Chemical Contaminants in Lake Simcoe and its Tributaries

Lake Simcoe Region
conservation authority

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Executive Summary

In 2015, a study was undertaken to investigate levels of chemical contaminants in the surface water and sediments of Lake Simcoe and its tributaries. The contaminants included in this study were chosen based on historical use within the watershed, previous research undertaken (such as the LSRCA 2004 study), and literature from similar areas in the Great Lakes Region. As such, this study included: petroleum hydrocarbons (or PHCs); polycyclic aromatic hydrocarbons (PAHs); phenols; metals, including chromium and mercury; organochlorine pesticides (OCPs), including DDT and its metabolites; neutral chlorinated compounds (NCCs), and polychlorinated biphenyls (PCBs).

In terms of PHCs, none were detected in surface waters of the lake or tributaries, but sediments had some high values related to Fraction 4G. No PHC guideline values currently exist but one site in Mill Creek (Orillia) had a concentration that was 11 times higher than the average of other tributary sites. In the lake, high PHCs were present in the lower East Holland River and in shallow water off Barrie. PAHs were not often detected in surface waters, but high results were found in sediments at Mill Creek in Orillia, the outlet of the Holland Marsh, and the East Holland River downstream from Aurora and Newmarket. In Lake Simcoe, high PAHs in sediment were found in the shallow and deeper water off Barrie. Although no NCCs were detected at our study sites, phenols exceeded guideline values at Colbar Marsh and the deepwater lake site near Barrie. At the shallow water site off Barrie, PCB concentrations exceeded guideline values.

Of more concern were the presence of OCPs and metals in the Lake Simcoe Watershed. OCPs were mostly found in, and downstream of, areas of intense agricultural use (e.g. Holland Marsh and other polders) where they were used extensively as pesticides in the mid-20th century. Among OCPs, the presence of DDT, and its metabolites DDD and DDE, are of concern in that the highest concentrations recorded in Ontario were found. DDT, DDD, and DDE are very persistent and can have large impacts to foodwebs, especially to top-level predators. Heavy metals (esp. cadmium, copper, arsenic, and zinc) were found in areas with heavy industrial uses (particularly Mill Creek in Orillia), but the presence of chromium is of special concern in the East Holland River, linked to the locations of former leather tanneries in Aurora and Newmarket.

Generally, the contaminants recorded in the Lake Simcoe Watershed are the result of non-point anthropogenic sources (e.g. automobile exhaust, fossil fuel combustion) and specific areas of industrial, urban, and agricultural land-use activities (e.g., pesticides). Although some contaminants may be linked to current uses (e.g. PHCs, PAHs, phenols), others are likely legacy contaminants (i.e. DDT and chromium) from historical activities. Overall, it is recommended that regular monitoring of specific contaminants (e.g. DDT and metabolites, chromium, heavy metals) be undertaken more frequently. Sampling should target areas of guideline exceedances such as urban centres (Aurora, Barrie, and Newmarket) and intensive agricultural areas (Holland Marsh and other polders). More frequent and targeted sampling will aid in better evaluating our understanding of changes in chemical contaminants, including decreases or increases in concentration, movement through the watershed, and the potential risks to aquatic organisms or human health.

Introduction

The sediment and surface water of aquatic systems can become polluted with chemical substances, or contaminants, originating from both natural and/or anthropogenic sources. Some of the anthropogenic sources of contaminants to the environment include combustion activities (e.g., burning of fossil fuels), pest control including insecticides and herbicides, a variety of industrial practices and the manufacture and use of materials like plastic. The many different uses of these chemicals in our society are as diverse as the number of individual chemicals.

These contaminants can pose a substantial threat to the health of aquatic ecosystems. Exposures to contaminants can reduce environmental quality, especially in benthic sediment habitats. These contaminants have toxic potential, bioaccumulate within organisms, and biomagnify through the food web [as listed in numerous factsheets by Canadian Council of Ministers of the Environment (CCME), 2014]. It is essential that people understand the sources and effects of contaminants to aquatic systems to enable them to better protect the environment, while staying within reasonable confines of the economy (Manahan, 1994).

The use of many chemicals recognized as environmental contaminants have been banned or highly restricted in Canada and Ontario through government regulations and international treaties. For example, the Stockholm Convention (2008) is a global treaty established to protect the environment (and human health) from persistent organic pollutants (POPs). Listed in the Convention for discontinued use are DDT and other organochlorine pesticides.

Two major types of chemical contaminants to aquatic systems are trace organic chemicals and trace elements (Manahan, 1994). The former, trace organic chemicals, are compounds that contain carbon in their structure and include phenols, pesticides, petroleum wastes and polychlorinated biphenyls (PCBs). The second type, trace elements, includes trace and heavy metals, such as mercury, lead, chromium, and others. These two types of contaminants are discussed in more detail below.

