88 | 0.17177 | 0.40690 | 0.1 | 4.32084 | <0.0001 |
| Copper | 88 | 0.59132 | 0.62836 | 1.5 | 4.44892 | 0.0037 |
| Lead | 87 | -0.10651 | 0.55834 | -0.3 | 3.53574 | <0.0001 |
| Nickel | 88 | 0.11472 | 0.32991 | -0.9 | 6.62326 | <0.0001 |
| Selenium | 75 | -0.01098 | 0.23289 | 0.0 | 7.12277 | <0.0001 |

According to Table 5.6, copper has the highest exceedance probability (0.0037), making it the most likely of the targeted contaminants to have an impact on the quality of drinking water. All other oil tar contaminants have exceedance probabilities below 0.0001. Therefore, if the utility is concerned about regulated oil tar contaminants, copper is the one that the Elgin Area WTP should monitor. Even so, the exceedance probability at 0.37% is extremely low.

5.6 Potential Treatment Alternatives

5.6.1 Evaluation of Treatment Alternatives

5.6.1.1 Treatment Efficiency Evaluation

The ability of a drinking-water supply system to treat contaminants to achieve specific guidelines depends on the contaminant concentration in raw water, control measures employed throughout the drinking-water system, nature of the raw water, and treatment processes already installed (WHO, 2008). Therefore, from a system perspective, treatment alternatives which can remove a broader range of oil tar contaminants are favored as they increase the robustness of treatment processes. This consideration is also important for the selection of treatment alternative(s) for the Elgin Area WTP to control contaminants that cannot be removed through current conventional processes. In the unlikely event that oil tar contaminant concentrations were to increase at some point in time, effective treatment

alternatives which are not available in the Elgin Area WTP are summarized in Table 5.7 which is based on Table 5.2:

Table 5.7 Summary of potential alternatives for consideration at the Elgin Area WTP

| | A | AA | AOPs | GAC | IX | MO | O ₃ | PS | UF | NF | RO |
|-----------------|---|----|------|-----|----|----|----------------|----|----|----|----|
| Antimony | | | | | | ● | | | | | ● |
| Arsenic | | ● | | | ● | | ● | ● | ● | ● | ● |
| Cadmium | | | | | ● | | | ● | | ● | ● |
| Chromium | | ● | | ● | | | | | ● | ● | ● |
| Copper | | ● | | ● | ● | | | | | ● | ● |
| Lead | | ● | | ● | ● | ● | | | | | ● |
| Nickel | | | | ● | ● | | | | | | ● |
| Selenium | | | | ● | ● | | | | | ● | ● |
| Benzene | ● | | ● | ● | | | ● | | | | |
| Toluene | ● | | ● | | | | ● | | | | |
| PAHs | | | ● | ● | | | | | | | |

A: aeration; AA: activated alumina; AOPs: advanced oxidation processes; GAC: granular activated carbon; MO: metal oxides; IX: ion exchange; NF: nanofiltration; O₃: ozonation; PS: precipitation softening; RO: reverse osmosis; UF: ultrafiltration

Group I and II contaminants are in bold

Symbols are as follows:

● 80% or more removal

No entry: no data available

5.6.1.2 Treatment Cost Evaluation

Along with treatment efficiency, treatment cost (capital, operating, and maintenance) is another fundamental issue when selecting and implementing a treatment alternative. Cost mainly depends on the technical complexity of any additional treatment or other control measures required as well as local costs for labor, chemical, electricity, waste disposal, civil and mechanical works (Mancini et al., 2005; WHO, 2008). Therefore, a general quantitative evaluation of the treatment costs is difficult to provide.

However, the WHO (2008) has qualitatively ranked treatment processes based on their degree of technical complexity in terms of maintenance and/or operation. A more

complicated process is considered to be associated with higher costs (WHO, 2008). However, the qualitative evaluation by WHO (2008) does not include activated alumina, metal oxide adsorption, and precipitation softening, which have been demonstrated at bench and pilot scale levels to be promising treatment alternatives for oil tar contaminants. As adsorptive technologies, activated alumina and metal oxide adsorption can be considered to have similar operation and maintenance features to activated carbon, for the level of quantitation required for the present comparison. The USEPA (2000) also indicates that activated alumina has relatively higher capital, operation, and maintenance costs compared to coagulation. Hence, it could potentially be ranked within the same group as activated carbon. Precipitation softening has similar capital, operation, and maintenance costs compared to chemical coagulation (USEPA, 2000) and hence can be ranked in Group 2. The ranking of complexity and cost of water alternatives is summarized in Table 5.8.

Table 5.8 Ranking of complexity and cost of water treatment processes

(adapted from WHO, 2008)

| Ranking* | Treatment Processes |
|-----------------|---|
| 1 | Simple chlorination; plain filtration (rapid sand, slow sand) |
| 2 | Pre-chlorination plus filtration; aeration |
| 3 | Chemical coagulation, process optimization for control of DBPs |
| 4 | Granular activated carbon (GAC); activated alumina; metal oxide; ion exchange |
| 5 | Ozonation |
| 6 | Advanced oxidation processes; membrane treatment (nanofiltration, ultrafiltration, reverse osmosis) |

*Higher number indicates more complexity and higher cost.

5.6.1.3 Cost-effectiveness Evaluation Using a Point System

A point system was developed to evaluate the cost-effectiveness of treatment alternatives and a Cost-Effectiveness Factor (CEF) was assigned to each treatment alternative. The CEF is rated according to costs and effectiveness of each alternative, which are two fundamental issues of technique selection for a drinking water treatment plant. In this research, they are considered to have equivalent importance. Cost factor (CF) and effectiveness factor (EF)

were assigned to each alternative, respectively. CEF can be calculated as the sum of CF and EF.

The cost factor is mainly determined based on the ranking of each alternative in Table 5.8. Alternatives ranked in Group 1 receive a maximum score of 6 and alternatives in Group 6 receive a minimum score of 1. Other groups of alternatives receive a score with respect to their ranking (Group 2 – 5, Group 3 – 4, Group 4 – 3; Group 5 - 2).

The effectiveness factor is determined based on treatment efficiency and treatment universality. Alternatives which can remove Group I and II contaminants in Table 2.5 receive a score of 1 for each contaminant. Comparatively, a treatment alternative which can remove one Group III contaminant or has a removal efficiency below 80%, receives a score of 0.5 for each contaminant. The alternative that can effectively remove copper with highest exceedance probability receives an additional 1 score based on the fact that this is the contaminant which was previously determined most likely to be problematic for this utility. The cost-effectiveness factors of each alternative are summarized and ranked in Table 5.9. Technologies with the highest CEFs should be given priority consideration.

Table 5.9 Ranking of treatment alternatives cost-effectiveness factors

| | GAC | IX | RO | AA | A | MO | NF | UF | O₃ | AOPs | PS |
|------------|------------|-----------|-----------|-----------|----------|-----------|-----------|-----------|----------------------|-------------|-----------|
| CF | 3 | 3 | 1 | 3 | 5 | 3 | 1 | 1 | 2 | 1 | 1 |
| EF | 6 | 5 | 7 | 3.5 | 1.5 | 3 | 4 | 2 | 1.5 | 2.5 | 2 |
| Cu | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| CEF | 10 | 9 | 9 | 7.5 | 6.5 | 6 | 6 | 4 | 3.5 | 3.5 | 3 |

A: aeration; AA: activated alumina; AOPs: advanced oxidation processes; GAC: granular activated carbon; MO: metal oxides; IX: ion exchange; NF: nanofiltration; O₃: ozonation; PS: precipitation softening; RO: reverse osmosis; UF: ultrafiltration

5.6.2 Treatment Alternative Recommendations

According to Table 5.9, granular activated carbon, reverse osmosis, and ion exchange are the three most cost-effective alternatives which can remove a wide range of contaminants and increase the robustness of current treatment processes in the Elgin Area WTP. GAC adsorption received the highest CFF score (10) and can effectively remove copper. The

implementation of a GAC process would represent the easiest process addition to a conventional treatment plant. If sufficient contact time could be achieved, GAC could potentially be applied as a cap substituting for anthracite in conventional filters. Therefore, GAC is considered to be the most suitable alternative for Elgin Area WTP with respect to dealing with the target heavy metals and PAHs.

5.7 Conclusions

In this chapter, the oil tar contaminant list was further condensed based on degree of health impact and exposure probability. Potential treatment techniques with detailed information on experiment conditions and removal efficiencies were identified and summarized for regulated contaminants. The treatment potential for oil tar contaminants within the Elgin Area WTP was qualitatively and quantitatively evaluated. Qualitative evaluation results demonstrated that the current Elgin Area WTP configuration is sufficiently effective with respect to the oil tar contaminants investigated in this study to ensure the safety of drinking water. To quantitatively evaluate the risk of breakthrough of oil tar contaminants, critical raw water concentrations and their exceedance probabilities were calculated, respectively. Copper was found to be the contaminant with the highest exceedance probability at 0.4%. Other treatment alternatives for heavy metals and PAHs which are not currently in use within the Elgin Area WTP were qualitatively evaluated based on their cost-effectiveness. Ultimately, granular activated carbon was identified as the most suitable technique to be considered for installation in the plant in order to deal with heavy metals and PAHs and contribute to the overall robustness of the currently available treatment processes.

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

In this study, potential adverse impacts of oil/coal tar contaminated sediments on the intake protection zones (IPZs) of the Elgin Area Water Treatment Plant (WTP) were evaluated through a literature review and a fingerprint analysis of leachate contaminants (FALCON) analysis. The effectiveness of conventional treatment processes currently available within the Elgin Area WTP in removing heavy metals and PAHs was also assessed using the concepts of critical raw water concentration (CRWC) and exceedance probability. Several conclusions can be drawn for oil tar contaminants and the Elgin Area WTP.

6.1.1 Conclusions for Site Characterization and Contaminant Identification

For contamination site characterization, the site history was comprehensively reviewed and the main industrial processes formerly on the site were identified. According to historical monitoring data from various compartments including soil, sediment, groundwater, and surface water, the composition of oil tar contaminated sediments was determined and classified. The main conclusions are as follows:

1. Evidence of both oil and coal gasification processes was found on the Port Stanley gasification complex site. The gasification wastes were comprised mainly of heavy metals and polycyclic aromatic hydrocarbons (PAHs). Those present in the intake protection zones and their maximum acceptable concentrations/maximum contaminant levels were reported (Table 3.10).
2. The identified oil/coal tar contaminants were classified according to their varying degrees of human health effects. The detailed results are illustrated in Table 3.19(a).

6.1.2 Conclusions for FALCON Analysis

The FALCON analysis was applied to identify the contribution of the oil tar contaminated sediments from Kettle Creek to detected contaminants within the drinking water intake protection zones and to track the migration pathway of those sediments. The following

conclusions can be drawn with respect to conducting a FALCON analysis on sediment data in Kettle Creek and Lake Erie.