Trace organic chemicals:

Organic compounds often have low solubility in water (i.e., hydrophobic) and high solubility in lipids (i.e., lipophilic). These properties can result in bioaccumulation of these compounds in the lipid-rich tissue (e.g. fatty tissues) of organisms. Trace organic chemicals can also build-up in areas with high amounts of organic material, such as sediments, in aquatic environments (Chaudhuri et al., 2017). Resuspension of these contaminants can occur when sediments are disturbed, such as during high flow events, transporting these compounds to other water bodies downstream.

Some organic contaminants are termed “legacy” because they are no longer being actively discharged to the environment yet continue to persist in the environment over long periods. Their chemical structures (containing carbon rings) are hard to break down through natural processes such as biodegradation. They are also known as persistent organic pollutants (POPs) and include halogenated hydrocarbons, such as PCBs, and organochlorine pesticides (OCPs) such as DDT. Often, OCPs are associated with areas of intensive agriculture as they were used extensively as herbicides, insecticides, and fungicides in Canada starting ~ 1940-1950s until the 1960-70s.

Other organic compounds exist in the environment from a variety of current and legacy sources. Often, they are associated with urbanized or industrial areas, but can also occur in agricultural areas. Examples of such compounds include polyaromatic hydrocarbons (PAHs) and petroleum hydrocarbons (PHCs) that are considered ubiquitous in the environment because of the many human activities that produce them. Unfortunately, these contaminants can reach levels that are of concern for aquatic ecosystems.

Persistent chemicals are of greatest concern, but others that degrade more readily can still be problematic when there is a continuous source. Phenols are soluble and degrade readily in the environment but there are many current and constant sources, especially from industry (e.g., pulp and paper mills, synthetic product manufacture) and sewage treatment.

Trace elements:

Metals occur naturally, distributed in rocks, soils, and water on the earth’s surface, often in the form of minerals or other multi-element complexes. Metals are extracted, used for anthropogenic purposes, and are re-introduced into the environment from many sources, such as industrial wastes, sometimes at levels that can impact plant and animal life. Heavy metals are metallic elements that have a relatively high density and are toxic at low concentrations, such as mercury and lead. Some heavy metals are essential elements for biological processes (e.g., iron), while others are toxic (e.g., cadmium). Both types of heavy metals can cause adverse effects in aquatic ecosystems under certain conditions. Trace metals occur at very low levels in the natural environment and include elements such as copper and zinc. As with heavy metals, some trace metals are essential to living things, but can be toxic in greater amounts.

The speciation, or changing molecular form of a metal, and whether a metal is in a dissolved or particulate phase, can dictate its bioavailability, bioaccumulation, toxicity, mobility and persistence in aquatic systems. For example, chromium (Cr) exists primarily in two species, trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) oxidations states. The former is non-toxic and essential for the growth of organisms, whereas hexavalent chromium is toxic and carcinogenic. Chromium-based compounds can be used in the tannery industry (where animal hides are tanned or processed into leather) to stabilize leather. Historically, environmental pollution has been associated with these facilities, and chromium (including toxic Cr^{6+}) and other metals can be found at high concentrations in aquatic systems adjacent to or downstream of tanneries, often long after the tanneries have ceased operation.

Chemical Contaminant Sampling Program in the Lake Simcoe Watershed

Based on current and historical land uses in the Lake Simcoe Watershed, there is a potential for trace organic or trace elements to cause adverse effects on aquatic life. As such, in 2004 the LSRCA initiated a sampling program (LSRCA, 2006) that would assess the presence of a range of organic and metal contaminants in surface water and sediments to identify areas where concentrations were exceeding relevant guidelines. This program was continued in 2015 and expanded to include samples from the lake itself. Building on the 2004 study results, the 2015 study targeted specific areas that were identified as a concern (by LSRCA, 2006) with additional sites sampled in and around these areas, as well as re-sampling some 2004 sites to capture changes over time. The areas sampled in 2015 focused on the larger urban centres in the watershed (Aurora, Barrie, Newmarket, Orillia), areas of intensive agriculture (vegetable polders) and naturalized areas to serve as a reference.

Another target area for this study was the East Holland River, specifically for chromium contamination associated with two historic tanneries: Collis Leather and Davis Leather. Collis Leather was in operation from 1910 to 1988 in the town of Aurora next to the Tannery Creek, an upper branch of the East Holland River. The Davis Leather Company was located on Davis Drive in Newmarket (now known as the “Tannery Mall”), adjacent to the East Holland River, and in operation from 1905 to 1962.