1. FALCON provided valuable information regarding contaminant characterization, source attribution, and transport within a surface water context without the need for knowledge of local hydrodynamic conditions potentially reducing reliance on complicated hydrodynamic analysis (e.g. modelling and simulation).
2. This fingerprint analysis could potentially be used to help delineate drinking water intake protection zones, not only for the contaminants discussed herein but for others which are resistant to chemical and microbial degradation. It may also be possible under some circumstances to use common water constituents (e.g. chloride, sulfate, calcium, sodium, nitrate, etc.) which may be present in different ratios in intersecting water courses as opposed to the contaminants of concern if data are lacking for those.
3. The fingerprint of the oil/coal tar contaminated sediment was distinguishable from those from other potential contamination sources including an upstream Kettle Creek site, an upwind/up current site to the west in Lake Erie, and the Little River site to the east.
4. Sediment from the identified point source was responsible for local PAH and heavy metal contamination inside and outside Port Stanley Harbour.
5. While contaminated sediments are generally dispersing in intake protection zone-2, they appear to be moving to the east and south through the prevailing Lake Erie littoral drift and mixing of sediment.
6. The high correlation between sediment collected in the drinking water intake and the point source fingerprint indicates that some contaminated sediments have reached the drinking water intake. However, the correlation has been decreasing in intake sediments since the contaminated site remediation. Drinking Water Surveillance Program data indicate that heavy metals and PAHs have not been detected above any existing Ontario regulatory Maximum Acceptable Concentrations in treated drinking water from this source.

6.1.3 Conclusions for Evaluation of Treatment Processes in Elgin Area WTP

The oil tar contaminant list was condensed based on the potential for health impacts and exposure probability. The existing conventional treatment processes and other techniques were qualitatively and quantitatively evaluated to ensure the safety of drinking water from the Elgin Area WTP. The following conclusions can be drawn with respect to the evaluation of currently available processes in the Elgin Area WTP.

1. Iron, vanadium, zinc, phenol and some PAHs were removed from the final contaminant list due to their low toxicity and exposure probability.
2. The current Elgin Area Water Treatment Plant configuration is capable of removing oil tar contaminants at the concentrations observed in this study such that the safety of drinking water is ensured.
3. Copper was found to be the contaminant with the highest probability of exceeding the critical raw water concentration.
4. Granular activated carbon (GAC) is the most cost-effective of the alternative techniques examined for heavy metals and PAHs. As such it is the most appropriate technique to be considered for implementation in the plant in order to improve the robustness of the currently available treatment processes.

6.2 Recommendations

6.2.1 Recommendations for a Monitoring Program within Elgin Area WTP Intake

According to surface water monitoring results within intake protection zones, the raw water concentrations of oil/coal tar contaminants are not sufficiently high to pose any adverse impacts on human health. Furthermore, the sediment sampling results from Kettle Creek also indicate that the contamination due to oil/coal tar has been successfully controlled through a series of *in situ* remediation projects. However, the leakage of oil tar wastes into Kettle Creek occurred for an undetermined period of time before the site remediation was conducted. There are uncertain amounts of contaminants bound to the deeply buried sediments. Extreme events such as floods could potentially re-suspend those buried sediments and transport oil/coal tar contaminants into the water phase. The FALCON analysis demonstrated that oil

tar contaminated sediments if present, will eventually move toward the drinking water intake. Therefore, it would be prudent to periodically monitor the sediment quality within Kettle Creek and Intake Protection Zone 1. A more practical and cost-effective alternative would be to periodically monitor and track any heavy metals or PAHs which appear above detection limits in raw water.

6.2.2 Recommendations for Elgin Area WTP

Even though literature review results show that copper is found to be refractory to conventional treatment processes, it will not likely pose any health concerns due to its low toxicity and low probability of exceeding its critical raw water concentration. Therefore, the existing conventional treatment processes within Elgin Area WTP are concluded to be sufficient for the removal of oil tar contaminants to ensure the quality of drinking water. However, in the event that oil tar contaminants were released from deeply buried sediments, granular activated carbon (GAC), which has the highest cost-effectiveness and can effectively remove chromium, is recommended for consideration at the Elgin Area WTP to enhance the robustness of the current treatment processes in Elgin Area WTP.

6.3 Future Work

The probability of oil tar contaminants appearing in drinking water in excess of drinking water guidelines/regulations for the existing treatment system within Elgin Area WTP were evaluated in Chapter 5. It should be noted that these exceedance probabilities were calculated based on information obtained under normal operating conditions (nominal mode) of the plant. That is, mechanical and operational failures within the plant were not considered in the analysis. However, at the concentrations encountered in this instance, health risks from these contaminants are not acute, as in the case of pathogens, and require long term exposure to be of health concern. Due to the scarcity of historical knowledge of non-optimal operation in the plant, a comprehensive risk analysis of Elgin Area WTP was beyond the scope of this study but it may be worthy of consideration.

To conduct a comprehensive water treatment plant risk analysis, failure mode and effect and criticality analysis (FMECA) could potentially be applied to identify a variety of

potential treatment unit failure modes x_i ($i = 1 \dots n$) and determine the corresponding parameters. Then, an appropriate risk analysis technique could be selected based on a set of selection criteria relating to the adaptability of the method to drinking water treatment systems and case specifics. The selected technique should be capable of:

- conducting quantitative evaluation of the risk
- assessing the uncertainty of the analysis
- modeling the inherent interactions (e.g. redundancy) within the treatment system
- diagnosing causes and potential mitigation measures for system failure

According to the above selection criteria, fault tree analysis (FTA) is considered to be the most appropriate technique to construct an integrated and probabilistic risk evaluation system due to its logical, systematic, and comprehensive characteristics. Failure mode and effect and criticality analysis (FMECA) is usually conducted as a precursor of fault tree analysis. Through the FMECA procedure, a failure mode list can be generated and the probability of a deviation from the nominal mode as well as reduced removal efficiencies can also be estimated. Then, the parameters obtained through FMECA procedure could be used as input data to fault tree analysis.

The fault tree is quantified through calculating the probabilities of the top event using probabilities of basic events and their corresponding logic gates. The probabilities of basic events can be obtained through statistical estimation and expert judgment. The limited availability of historical information is always the biggest challenge for probability estimation. The dominant basic events which are main contributors to the top event probability can be also identified through FT quantifying procedure. This can help prioritize the major failure causes when selecting risk mitigation measures and achieve the overall optimization of risk reduction options.

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Appendix A

Distribution of Sediment and Soil Sampling Locations

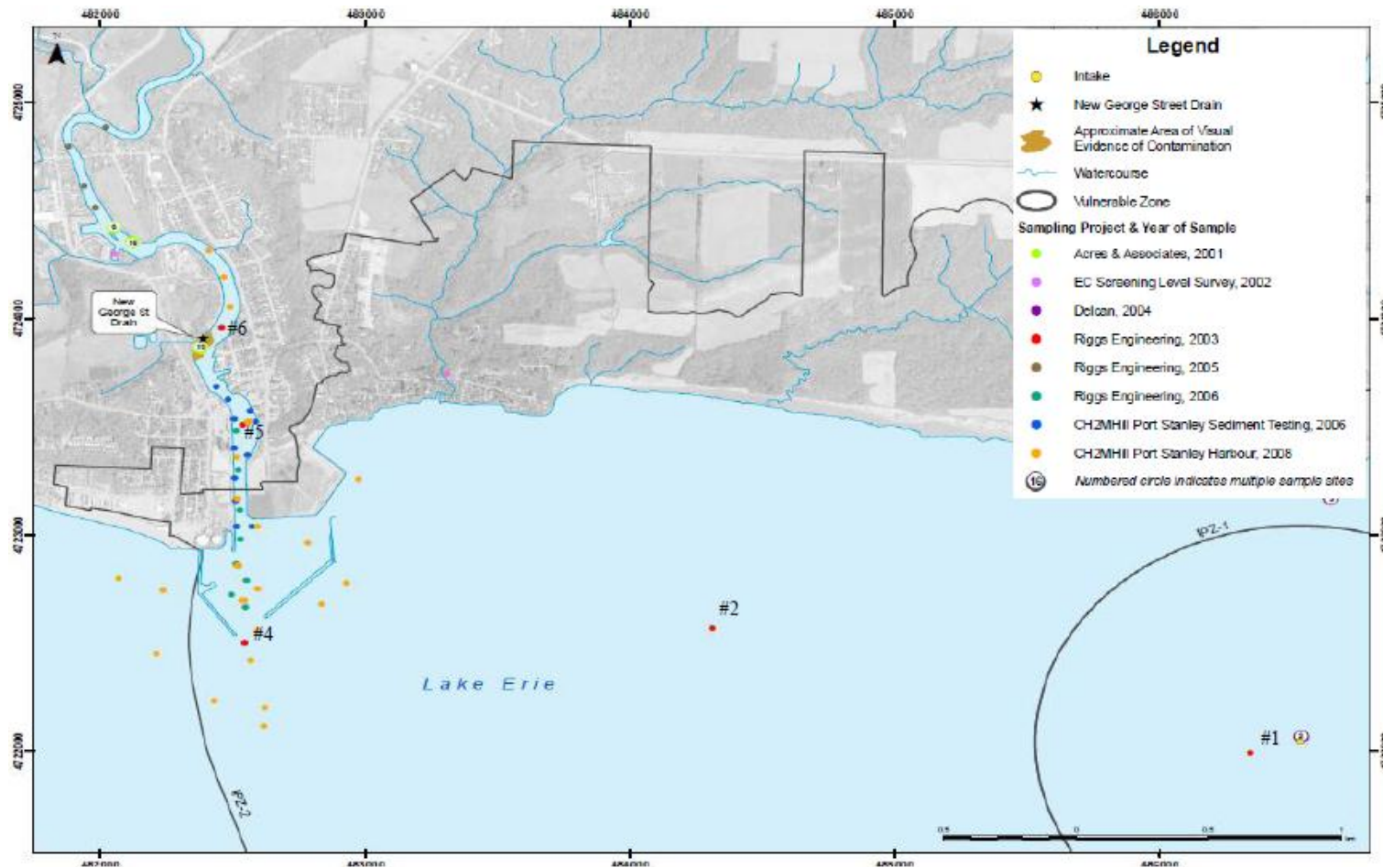


Figure A.1 Distribution of sediment sampling locations (Stantec Consulting Ltd., 2009a)

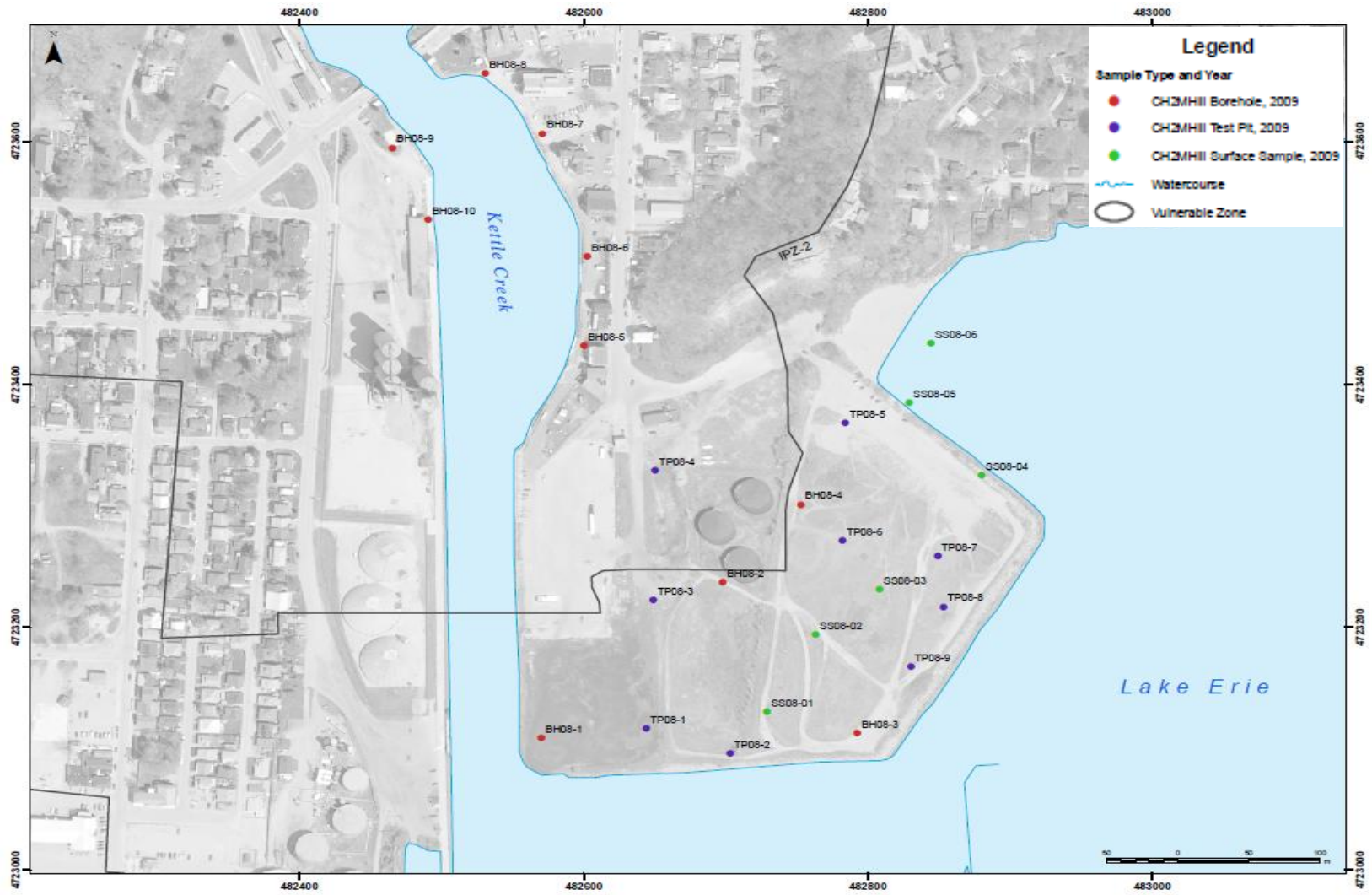


Figure A.2 Distribution of soil sampling locations (Stantec Consulting Ltd., 2009a)

Appendix B

Ontario MOE Guidelines

Table B.1 Ontario Drinking water Quality Standards, Objectives and Guidelines – Chemical Standards (Ontario MOE, 2006a)

| PARAMETER | MAC (mg/L) | IMAC (mg/L) |
|--------------------------------------|------------|-------------|
| Alachlor | | 0.005 |
| Aldicarb | 0.009 | |
| Aldrin + Dieldrin | 0.0007 | |
| Antimony | | 0.006 |
| Arsenic | | 0.025 |
| Atrazine + N-dealkylated metabolites | | 0.005 |
| Azinphos-methyl | 0.02 | |
| Barium | 1 | |
| Bendiocarb | 0.04 | |
| Benzene | 0.005 | |
| Benzo(a)pyrene | 0.00001 | |
| Boron | | 5 |
| Bromate | | 0.01 |
| Bromoxynil | | 0.005 |
| Cadmium | 0.005 | |
| Carbaryl | 0.09 | |
| Carbofuran | 0.09 | |
| Carbon Tetrachloride | 0.005 | |
| Chloramines | 3 | |
| Chlordane (Total) | 0.007 | |
| Chlorpyrifos | 0.09 | |
| Chromium | 0.05 | |
| Cyanazine | | 0.01 |
| Cyanide(free) | 0.2 | |
| Diazinon | 0.02 | |
| Dicamba | 0.12 | |
| 1,2-Dichlorobenzene | 0.2 | |

Table B.1 (Continued)

| PARAMETER | MAC (mg/L) | IMAC (mg/L) |
|---|-------------------|--------------------------|
| 1,4-Dichlorobenzene | 0.005 | |
| Dichlorodiphenyltrichloroethane (DDT) + metabolites | 0.03 | |
| 1,2-Dichloroethane | | 0.005 |
| 1,1-Dichloroethylene(vinylidene chloride) | 0.014 | |
| Dichloromethane | 0.05 | |
| 2,4-Dichlorophenol | 0.9 | |
| 2,4-Dichlorophenoxy acetic acid(2,4-D) | | 0.1 |
| Diclofop-methyl | 0.009 | |
| Dimethoate | | 0.02 |
| Dinoseb | 0.01 | |
| Dioxin and Furan | | 0.000000015 ^a |
| Diquat | 0.07 | |
| Diuron | 0.15 | |
| Fluoride | 1.5 ^b | |
| Glyphosate | | 0.28 |
| Heptachlor + Heptachlor Epoxide | 0.003 | |
| Lead | 0.01 ^c | |
| Lindane (Total) | 0.004 | |
| Malathion | 0.19 | |
| Mercury | 0.001 | |
| Methoxychlor | 0.9 | |
| Metolachlor | | 0.05 |
| Metribuzin | 0.08 | |
| Microcystin-LR | 0.0015 | |
| Monochlorobenzene | 0.08 | |
| Nitrate (as nitrogen) | 10.0 ^d | |
| Nitrite (as nitrogen) | 1.0 ^d | |
| Nitrate + Nitrite (as nitrogen) | 10.0 ^d | |
| Nitrilotriacetic Acid (NTA) | 0.4 | |
| N-Nitrosodimethylamine (NDMA) | | 0.000009 |
| Paraquat | | 0.01 |
| Parathion | 0.05 | |
| Pentachlorophenol | 0.06 | |

Table B.1 (Continued)

| PARAMETER | MAC (mg/L) | IMAC (mg/L) |
|--|--------------------|-------------|
| Phorate | | 0.002 |
| Picloram | | 0.19 |
| Polychlorinated Biphenyls (PCB) | | 0.003 |
| Prometryne | | 0.001 |
| Selenium | 0.01 | |
| Simazine | | 0.01 |
| Temephos | | 0.28 |
| Terbufos | | 0.001 |
| Tetrachloroethylene (perchloroethylene) | 0.03 | |
| 2,3,4,6-Tetrachlorophenol | 0.1 | |
| Triallate | 0.23 | |
| Trichloroethylene | 0.005 | |
| 2,4,6-Trichlorophenol | 0.005 | |
| 2,4,5-Trichlorophenoxy acetic acid (2,4,5-T) | 0.28 | |
| Trifluralin | | 0.045 |
| Trihalomethanes | 0.100 ^e | |
| Uranium | 0.02 | |
| Vinyl Chloride | 0.002 | |

Short forms:

mg/L - milligrams per litre

Footnotes:

- a) Total toxic equivalents when compared with 2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin).
- b) Where fluoride is added to drinking water, it is recommended that the concentration be adjusted to 0.5 -0.8 mg/L the optimum level for control of tooth decay. Where supplies contain naturally occurring fluoride at levels higher than 1.5 mg/L but less than 2.4 mg/L the Ministry of Health and Long Term Care recommends an approach through local boards of health to raise public and professional awareness to control excessive exposure to fluoride from other sources.
- c) This standard applies to water at the point of consumption. Since lead is a component in some plumbing systems, first flush water may contain higher concentrations of lead than water that has been flushed for five minutes.
- d) Where both nitrate and nitrite are present, the total of the two should not exceed 10 mg/L (as nitrogen).
- e) This standard is expressed as a running annual average of quarterly samples measured at point reflecting the maximum residence time in the distribution system.

Table B.2 Ontario Drinking water Quality Standards, Objectives and Guidelines – Objectives and Guidelines (Ontario MOE, 2006a)

| PARAMETER | AO (mg/L - unless otherwise specified) | OG (mg/L - unless otherwise specified) |
|---|---|---|
| 1,2-Dichlorobenzene | 0.003 ^a | |
| 1,4-Dichlorobenzene | 0.001 ^a | |
| 2,4-Dichlorophenol | 0.0003 ^a | |
| 2,3,4,6-Tetrachlorophenol | 0.001 ^a | |
| 2,4,6-Trichlorophenol | 0.002 ^a | |
| 2,4,5-Trichlorophenoxy acetic acid (2,4,5-T) | 0.02 ^a | |
| Alkalinity (as CaCO ₃) | | 30-500 |
| Aluminum | | 0.1 |
| Chloride | 250 | |
| Colour | 5 TCU | |
| Copper | 1 | |
| Dissolved Organic Carbon | 5 | |
| Ethylbenzene | 0.0024 | |
| Hardness (as CaCO ₃) | | 80-100 |
| Heterotrophic Plate Count (HPC)- General bacteria population expressed as colony counts on a heterotrophic plate count | | f |
| Iron | 0.3 | |
| Manganese | 0.05 | |
| Methane | 3L/ m ³ | |
| Monochlorobenzene | 0.03 ^a | |
| Odour | Inoffensive | |

Table B.2 (Continued)

| PARAMETER | AO (mg/L - unless otherwise specified) | OG (mg/L - unless otherwise specified) |
|------------------------|---|---|
| Organic Nitrogen | | 0.15 |
| pH | | 6.5-8.5 (no units) |
| Pentachlorophenol | 0.03 ^a | |
| Sodium | b | |
| Sulphate | 500 ^c | |
| Sulphide | 0.05 | |
| Taste | Inoffensive | |
| Temperature | 15 ^o C | |
| Toluene | 0.024 | |
| Total Dissolved Solids | 500 | |
| Turbidity | 5 NTU ^d | e |
| Xylenes | 0.3 | |
| Zinc | 5 | |

Short Forms:

NTU - Nephelometric Turbidity unit

Footnotes:

- a) Refer to Table 2 for standard
- b) The aesthetic objective for sodium in drinking water is 200 mg/L. The local Medical Officer of Health should be notified when the sodium concentration exceeds 20 mg/L so that this information may be communicated to local physicians for their use with patients on sodium restricted diets
- c) When sulphate levels exceed 500 mg/L, water may have a laxative effect on some people
- d) Applicable for all waters at the point of consumption.
- e) The Operational Guidelines for filtration processes are provided as performance criteria in the Procedure for Disinfection of Drinking Water in Ontario.
- f) Increases in HPC concentrations above baseline levels are considered undesirable.