Study Objectives

This study evaluated the levels of chemical contaminants in the surface water and sediments of Lake Simcoe and its tributaries with the specific objectives of:

- Investigating contaminants likely occurring in the Lake Simcoe watershed from suspected or known legacy or current use
- Identify areas where contaminants are unacceptably high (compared to sediment / water quality guidelines, if available), specifically targeting urban areas and areas of intensive agricultural activity
- Assessing the movement, spread, or change in levels of contaminants as identified through prior sampling or studies, including a comparison of the 2015 and 2004 sampling carried-out by LSRCA

The contaminants studied include petroleum hydrocarbons (PHCs), polycyclic aromatic hydrocarbons (PAHs), phenols, metals, organochlorine pesticides (OCPs), neutral chlorinated compounds (NCCs) and polychlorinated biphenyls (PCBs). While this list is not exhaustive, these were the contaminants deemed most likely to be detected in the Lake Simcoe Watershed based on historical use, previous research, and literature.

Methods

Sample Locations

Sites were selected in urban tributaries of Aurora, Barrie, Innisfil, Newmarket and Orillia. Agricultural tributary sites included West Holland River, with a focus on Holland Marsh and other polders, as well as the Maskinonge and Beaver rivers. Lake sites were chosen to complement these areas, being downstream or adjacent to them, in shallow (<20 m water depth) and deeper (>20 m water depth) in bays (i.e., Cook's, Kempenfelt, Shannon and Shingle bays), the main basin and also at boat-accessible sites in the Holland River). As potential reduced impact sites, less developed areas were assessed: Hawkestone Creek, lake areas adjacent to the Oro Creeks South Subwatershed, and near the mouth of the Talbot River. In total, 27 tributary sites and 12 lake sites were sampled (Figure 1).

In addition to the sites above, 20 sites were sampled for chromium along the East Holland River. These sites were located from approximately 600 m upstream (north) of the Collis Leather site in Aurora through Newmarket to Holland Landing (Figure 2).