Appendix C

Health Canada Guidelines

Table C.1 Guidelines for chemical and physical parameters
(FPT Committee on Drinking Water, 2008)

| Parameter | MAC (mg/L) | AO [or OG] (mg/L) | Year of approval (or reaffirmation) |
|-----------------------------|---------------|-------------------------|--|
| Aldicarb | 0.009 | | 1994 |
| Aldrin + dieldrin | 0.0007 | | 1994 |
| Aluminum ^a | | [0.1/0.2] | 1998 |
| *Antimony ^b | 0.006 | | 1997 |
| Arsenic | 0.010 | | 2006 |
| *Atrazine + metabolites | 0.005 | | 1993 |
| Azinphos-methyl | 0.02 | | 1989 (2005) |
| Barium | 1 | | 1990 |
| Bendiocarb | 0.04 | | 1990 (2005) |
| Benzene | 0.005 | | 1986 |
| Benzo[a]pyrene | 0.00001 | | 1988 (2005) |
| *Boron | 5 | | 1990 |
| *Bromate | 0.01 | | 1998 |
| Bromodichloromethane (BDCM) | 0.016 | | 2006 |
| *Bromoxynil | 0.005 | | 1989 (2005) |
| Cadmium | 0.005 | | 1986 (2005) |
| Carbaryl | 0.09 | | 1991 (2005) |
| Carbofuran | 0.09 | | 1991 (2005) |
| Carbon tetrachloride | 0.005 | | 1986 |
| Chloramines—total | 3 | | 1995 |
| Chlorate | 1.0 | | 2008 |
| Chloride | | ≤250 | 1979 (2005) |
| Chlorite | 1.0 | | 2008 |
| Chlorpyrifos | 0.09 | | 1986 |
| Chromium | 0.05 | | 1986 |
| Colour ^d | | ≤15 TCU | 1979 (2005) |

Table C.1 (Continued)

| Parameter | MAC (mg/L) | AO [or OG] (mg/L) | Year of approval (or reaffirmation) |
|---|---------------|-------------------------|--|
| Copper ^b | | ≤1.0 | 1992 |
| *Cyanazine | 0.01 | | 1986 (2005) |
| Cyanide | 0.2 | | 1991 |
| Cyanobacterial toxins–Microcystin-LR ^c | 0.0015 | | 2002 |
| Diazinon | 0.02 | | 1986 (2005) |
| Dicamba | 0.12 | | 1987 (2005) |
| 1,2-Dichlorobenzene ^e | 0.2 | ≤0.003 | 1987 |
| 1,4-Dichlorobenzene ^e | 0.005 | ≤0.001 | 1987 |
| *1,2-Dichloroethane | 0.005 | | 1987 |
| 1,1-Dichloroethylene | 0.014 | | 1994 |
| Dichloromethane | 0.05 | | 1987 |
| 2,4-Dichlorophenol. | 0.9 | ≤0.0003 | 1987 (2005) |
| *2,4-Dichlorophenoxyacetic acid (2,4 -D) | 0.1 | | 1991 |
| Diclofop-methyl | 0.009 | | 1987 (2005) |
| *Dimethoate | 0.02 | | 1986 (2005) |
| Dinoseb | 0.01 | | 1991 |
| Diquat | 0.07 | | 1986 (2005) |
| Diuron | 0.15 | | 1987 (2005) |
| Ethylbenzene | | ≤0.0024 | 1986 (2005) |
| Fluoride | 1.5 | | 1996 |
| *Glyphosate | 0.28 | | 1987 (2005) |
| Haloacetic Acids–Total (HAAs) | 0.080 | | 2008 |
| Iron | | ≤0.3 | 1978 (2005) |
| Lead ^b | 0.01 | | 1992 |
| Malathion | 0.19 | | 1986 (2005) |
| Manganese | | ≤0.05 | 1987 |
| Mercury | 0.001 | | 1986 |
| Methoxychlor | 0.9 | | 1986 (2005) |
| Methyl tertiary-butyl ether (MTBE) | | 0.015 | 2006 |
| *Metolachlor | 0.05 | | 1986 |
| Metribuzin | 0.08 | | 1986 (2005) |
| Monochlorobenzene | 0.08 | ≤0.03 | 1987 |
| Nitrate ^f | 45 | | 1987 |
| Nitritotriacetic acid (NTA) | 0.4 | | 1990 |
| Odour | | Inoffensive | 1979 (2005) |

Table C.1 (Continued)

| Parameter | MAC (mg/L) | AO [or OG] (mg/L) | Year of approval (or reaffirmation) |
|---|---------------|-------------------------|--|
| *Paraquat (as dichloride) ^g | 0.01 | | 1986 (2005) |
| Parathion | 0.05 | | 1986 |
| Pentachlorophenol | 0.06 | ≤0.030 | 1987 (2005) |
| pH ^h | | 6.5–8.5 | 1995 |
| Phorate | 0.002 | | 1986 (2005) |
| *Picloram | 0.19 | | 1988 (2005) |
| Selenium | 0.01 | | 1992 |
| *Simazine | 0.01 | | 1986 |
| Sodium ⁱ | | ≤200 | 1992 |
| Sulphate ^j | | ≤500 | 1994 |
| Sulphide (as H ₂ S) | | ≤0.05 | 1992 |
| Taste | | Inoffensive | 1979 (2005) |
| Temperature | | ≤15°C | 1979 (2005) |
| *Terbufos | 0.001 | | 1987 (2005) |
| Tetrachloroethylene | 0.03 | | 1995 |
| 2,3,4,6-Tetrachlorophenol | 0.1 | ≤0.001 | 1987 (2005) |
| Toluene | | ≤0.024 | 1986 (2005) |
| Total dissolved solids (TDS) | | ≤500 | 1991 |
| Trichloroethylene | 0.005 | | 2005 |
| 2,4,6-Trichlorophenol | 0.005 | ≤0.002 | 1987 (2005) |
| *Trifluralin | 0.045 | | 1989 (2005) |
| Trihalomethanes-total (THMs) ^k | 0.100 | | 2006 |
| Turbidity ^l | | | 2004 |
| *Uranium | 0.02 | | 1999 |
| Vinyl chloride | 0.002 | | 1992 |
| Xylenes—total | | ≤0.3 | 1986 (2005) |
| Zinc ^b | | ≤5.0 | 1979 (2005) |

Appendix D

USEPA Guidelines

Table D.1 National primary drinking water regulations (USEPA, 2009)

| Contaminant | MCL or TT* (mg/L) [†] | Potential health effects from long-term [‡] exposure above the MCL | Common sources of contaminant in drinking water | Public Health Goal (mg/L) [‡] |
|--|----------------------------------|---|---|--|
| OC Acrylamide | TT* | Nervous system or blood problems; increased risk of cancer | Added to water during sewage/wastewater treatment | zero |
| OC Alachlor | 0.002 | Eye, liver, kidney or spleen problems; anemia; increased risk of cancer | Runoff from herbicide used on row crops | zero |
| R Alpha photon emitters | 15 picocuries per Liter (pCi/L) | Increased risk of cancer | Erosion of natural deposits of certain minerals that are radioactive and may emit a form of radiation known as alpha radiation | zero |
| IOC Antimony | 0.006 | Increase in blood cholesterol; decrease in blood sugar | Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder | 0.006 |
| IOC Arsenic | 0.010 | Skin damage or problems with circulatory systems, and may have increased risk of getting cancer | Erosion of natural deposits; runoff from orchards; runoff from glass & electronics production wastes | 0 |
| IOC Asbestos (fibers >10 micrometers) | 7 million fibers per Liter (MFL) | Increased risk of developing benign intestinal polyps | Decay of asbestos cement in water mains; erosion of natural deposits | 7 MFL |
| OC Atrazine | 0.003 | Cardiovascular system or reproductive problems | Runoff from herbicide used on row crops | 0.003 |
| IOC Barium | 2 | Increase in blood pressure | Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits | 2 |
| OC Benzene | 0.005 | Anemia; decrease in blood platelets; increased risk of cancer | Discharge from factories; leaching from gas storage tanks and landfills | zero |
| OC Benzo(a)pyrene (PAHs) | 0.0002 | Reproductive difficulties; increased risk of cancer | Leaching from linings of water storage tanks and distribution lines | zero |
| IOC Beryllium | 0.004 | Intestinal lesions | Discharge from metal refineries and coal-burning factories; discharge from electrical, aerospace, and defense industries | 0.004 |
| R Beta photon emitters | 4 millirems per year | Increased risk of cancer | Decay of natural and man-made deposits of certain minerals that are radioactive and may emit forms of radiation known as photons and beta radiation | zero |
| DBP Bromate | 0.010 | Increased risk of cancer | Byproduct of drinking water disinfection | zero |
| IOC Cadmium | 0.005 | Kidney damage | Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints | 0.005 |
| OC Carbofuran | 0.04 | Problems with blood, nervous system, or reproductive system | Leaching of soil fumigant used on rice and alfalfa | 0.04 |
| OC Carbon tetrachloride | 0.005 | Liver problems; increased risk of cancer | Discharge from chemical plants and other industrial activities | zero |
| D Chloramines (as Cl ₂) | MRDL=4.0 [§] | Eye/nose irritation; stomach discomfort; anemia | Water additive used to control microbes | MRDLG=4 [§] |
| OC Chlordane | 0.002 | Liver or nervous system problems; increased risk of cancer | Residue of banned termiticide | zero |
| D Chlorine (as Cl ₂) | MRDL=4.0 [§] | Eye/nose irritation; stomach discomfort | Water additive used to control microbes | MRDLG=4 [§] |
| D Chlorine dioxide (as ClO ₂) | MRDL=0.8 [§] | Anemia; infants, young children, and fetuses of pregnant women: nervous system effects | Water additive used to control microbes | MRDLG=0.8 [§] |
| DBP Chlorite | 1.0 | Anemia; infants, young children, and fetuses of pregnant women: nervous system effects | Byproduct of drinking water disinfection | 0.8 |
| OC Chlorobenzene | 0.1 | Liver or kidney problems | Discharge from chemical and agricultural chemical factories | 0.1 |
| IOC Chromium (total) | 0.1 | Allergic dermatitis | Discharge from steel and pulp mills; erosion of natural deposits | 0.1 |
| IOC Copper | TT*; Action Level = 1.3 | Short-term exposure: Gastrointestinal distress. Long-term exposure: Liver or kidney damage. People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level | Corrosion of household plumbing systems; erosion of natural deposits | 1.3 |
| M Cryptosporidium | TT* | Short-term exposure: Gastrointestinal illness (e.g., diarrhea, vomiting, cramps) | Human and animal fecal waste | zero |

LEGEND

| | | |
|-----------------------------------|-------------------------------|----------------------------|
| D Disinfectant | IOC Inorganic Chemical | OC Organic Chemical |
| DBP Disinfection Byproduct | M Microorganism | R Radionuclides |

| Contaminant | MCL or TT ^a (mg/L) ^b | Potential health effects from long-term ^c exposure above the MCL | Common sources of contaminant in drinking water | Public Health Goal (mg/L) ^d |
|--|--|---|---|--|
| IOC Cyanide (as free cyanide) | 0.2 | Nerve damage or thyroid problems | Discharge from steel/metal factories; discharge from plastic and fertilizer factories | 0.2 |
| OC 2,4-D | 0.07 | Kidney, liver, or adrenal gland problems | Runoff from herbicide used on row crops | 0.07 |
| OC Dalapon | 0.2 | Minor kidney changes | Runoff from herbicide used on rights of way | 0.2 |
| OC 1,2-Dibromo-3-chloropropane (DBCP) | 0.0002 | Reproductive difficulties; increased risk of cancer | Runoff/leaching from soil fumigant used on soybeans, cotton, pineapples, and orchards | zero |
| OC o-Dichlorobenzene | 0.6 | Liver, kidney, or circulatory system problems | Discharge from industrial chemical factories | 0.6 |
| OC p-Dichlorobenzene | 0.075 | Anemia; liver, kidney or spleen damage; changes in blood | Discharge from industrial chemical factories | 0.075 |
| OC 1,2-Dichloroethane | 0.005 | Increased risk of cancer | Discharge from industrial chemical factories | zero |
| OC 1,1-Dichloroethylene | 0.007 | Liver problems | Discharge from industrial chemical factories | 0.007 |
| OC cis-1,2-Dichloroethylene | 0.07 | Liver problems | Discharge from industrial chemical factories | 0.07 |
| OC trans-1,2-Dichloroethylene | 0.1 | Liver problems | Discharge from industrial chemical factories | 0.1 |
| OC Dichloromethane | 0.005 | Liver problems; increased risk of cancer | Discharge from drug and chemical factories | zero |
| OC 1,2-Dichloropropane | 0.005 | Increased risk of cancer | Discharge from industrial chemical factories | zero |
| OC Di(2-ethylhexyl) adipate | 0.4 | Weight loss, liver problems, or possible reproductive difficulties | Discharge from chemical factories | 0.4 |
| OC Di(2-ethylhexyl) phthalate | 0.006 | Reproductive difficulties; liver problems; increased risk of cancer | Discharge from rubber and chemical factories | zero |
| OC Dinoseb | 0.007 | Reproductive difficulties | Runoff from herbicide used on soybeans and vegetables | 0.007 |
| OC Dioxin (2,3,7,8-TCDD) | 0.0000003 | Reproductive difficulties; increased risk of cancer | Emissions from waste incineration and other combustion; discharge from chemical factories | zero |
| OC Diquat | 0.02 | Cataracts | Runoff from herbicide use | 0.02 |
| OC Endosulfan | 0.1 | Stomach and intestinal problems | Runoff from herbicide use | 0.1 |
| OC Endrin | 0.002 | Liver problems | Residue of banned insecticide | 0.002 |
| OC Epichlorohydrin | TT ^a | Increased cancer risk; stomach problems | Discharge from industrial chemical factories; an impurity of some water treatment chemicals | zero |
| OC Ethylbenzene | 0.7 | Liver or kidney problems | Discharge from petroleum refineries | 0.7 |
| OC Ethylene dibromide | 0.00005 | Problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer | Discharge from petroleum refineries | zero |
| M Fecal coliform and <i>E. coli</i> | MCL ^a | Fecal coliforms and <i>E. coli</i> are bacteria whose presence indicates that the water may be contaminated with human or animal wastes. Microbes in these wastes may cause short term effects, such as diarrhea, cramps, nausea, headaches, or other symptoms. They may pose a special health risk for infants, young children, and people with severely compromised immune systems. | Human and animal fecal waste | zero ^e |
| IOC Fluoride | 4.0 | Bone disease (pain and tenderness of the bones); children may get mottled teeth | Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories | 4.0 |
| M <i>Giardia lamblia</i> | TT ^a | Short-term exposure: Gastrointestinal illness (e.g., diarrhea, vomiting, cramps) | Human and animal fecal waste | zero |
| OC Glyphosate | 0.7 | Kidney problems; reproductive difficulties | Runoff from herbicide use | 0.7 |
| DBP Haloacetic acids (HAA3) | 0.060 | Increased risk of cancer | Byproduct of drinking water disinfection | n/a ^f |
| OC Heptachlor | 0.0004 | Liver damage; increased risk of cancer | Residue of banned termiticide | zero |
| OC Heptachlor epoxide | 0.0002 | Liver damage; increased risk of cancer | Breakdown of heptachlor | zero |
| M Heterotrophic plate count (HPC) | TT ^a | HPC has no health effects; it is an analytic method used to measure the variety of bacteria that are common in water. The lower the concentration of bacteria in drinking water, the better maintained the water system is. | HPC measures a range of bacteria that are naturally present in the environment | n/a |

LEGEND

| | | |
|-----------------------------------|-------------------------------|----------------------------|
| D Disinfectant | IOC Inorganic Chemical | OC Organic Chemical |
| DBP Disinfection Byproduct | M Microorganism | R Radionuclides |

| Contaminant | MCL or TT ¹ (mg/L) ² | Potential health effects from long-term ³ exposure above the MCL | Common sources of contaminant in drinking water | Public Health Goal (mg/L) ² |
|---|--|---|---|--|
| OC Hexachlorobenzene | 0.001 | Liver or kidney problems; reproductive difficulties; increased risk of cancer | Discharge from metal refineries and agricultural chemical factories | zero |
| OC Hexachlorocyclopentadiene | 0.05 | Kidney or stomach problems | Discharge from chemical factories | 0.05 |
| IOC Lead | TT ⁵ ; Action Level=0.015 | Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities; Adults: Kidney problems; high blood pressure | Corrosion of household plumbing systems; erosion of natural deposits | zero |
| M Legionella | 177 | Legionnaire's Disease, a type of pneumonia | Found naturally in water; multiplies in heating systems | zero |
| OC Lindane | 0.0002 | Liver or kidney problems | Runoff/leaching from insecticide used on cattle, lumber, gardens | 0.0002 |
| IOC Mercury (inorganic) | 0.002 | Kidney damage | Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands | 0.002 |
| OC Methoxychlor | 0.04 | Reproductive difficulties | Runoff/leaching from insecticide used on fruits, vegetables, alfalfa, livestock | 0.04 |
| IOC Nitrate (measured as Nitrate) | 10 | Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome. | Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits | 10 |
| IOC Nitrite (measured as Nitrite) | 1 | Infants below the age of six months who drink water containing nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome. | Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits | 1 |
| OC Oxydemeton Methyl (Vydate) | 0.2 | Slight nervous system effects | Runoff/leaching from insecticide used on apples, potatoes, and tomatoes | 0.2 |
| OC Pentachlorophenol | 0.001 | Liver or kidney problems; increased cancer risk | Discharge from wood-preserving factories | zero |
| OC Picloram | 0.5 | Liver problems | Herbicide runoff | 0.5 |
| OC Polychlorinated biphenyls (PCBs) | 0.0005 | Skin changes; thyroid gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer | Runoff from landfills; discharge of waste chemicals | zero |
| R Radium 226 and Radium 228 (combined) | 5 pCi/L | Increased risk of cancer | Erosion of natural deposits | zero |
| IOC Selenium | 0.05 | Hair or fingernail loss; numbness in fingers or toes; circulatory problems | Discharge from petroleum and metal refineries; erosion of natural deposits; discharge from mines | 0.05 |
| OC Simazine | 0.004 | Problems with blood | Herbicide runoff | 0.004 |
| OC Styrene | 0.1 | Liver, kidney, or circulatory system problems | Discharge from rubber and plastic factories; leaching from landfills | 0.1 |
| OC Tetrachloroethylene | 0.005 | Liver problems; increased risk of cancer | Discharge from factories and dry cleaners | zero |
| IOC Thallium | 0.002 | Hair loss; changes in blood; kidney, intestine, or liver problems | Leaching from ore-processing sites; discharge from electronics, glass, and drug factories | 0.0005 |
| OC Toluene | 1 | Nervous system, kidney, or liver problems | Discharge from petroleum factories | 1 |
| M Total Coliforms | 5.0 percent ⁴ | Coliforms are bacteria that indicate that other, potentially harmful bacteria may be present. See fecal coliforms and <i>E. coli</i> . | Naturally present in the environment | zero |
| DBP Total Trihalomethanes (TTHMs) | 0.080 | Liver, kidney or central nervous system problems; increased risk of cancer | Byproduct of drinking water disinfection | n/a ⁶ |
| OC Toxaphene | 0.003 | Kidney, liver, or thyroid problems; increased risk of cancer | Runoff/leaching from insecticide used on cotton and cattle | zero |
| OC 2,4,5-TP (Silvex) | 0.05 | Liver problems | Residue of banned herbicide | 0.05 |
| OC 1,2,4-Trichlorobenzene | 0.07 | Changes in adrenal glands | Discharge from textile finishing factories | 0.07 |
| OC 1,1,1-Trichloroethane | 0.2 | Liver, nervous system, or circulatory problems | Discharge from metal degreasing sites and other factories | 0.2 |
| OC 1,1,2-Trichloroethane | 0.005 | Liver, kidney, or immune system problems | Discharge from industrial chemical factories | 0.003 |
| OC Trichloroethylene | 0.005 | Liver problems; increased risk of cancer | Discharge from metal degreasing sites and other factories | zero |

| LEGEND | | | |
|-----------------------------------|-------------------------------|----------------------------|--|
| D Disinfectant | IOC Inorganic Chemical | OC Organic Chemical | |
| DBP Disinfection Byproduct | M Microorganism | R Radionuclides | |

| Contaminant | MCL or TT ⁶ (mg/L) ² | Potential health effects from long-term ³ exposure above the MCL | Common sources of contaminant in drinking water | Public Health Goal (mg/L) ² |
|----------------------------|--|---|---|--|
| M Turbidity | TT ⁶ | Turbidity is a measure of the cloudiness of water. It is used to indicate water quality and filtration effectiveness (e.g., whether disease-causing organisms are present). Higher turbidity levels are often associated with higher levels of disease-causing microorganisms such as viruses, parasites and some bacteria. These organisms can cause short term symptoms such as nausea, cramps, diarrhea, and associated headaches. | Soil runoff | n/a |
| R Uranium | 30µg/L | Increased risk of cancer, kidney toxicity | Erosion of natural deposits | zero |
| OC Vinyl chloride | 0.002 | Increased risk of cancer | Leaching from PVC pipes; discharge from plastic factories | zero |
| M Viruses (enteric) | TT ⁶ | Short-term exposure: Gastrointestinal illness (e.g., diarrhea, vomiting, cramps) | Human and animal fecal waste | zero |
| OC Xylenes (total) | 10 | Nervous system damage | Discharge from petroleum factories; discharge from chemical factories | 10 |

| LEGEND | | | |
|-----------------------------------|-------------------------------|----------------------------|--|
| D Disinfectant | IOC Inorganic Chemical | OC Organic Chemical | |
| DBP Disinfection Byproduct | M Microorganism | R Radionuclides | |

NOTES:

1 Definitions

- Maximum Contaminant Level Goal (MCLG) – The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.
- Maximum Contaminant Level (MCL) – The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.
- Maximum Residual Disinfectant Level Goal (MRDLG) – The level of a drinking water disinfectant below which there is no known or expected risk to health. MRDLGs do not reflect the benefits of the use of disinfectants to control microbial contaminants.
- Maximum Residual Disinfectant Level (MRDL) – The highest level of a disinfectant allowed in drinking water. There is convincing evidence that addition of a disinfectant is necessary for control of microbial contaminants.
- Treatment Technique (TT) – A required process intended to reduce the level of a contaminant in drinking water.

2 Units are in milligrams per liter (mg/L) unless otherwise noted. Milligrams per liter are equivalent to parts per million (ppm).

3 Health effects are from long-term exposure unless specified as short-term exposure.

4 Each water system must certify annually, in writing, to the state (using third-party or manufacturer certification) that when it uses acrylamide and/or epichlorohydrin to treat water, the combination (or product) of dose and monomer level does not exceed that levels specified, as follows: Acrylamide = 0.05 percent dosed at 1mg/L (or equivalent); Epichlorohydrin = 0.01 percent dosed at 20 mg/L (or equivalent).

5 Lead and copper are regulated by a Treatment Technique that requires systems to control the corrosiveness of their water. If more than 10 percent of tap water samples exceed the action level, water systems must take additional steps. For copper, the action level is 1.3 mg/L, and for lead is 0.015 mg/L.

6 A routine sample that is fecal coliform-positive or E. coli-positives triggers repeat samples – if any repeat sample is total coliform-positive, the system has an acute MCL violation. A routine sample that is total coliform-positive and fecal coliform-negative or E.coli-negative triggers repeat samples – if

any repeat sample is fecal coliform-positive or E.coli-positive, the system has an acute MCL violation. See also Total Coliforms.

7 EPA's surface water treatment rules require systems using surface water or ground water under the direct influence of surface water to (1) disinfect their water, and (2) filter their water or meet criteria for avoiding filtration so that the following contaminants are controlled at the following levels:

- Cryptosporidium: 99 percent removal for systems that filter. Unfiltered systems are required to include Cryptosporidium in their existing watershed control provisions.
- Giardia lamblia: 99.9 percent removal/inactivation.
- Viruses: 99.99 percent removal/inactivation
- Legionella: No limit but EPA believes that if Giardia and viruses are removed/inactivated according to the treatment techniques in the surface water treatment rule, Legionella will also be controlled.
- Turbidity: For systems that use conventional or direct filtration, at no time can turbidity (cloudiness of water) go higher than 1 nephelometric turbidity unit (NTU), and samples for turbidity must be less than or equal to 0.3 NTU in at least 95 percent of the samples in any month. Systems that use filtration other than conventional or direct filtration must follow state limits, which must include turbidity at no time exceeding 5 NTU.
- HPC: No more than 500 bacterial colonies per milliliter
- Long Term 1 Enhanced Surface Water Treatment; Surface water systems or ground water systems under the direct influence of surface water serving fewer than 10,000 people must comply with the applicable Long Term 1 Enhanced Surface Water Treatment Rule provisions (e.g. turbidity standards, individual filter monitoring, Cryptosporidium removal requirements, updated watershed control requirements for unfiltered systems).
- Long Term 2 Enhanced Surface Water Treatment; This rule applies to all surface water systems or ground water systems under the direct influence of surface water. The rule targets additional Cryptosporidium treatment requirements for higher risk systems and includes provisions to reduce risks from uncovered finished water storage facilities and to ensure that the systems maintain microbial protection as they take steps to reduce the formation of disinfection byproducts. (Monitoring start dates are staggered by system size. The largest systems (serving at least 100,000 people) will begin monitoring in October 2006 and the smallest systems (serving fewer than 10,000 people) will not begin monitoring until October 2008. After completing monitoring and determining their treatment bin, systems generally have three years to comply with any additional treatment requirements.)
- Filter Backwash Recycling: The Filter Backwash Recycling Rule requires systems that recycle to return specific recycle flows through all processes of the system's existing conventional or direct filtration system or at an alternate location approved by the state.

8 No more than 5.0 percent samples total coliform-positive in a month. (For water systems that collect fewer than 40 routine samples per month, no more than one sample can be total coliform-positive per month.) Every sample that has total coliform must be analyzed for either fecal coliforms or E.coli. If two consecutive TC-positive samples, and one is also positive for E.coli or fecal coliforms, system has an acute MCL violation.

9 Although there is no collective MCLG for this contaminant group, there are individual MCLGs for some of the individual contaminants:

Haloacetic acids: dichloroacetic acid (zero); trichloroacetic acid (0.3 mg/L)

Trihalomethanes: bromodichloromethane (zero); bromoform (zero); dibromochloromethane (0.06 mg/L)

Table D.2 USEPA national secondary drinking water regulations

| Contaminant | Secondary Maximum Contaminant Level |
|------------------------|--|
| Aluminum | 0.05 to 0.2 mg/L |
| Chloride | 250 mg/L |
| Color | 15 (color units) |
| Copper | 1.0 mg/L |
| Corrosivity | noncorrosive |
| Fluoride | 2.0 mg/L |
| Foaming Agents | 0.5 mg/L |
| Iron | 0.3 mg/L |
| Manganese | 0.05 mg/L |
| Odor | 3 threshold odor number |
| pH | 6.5-8.5 |
| Silver | 0.10 mg/L |
| Sulfate | 250 mg/L |
| Total Dissolved Solids | 500 mg/L |
| Zinc | 5 mg/L |

National Secondary Drinking Water Regulations are non-enforceable guidelines regarding contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. EPA recommends secondary standards to water systems but does not require systems to comply. However, some states may choose to adopt them as enforceable standards.

Appendix E

WHO Guidelines

Table E.1 Guideline values for chemicals that are of health significance in drinking water
(WHO, 2008)

| Chemical | Guideline value ^a (mg/litre) | Remarks |
|--|--|--|
| Acrylamide | 0.0005 ^b | |
| Alachlor | 0.02 ^b | |
| Aldicarb | 0.01 | Applies to aldicarb sulfoxide and aldicarb sulfone |
| Aldrin and dieldrin | 0.00003 | For combined aldrin plus dieldrin |
| Antimony | 0.02 | |
| Arsenic | 0.01 (P) | |
| Atrazine | 0.002 | |
| Barium | 0.7 | |
| Benzene | 0.01 ^b | |
| Benzo[<i>a</i>]pyrene | 0.0007 ^b | |
| Boron | 0.5 (T) | |
| Bromate | 0.01 ^b (A, T) | |
| Bromodichloromethane | 0.06 ^b | |
| Bromoform | 0.1 | |
| Cadmium | 0.003 | |
| Carbofuran | 0.007 | |
| Carbon tetrachloride | 0.004 | |
| Chlorate | 0.7 (D) | |
| Chlordane | 0.0002 | |
| Chlorine | 5 (C) | For effective disinfection, there should be a residual concentration of free chlorine of ≥ 0.5 mg/litre after at least 30 min contact time at pH <8.0 |
| Chlorite | 0.7 (D) | |
| Chloroform | 0.3 | |
| Chlorotoluron | 0.03 | |
| Chlorpyrifos | 0.03 | |
| Chromium | 0.05 (P) | For total chromium |
| Copper | 2 | Staining of laundry and sanitary ware may occur below guideline value |
| Cyanazine | 0.0006 | |
| Cyanide | 0.07 | |
| Cyanogen chloride | 0.07 | For cyanide as total cyanogenic compounds |
| 2,4-D (2,4-dichlorophenoxyacetic acid) | 0.03 | Applies to free acid |
| 2,4-DB | 0.09 | |
| DDT and metabolites | 0.001 | |
| Di(2-ethylhexyl)phthalate | 0.008 | |
| Dibromoacetonitrile | 0.07 | |
| Dibromochloromethane | 0.1 | |
| 1,2-Dibromo-3-chloropropane | 0.001 ^b | |
| 1,2-Dibromoethane | 0.0004 ^b (P) | |
| Dichloroacetate | 0.05 ^b (T, D) | |
| Dichloroacetonitrile | 0.02 (P) | |
| Dichlorobenzene, 1,2- | 1 (C) | |

Table E.1 (Continued)

| Chemical | Guideline value (mg/litre) | Remarks |
|--|-------------------------------|--|
| Dichlorobenzene, 1,4- | 0.3 (C) | |
| Dichloroethane, 1,2- | 0.03 ^b | |
| Dichloroethene, 1,2- | 0.05 | |
| Dichloromethane | 0.02 | |
| 1,2-Dichloropropane (1,2-DCP) | 0.04 (P) | |
| 1,3-Dichloropropene | 0.02 ^b | |
| Dichlorprop | 0.1 | |
| Dimethoate | 0.006 | |
| Dioxane, 1,4- | 0.05 ^b | |
| Edetic acid (EDTA) | 0.6 | Applies to the free acid |
| Endrin | 0.0006 | |
| Epichlorohydrin | 0.0004 (P) | |
| Ethylbenzene | 0.3 (C) | |
| Fenoprop | 0.009 | |
| Fluoride | 1.5 | Volume of water consumed and intake from other sources should be considered when setting national standards |
| Hexachlorobutadiene | 0.0006 | |
| Isoproturon | 0.009 | |
| Lead | 0.01 | |
| Lindane | 0.002 | |
| Manganese | 0.4 (C) | |
| MCPA | 0.002 | |
| Mecoprop | 0.01 | |
| Mercury | 0.006 | For inorganic mercury |
| Methoxychlor | 0.02 | |
| Metolachlor | 0.01 | |
| Microcystin-LR | 0.001 (P) | For total microcystin-LR (free plus cell-bound) |
| Molinate | 0.006 | |
| Molybdenum | 0.07 | |
| Monochloramine | 3 | |
| Monochloroacetate | 0.02 | |
| Nickel | 0.07 | |
| Nitrate (as NO ₃ ⁻) | 50 | Short-term exposure |
| Nitrilotriacetic acid (NTA) | 0.2 | |
| Nitrite (as NO ₂ ⁻) | 3 | Short-term exposure |
| | 0.2 (P) | Long-term exposure |
| <i>N</i> -Nitrosodimethylamine (NDMA) | 0.1 | |
| Pendimethalin | 0.02 | |
| Pentachlorophenol | 0.009 ^b (P) | |
| Permethrin | 0.3 | Only when used as a larvicide for public health purposes |
| Pyriproxyfen | 0.3 | |
| Pyriproxyfen | 0.3 | This is not to be used as a guideline value where pyriproxyfen is added to water for public health purposes. |
| Selenium | 0.01 | |
| Simazine | 0.002 | |
| Sodium dichloroisocyanurate | 50 | As sodium dichloroisocyanurate |
| | 40 | As cyanuric acid |
| Styrene | 0.02 (C) | |
| 2,4,5-T | 0.009 | |
| Terbutylazine | 0.007 | |
| Tetrachloroethene | 0.04 | |
| Toluene | 0.7 (C) | |

Table E.1 (Continued)

| Chemical | Guideline value (mg/litre) | Remarks |
|-------------------------|-------------------------------|---|
| Trichloroacetate | 0.2 | |
| Trichloroethene | 0.02 (P) | |
| Trichlorophenol, 2,4,6- | 0.2 ^b (C) | |
| Trifluralin | 0.02 | |
| Trihalomethanes | | The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1 |
| Uranium | 0.015 (P,T) | Only chemical aspects of uranium addressed |
| Vinyl chloride | 0.0003 ^b | |
| Xylenes | 0.5 (C) | |

^a P = provisional guideline value, as there is evidence of a hazard, but the available information on health effects is limited; T = provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.; A = provisional guideline value because calculated guideline value is below the achievable quantification level; D = provisional guideline value because disinfection is likely to result in the guideline value being exceeded; C = concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, leading to consumer complaints.

^b For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking-water associated with an upper-bound excess lifetime cancer risk of 10^{-5} (one additional cancer per 100 000 of the population ingesting drinking-water containing the substance at the guideline value for 70 years). Concentrations associated with upper-bound estimated excess lifetime cancer risks of 10^{-4} and 10^{-6} can be calculated by multiplying and dividing, respectively, the guideline value by 10.

Appendix F

Elgin Area DWSP Raw Water Data from 1987 – 2010

Table F.1 Elgin Area DWSP raw water data from 1987 – 2010 (µg/L)

| | Sb | As | Cd | Cr | Cu | Pb | Ni | Se | Benzene | Toluene |
|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------------|----------------|
| 1987 | | 1.00 | 0.30 | 1.00 | 6.00 | 9.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 25.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 3.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 2.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 2.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 2.00 | 3.00 | 3.00 | 3.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 2.00 | 2.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 2.00 | 2.00 | 4.00 | 3.00 | 1.00 | | |
| 1988 | 0.18 | 1.30 | 0.07 | 1.40 | 2.60 | 2.20 | 3.20 | 0.66 | | |
| 1988 | 0.23 | 0.69 | 0.05 | 3.90 | 1.30 | 0.28 | 0.90 | 0.73 | | |
| 1988 | 0.19 | 0.36 | 0.05 | 0.34 | 2.10 | 0.35 | 1.00 | 0.74 | | |
| 1988 | 0.13 | 0.05 | 0.05 | 0.80 | 2.00 | 0.56 | 2.50 | 1.10 | | |
| 1988 | 0.21 | 0.60 | 0.05 | 0.95 | 1.30 | 0.27 | 1.90 | 2.00 | | |
| 1988 | 0.22 | 0.84 | 0.06 | 0.33 | 1.40 | 0.32 | 1.00 | 0.35 | | |
| 1988 | 0.24 | 0.78 | 0.05 | 1.30 | 1.70 | 0.30 | 1.50 | 2.60 | | |
| 1988 | 0.50 | 0.64 | 0.05 | 0.49 | 2.20 | 0.40 | 0.99 | 0.22 | | |
| 1988 | 0.34 | 0.95 | 0.05 | 1.60 | 1.10 | 0.02 | 0.72 | 1.40 | | |
| 1988 | 0.48 | 1.90 | 0.05 | 6.40 | 1.70 | 0.60 | 3.40 | 0.20 | | |
| 1988 | 0.34 | 1.90 | 0.09 | 2.50 | 3.90 | 2.90 | 0.52 | 0.28 | | |
| 1988 | 0.26 | 1.20 | 0.05 | 0.85 | 2.70 | 1.90 | 1.70 | 0.55 | | |
| 1989 | 0.36 | 1.40 | 0.05 | 5.20 | 2.30 | 1.80 | 1.70 | 0.42 | | |
| 1989 | 0.30 | 1.30 | 0.07 | 1.80 | 3.50 | 2.30 | 1.50 | 1.40 | | |
| 1989 | 0.99 | 1.10 | 0.15 | 0.21 | 6.40 | 0.09 | 0.27 | 6.80 | | |
| 1989 | 0.36 | 1.20 | 0.24 | 0.85 | 4.70 | 2.80 | 1.80 | 1.40 | | |
| 1989 | 0.84 | 1.80 | 0.05 | 9.00 | 2.30 | 0.89 | 2.10 | 1.10 | | |
| 1989 | 0.95 | 1.10 | 0.05 | 0.24 | 1.60 | 0.25 | 0.78 | 0.75 | | |
| 1989 | 0.54 | 1.60 | 0.07 | 4.00 | 3.90 | 2.30 | 1.60 | 1.00 | | |
| 1989 | 0.84 | 1.30 | 0.05 | 7.20 | 1.30 | 0.46 | 2.10 | 1.30 | | |
| 1989 | 0.60 | 2.00 | 0.05 | 5.50 | 3.60 | 2.20 | 1.80 | 5.30 | | |
| 1989 | 0.43 | 0.80 | 0.05 | 0.93 | 1.50 | 0.51 | 1.20 | 1.00 | | |
| 1989 | 0.27 | 1.00 | 0.05 | 0.87 | 4.60 | 2.80 | 3.60 | 1.00 | | |
| 1989 | 0.25 | 1.20 | 0.05 | 0.85 | 4.40 | 3.10 | 1.90 | 1.00 | | |
| 1990 | 0.49 | 0.78 | 0.05 | 0.50 | 1.40 | 0.21 | 0.44 | 1.00 | | |

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|-------------|------|------|------|-------|--------|-------|------|------|------|------|
| 1990 | 0.30 | 0.78 | 0.11 | 0.55 | 2.60 | 1.20 | 0.61 | 1.00 | | |
| 1990 | 0.20 | 0.75 | 0.05 | 2.00 | 2.30 | 0.89 | 1.50 | 1.00 | | |
| 1990 | 0.66 | 0.60 | 0.05 | 0.50 | 1.60 | 0.22 | 0.75 | 1.00 | | |
| 1990 | 0.32 | 0.89 | 0.05 | 2.30 | 1.50 | 0.14 | 0.66 | 1.00 | | |
| 1990 | 0.31 | 1.70 | 0.07 | 3.00 | 8.40 | 3.00 | 2.30 | 1.00 | | |
| 1991 | 0.26 | 1.10 | 0.05 | 3.30 | 3.70 | 1.10 | 0.64 | 1.00 | | |
| 1991 | 0.54 | 0.88 | 0.05 | 2.70 | 1.80 | 0.45 | 0.20 | 1.00 | | |
| 1991 | 0.36 | 0.91 | 0.05 | 1.00 | 2.40 | 0.71 | 2.00 | 1.00 | | |
| 1991 | 0.70 | 0.73 | 0.05 | 3.10 | 1.70 | 0.25 | 0.20 | 1.00 | | |
| 1991 | 0.37 | 0.84 | 0.05 | 0.57 | 1.50 | 0.19 | 0.88 | 1.00 | | |
| 1991 | 0.36 | 1.40 | 0.05 | 2.10 | 4.10 | 2.10 | 1.30 | 1.00 | | |
| 1992 | 0.65 | 0.77 | 0.05 | 0.98 | 1.40 | 0.33 | 0.46 | 1.00 | | |
| 1992 | 0.45 | 0.94 | 0.05 | 0.76 | 1.90 | 0.44 | 3.20 | 1.00 | | |
| 1992 | 0.52 | 0.87 | 0.05 | 2.10 | 1.40 | 0.13 | 2.70 | 1.00 | | |
| 1992 | 0.47 | 1.20 | 0.05 | 2.20 | 1.80 | 0.50 | 3.40 | 1.80 | | |
| 1993 | 0.26 | 1.00 | 0.05 | 3.20 | 3.60 | 1.70 | 0.55 | 1.00 | | |
| 1993 | 0.44 | 1.10 | 0.05 | 3.60 | 2.40 | 0.88 | 0.86 | 1.00 | | |
| 1993 | 0.66 | 0.70 | 0.05 | 1.60 | 1.30 | 0.10 | 2.30 | 1.00 | | |
| 1993 | 0.31 | 1.50 | 0.05 | 4.00 | 5.60 | 3.10 | 3.80 | 1.00 | | |
| 1994 | 0.50 | 0.70 | 0.05 | 0.50 | 1.20 | 0.30 | 3.00 | 1.00 | | |
| 1994 | 0.38 | 0.66 | 0.05 | 1.70 | 3.20 | 1.30 | 2.80 | 1.00 | | |
| 1994 | 0.68 | 0.90 | 0.05 | 1.90 | 1.40 | 0.27 | 0.20 | 1.00 | | |
| 1994 | 0.61 | 1.07 | 0.05 | 1.78 | 2.12 | 30.96 | 1.54 | 1.00 | | |
| 1995 | 0.50 | 1.05 | 0.10 | 2.94 | 3.52 | 1.95 | 2.08 | 1.92 | | |
| 1995 | 0.40 | 0.80 | 0.05 | 2.00 | 2.50 | 0.50 | 0.20 | 1.00 | | |
| 1995 | 0.50 | 0.90 | 0.05 | 4.50 | 2.00 | 0.35 | 0.80 | 1.00 | | |
| 1996 | 0.55 | 1.00 | 0.05 | 2.00 | 1.00 | 0.15 | 0.40 | 1.00 | | |
| 1997 | 0.55 | 0.90 | 0.05 | 2.50 | 1.00 | 0.45 | 0.20 | 1.00 | | |
| 1997 | 0.38 | 0.93 | 0.19 | 3.73 | 1.71 | 0.48 | 0.90 | 1.00 | | |
| 1997 | 0.34 | 1.20 | 0.07 | 2.41 | 1.48 | 0.73 | 1.22 | 1.00 | | |
| 1998 | 0.39 | 0.74 | 0.05 | 5.33 | 1.48 | 0.12 | 0.25 | 1.00 | | |
| 1998 | 0.48 | 1.57 | 0.10 | 9.99 | 2.87 | 1.73 | 2.69 | 0.34 | 0.05 | 0.05 |
| 1999 | 0.65 | 0.80 | 0.20 | 9.30 | 1.20 | 0.00 | 0.70 | 2.00 | 0.05 | 0.05 |
| 1999 | 0.90 | 1.50 | 0.04 | 1.30 | 2.10 | 0.99 | 1.40 | 1.00 | 0.05 | 0.05 |
| 2000 | 0.97 | 0.80 | 0.45 | 0.50 | 14.00 | 0.83 | 4.20 | 1.00 | 0.05 | 0.05 |
| 2000 | 0.43 | 1.80 | 0.07 | 1.40 | 3.20 | 2.21 | 2.10 | 0.00 | 0.05 | 0.05 |
| 2001 | 0.38 | 0.90 | 0.01 | 0.70 | 1.10 | 0.18 | 1.40 | 0.00 | 0.05 | 0.05 |
| 2002 | 0.33 | 0.80 | 0.00 | 13.60 | 91.60 | 0.64 | 2.00 | 1.00 | 0.05 | 0.05 |
| 2002 | 0.49 | 1.40 | 0.04 | 1.40 | 109.00 | 1.93 | 1.30 | 1.00 | 0.05 | 0.05 |
| 2004 | 0.46 | 0.90 | 0.02 | 0.90 | 52.70 | 0.46 | 0.90 | 0.00 | 0.05 | 0.05 |

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|-------------|------|------|------|-------|--------|------|------|------|------|------|
| 2004 | 0.58 | 1.00 | 0.00 | 0.90 | 87.70 | 1.52 | 1.30 | 0.00 | 0.05 | 0.05 |
| 2005 | 0.45 | 1.70 | 0.05 | 2.30 | 92.50 | 4.50 | 2.90 | 0.00 | 0.05 | 0.05 |
| 2007 | 0.63 | 1.00 | 0.02 | 1.30 | 2.40 | 0.89 | 1.40 | 0.00 | 0.05 | 0.05 |
| 2007 | 0.42 | 1.00 | 0.01 | 0.40 | 1.40 | 0.05 | 1.20 | 0.00 | 0.05 | 0.05 |
| 2007 | 0.45 | 2.40 | 0.07 | 1.60 | 57.20 | 2.98 | 3.30 | 0.00 | 0.05 | 0.1 |
| 2008 | 0.35 | 1.60 | 0.08 | 1.60 | 116.00 | 3.24 | 2.90 | 1.00 | 0.05 | 0.05 |
| 2008 | 0.76 | 0.90 | 0.01 | 1.20 | 1.20 | 0.03 | 1.00 | 0.00 | 0.05 | 0.05 |
| 2008 | 0.57 | 0.85 | 0.02 | 0.80 | 107.00 | 0.55 | 1.30 | 0.00 | 0.05 | 0.05 |
| 2008 | 0.61 | 1.03 | 0.01 | 0.30 | 59.10 | 0.29 | 1.00 | 1.00 | 0.05 | 0.05 |
| 2009 | 0.54 | 1.03 | 0.01 | 0.30 | 116.00 | 0.38 | 1.20 | 0.00 | 0.05 | 0.05 |
| 2009 | 0.34 | 1.17 | 0.02 | 10.20 | 160.00 | 1.26 | 2.10 | 0.00 | 0.05 | 0.05 |
| 2009 | 0.40 | 1.20 | 0.00 | 0.30 | 94.40 | 0.60 | 1.30 | 0.00 | 0.05 | 0.05 |
| 2010 | 0.50 | 1.20 | 0.00 | 0.30 | 133.00 | 0.90 | 2.20 | 0.30 | 0.05 | 0.05 |

Blank: No data were reported.

Appendix G

Elgin Area DWSP Treated Water Data from 1987 – 2010

Table G.1 Elgin Area DWSP treated water data from 1987 – 2010 (µg/L)

| | Sb | As | Cd | Cr | Cu | Pb | Ni | Se | Benzene | Toluene |
|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------------|----------------|
| 1987 | | 1.00 | 0.30 | 1.00 | 2.00 | 6.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 3.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 2.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 1.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1987 | | 1.00 | 0.30 | 1.00 | 1.00 | 3.00 | 2.00 | 1.00 | | |
| 1988 | 0.19 | 0.32 | 0.05 | 0.12 | 0.93 | 0.19 | 1.00 | 0.90 | | |
| 1988 | 0.18 | 0.05 | 0.05 | 0.17 | 0.78 | 0.04 | 0.58 | 0.61 | | |
| 1988 | 0.20 | 0.05 | 0.05 | 0.15 | 1.10 | 0.02 | 1.60 | 0.48 | | |
| 1988 | 0.20 | 0.40 | 0.05 | 0.18 | 0.90 | 0.05 | 1.20 | 1.80 | | |
| 1988 | 0.27 | 0.33 | 0.06 | 0.13 | 1.00 | 0.04 | 0.55 | 0.20 | | |
| 1988 | 0.23 | 0.54 | 0.06 | 0.22 | 1.10 | 0.04 | 1.10 | 1.00 | | |
| 1988 | 0.55 | 0.12 | 0.05 | 0.21 | 0.91 | 0.02 | 0.64 | 1.20 | | |
| 1988 | 0.46 | 0.60 | 0.05 | 0.47 | 1.10 | 0.04 | 0.66 | 1.40 | | |
| 1988 | 0.72 | 0.54 | 0.05 | 2.00 | 0.97 | 0.02 | 1.70 | 2.70 | | |
| 1988 | 0.68 | 0.31 | 0.05 | 5.70 | 2.60 | 0.16 | 0.10 | 2.30 | | |
| 1988 | 0.31 | 0.23 | 0.05 | 0.47 | 1.20 | 0.08 | 0.71 | 1.40 | | |
| 1989 | 0.39 | 0.25 | 0.05 | 0.56 | 0.98 | 0.07 | 0.24 | 0.24 | | |
| 1989 | 0.46 | 0.14 | 0.05 | 0.10 | 1.20 | 0.06 | 0.10 | 0.60 | | |
| 1989 | 0.73 | 0.91 | 0.12 | 2.80 | 1.90 | 0.19 | 1.50 | 4.50 | | |
| 1989 | 0.55 | 0.49 | 0.12 | 2.20 | 1.40 | 0.34 | 0.40 | 3.60 | | |
| 1989 | 0.74 | 1.10 | 0.05 | 2.80 | 1.40 | 0.02 | 1.50 | 2.60 | | |
| 1989 | 0.62 | 0.76 | 0.05 | 1.30 | 1.30 | 0.18 | 0.42 | 2.20 | | |
| 1989 | 0.62 | 0.82 | 0.05 | 1.00 | 0.65 | 0.02 | 1.60 | 2.90 | | |
| 1989 | 0.73 | 0.98 | 0.05 | 2.50 | 1.10 | 0.10 | 0.35 | 6.10 | | |
| 1989 | 0.44 | 0.43 | 0.05 | 2.70 | 0.84 | 0.07 | 0.24 | 1.00 | | |
| 1989 | 0.32 | 1.30 | 0.05 | 0.10 | 0.98 | 0.03 | 0.96 | 1.00 | | |
| 1989 | 0.44 | 0.10 | 0.05 | 0.11 | 0.91 | 0.02 | 0.82 | 1.00 | | |
| 1990 | 0.60 | 0.41 | 0.05 | 0.50 | 1.00 | 0.07 | 0.80 | 1.00 | | |
| 1990 | 0.40 | 0.22 | 0.08 | 1.10 | 1.00 | 0.07 | 2.80 | 1.50 | | |
| 1990 | 0.36 | 0.36 | 0.05 | 1.70 | 0.94 | 0.10 | 0.61 | 1.20 | | |

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|-------------|------|------|------|------|-------|------|------|------|------|------|
| 1990 | 0.64 | 0.30 | 0.05 | 0.71 | 1.20 | 0.05 | 0.87 | 1.80 | | |
| 1990 | 0.41 | 0.37 | 0.05 | 1.30 | 1.10 | 0.05 | 0.60 | 1.00 | | |
| 1990 | 0.39 | 0.16 | 0.05 | 1.30 | 0.97 | 0.31 | 0.20 | 1.00 | | |
| 1991 | 0.44 | 0.29 | 0.05 | 1.70 | 1.00 | 0.05 | 0.20 | 1.30 | | |
| 1991 | 0.50 | 0.13 | 0.05 | 0.85 | 0.92 | 0.05 | 0.20 | 1.00 | | |
| 1991 | 0.51 | 0.51 | 0.05 | 0.98 | 0.99 | 0.05 | 1.30 | 1.00 | | |
| 1991 | 0.66 | 0.33 | 0.05 | 2.60 | 0.90 | 0.05 | 0.20 | 1.50 | | |
| 1991 | 0.49 | 0.55 | 0.05 | 0.50 | 0.85 | 0.05 | 0.58 | 1.00 | | |
| 1991 | 0.55 | 0.26 | 0.05 | 1.60 | 1.10 | 0.06 | 0.20 | 1.00 | | |
| 1992 | 0.48 | 0.23 | 0.05 | 0.50 | 0.92 | 0.11 | 0.20 | 1.30 | | |
| 1992 | 0.58 | 0.50 | 0.05 | 0.50 | 1.10 | 0.28 | 2.40 | 1.00 | | |
| 1992 | 0.46 | 0.50 | 0.05 | 0.50 | 1.10 | 2.90 | 2.50 | 1.00 | | |
| 1992 | 0.49 | 0.42 | 0.05 | 1.70 | 0.93 | 0.05 | 2.10 | 1.00 | | |
| 1993 | 0.48 | 0.18 | 0.05 | 1.10 | 1.10 | 0.05 | 0.20 | 1.50 | | |
| 1993 | 0.54 | 0.27 | 0.05 | 2.80 | 1.50 | 0.05 | 0.20 | 1.20 | | |
| 1993 | 0.63 | 0.49 | 0.05 | 1.50 | 0.73 | 0.05 | 2.10 | 1.50 | | |
| 1993 | 0.58 | 0.21 | 0.05 | 0.50 | 0.80 | 0.05 | 0.80 | 1.00 | | |
| 1994 | 0.65 | 0.16 | 0.05 | 0.50 | 0.89 | 0.05 | 2.80 | 1.00 | | |
| 1994 | 0.71 | 0.10 | 0.05 | 0.50 | 0.83 | 0.05 | 0.92 | 1.00 | | |
| 1994 | 0.59 | 0.42 | 0.05 | 1.70 | 0.87 | 0.05 | 0.20 | 1.30 | | |
| 1994 | 0.64 | 0.42 | 0.05 | 1.08 | 0.91 | 0.13 | 0.93 | 1.00 | | |
| 1995 | 0.57 | 0.26 | 0.05 | 3.70 | 1.50 | 0.25 | 0.20 | 1.40 | | |
| 1995 | 0.30 | 0.40 | 0.05 | 1.50 | 1.50 | 0.30 | 0.20 | 1.00 | | |
| 1995 | 0.70 | 0.30 | 0.05 | 3.00 | 1.00 | 0.10 | 0.60 | 1.00 | | |
| 1996 | 0.45 | 0.20 | 0.05 | 3.00 | 0.50 | 0.40 | 0.20 | 1.00 | | |
| 1997 | 0.50 | 0.10 | 0.05 | 1.50 | 1.00 | 0.05 | 0.20 | 1.00 | | |
| 1997 | 0.39 | 0.34 | 0.13 | 3.45 | 0.87 | 0.06 | 0.39 | 1.01 | | |
| 1997 | 0.62 | 0.21 | 0.05 | 1.73 | 0.83 | 0.05 | 0.40 | 1.00 | | |
| 1998 | 0.43 | 0.52 | 0.08 | 6.18 | 1.33 | 0.05 | 0.24 | 1.43 | | |
| 1998 | 0.73 | 0.30 | 0.03 | 7.13 | 0.92 | 0.05 | 1.15 | 1.25 | 0.05 | 0.05 |
| 1999 | 0.73 | 0.00 | 0.00 | 6.60 | 1.80 | 0.14 | 1.20 | 9.00 | 0.05 | 0.10 |
| 1999 | 0.96 | 0.40 | 0.00 | 1.60 | 1.10 | 0.05 | 0.40 | 1.00 | 0.05 | 0.05 |
| 2000 | 0.81 | 0.40 | 0.02 | 0.20 | 3.40 | 0.12 | 0.90 | 0.00 | 0.05 | 0.05 |
| 2000 | 0.65 | 0.20 | 0.01 | 1.60 | 1.00 | 0.04 | 0.70 | 0.00 | 0.05 | 0.05 |
| 2001 | 0.55 | 0.60 | 0.00 | 0.80 | 2.10 | 0.00 | 1.40 | 1.00 | 0.05 | 0.05 |
| 2002 | 0.34 | 0.40 | 0.00 | 1.80 | 2.70 | 0.02 | 1.50 | 1.00 | 0.05 | 0.05 |
| 2002 | 0.49 | 0.60 | 0.01 | 0.90 | 1.50 | 0.02 | 1.50 | 0.00 | 0.05 | 0.05 |
| 2004 | 0.45 | 0.40 | 0.04 | 1.10 | 12.70 | 0.08 | 1.20 | 0.00 | 0.05 | 0.05 |
| 2004 | 0.58 | 0.50 | 0.00 | 0.90 | 10.70 | 0.00 | 0.90 | 0.00 | 0.05 | 0.05 |
| 2005 | 0.64 | 0.40 | 0.04 | 1.90 | 38.20 | 0.05 | 1.80 | 0.00 | 0.05 | 0.05 |

| | | | | | | | | | | |
|-------------|------|------|------|-------|-------|------|------|------|------|------|
| 2007 | 0.43 | 0.30 | 0.02 | 0.30 | 1.40 | 0.01 | 0.20 | 1.00 | 0.05 | 0.05 |
| 2007 | 0.39 | 0.30 | 0.01 | 0.30 | 3.80 | 0.19 | 1.10 | 1.00 | 0.05 | 0.05 |
| 2007 | 0.65 | 0.40 | 0.02 | 0.80 | 2.30 | 0.02 | 1.00 | 0.00 | 0.05 | 0.05 |
| 2008 | 0.68 | 0.40 | 0.02 | 0.80 | 12.70 | 0.02 | 0.60 | 0.00 | 0.05 | 0.05 |
| 2008 | 0.74 | 0.40 | 0.01 | 1.00 | 1.30 | 0.01 | 0.90 | 0.00 | 0.05 | 0.05 |
| 2008 | 0.47 | 0.42 | 0.01 | 0.50 | 6.30 | 0.05 | 0.70 | 1.00 | 0.05 | 0.05 |
| 2008 | 0.68 | 0.57 | 0.01 | 0.20 | 2.00 | 0.01 | 0.70 | 1.00 | 0.05 | 0.05 |
| 2009 | 0.73 | 0.50 | 0.01 | 0.10 | 1.30 | 0.02 | 0.80 | 0.00 | 0.05 | 0.05 |
| 2009 | 0.36 | 0.57 | 0.01 | 11.00 | 3.00 | 0.11 | 0.70 | 0.00 | 0.05 | 0.05 |
| 2009 | 0.60 | 0.50 | 0.00 | 0.10 | 1.10 | 0.00 | 0.80 | 0.00 | 0.05 | 0.05 |

Blank: No data were reported.