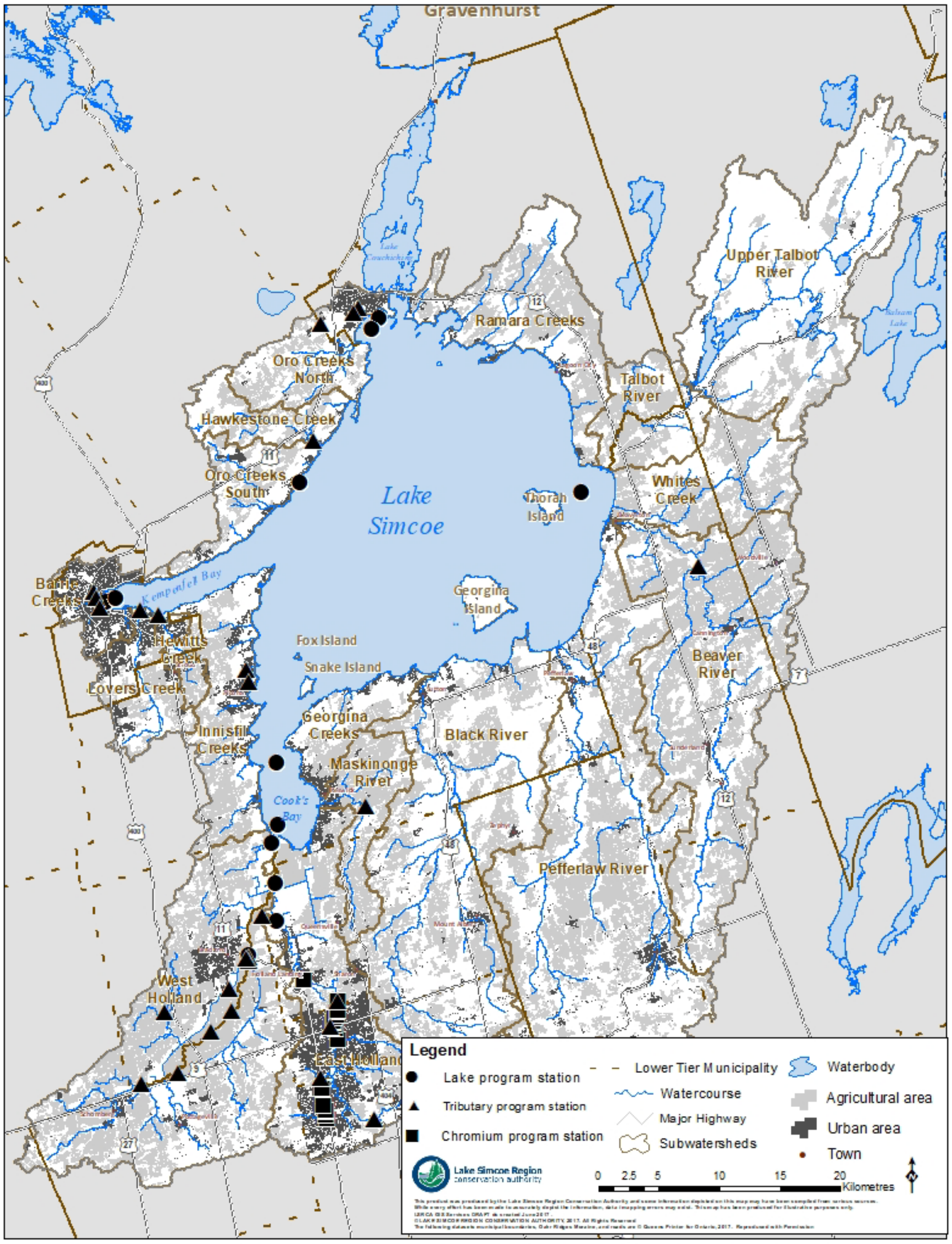

Figure 1. Map of the Lake Simcoe Watershed showing sample site used for the 2015 chemical contaminant study.

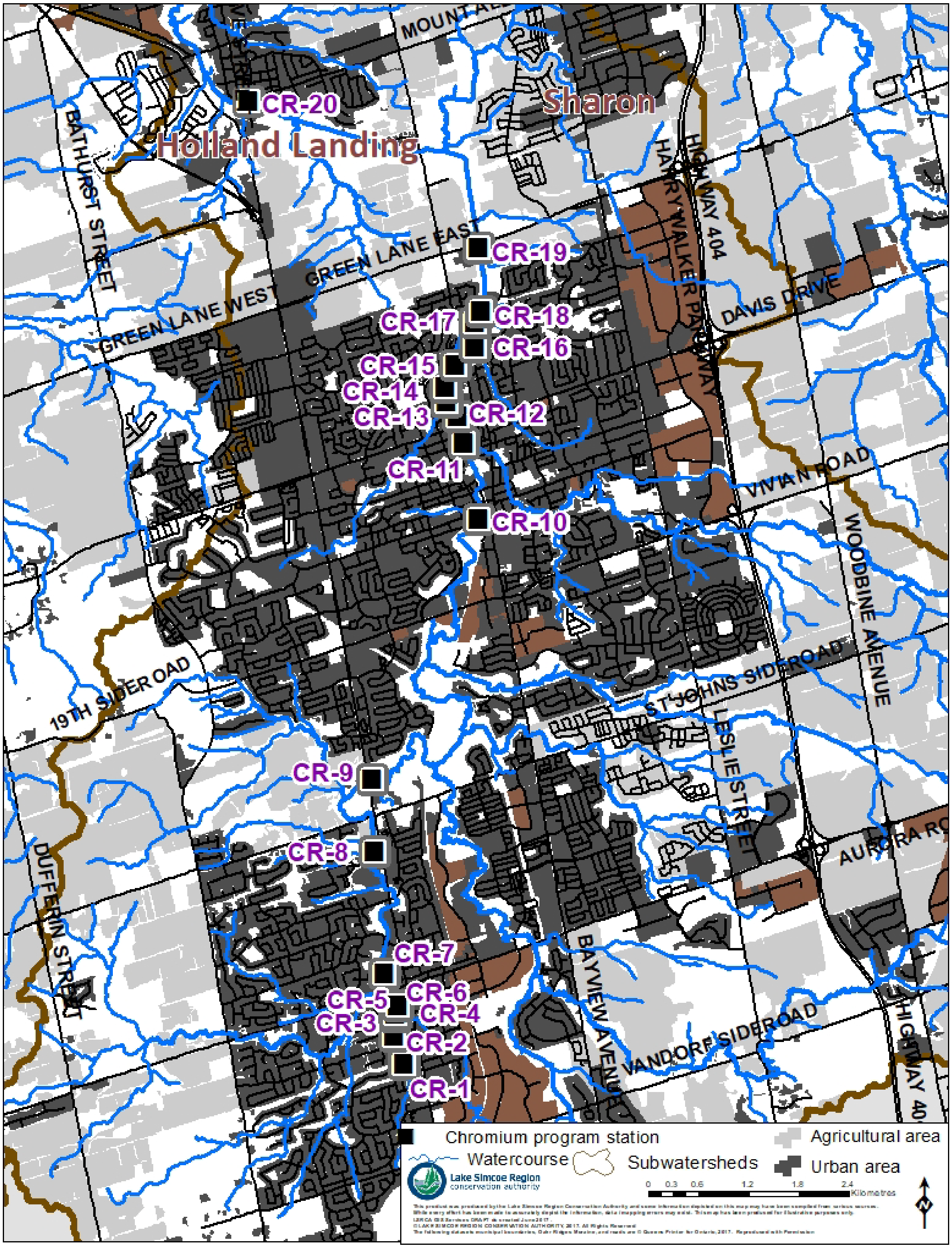

Figure 2. detailing sampling locations for chromium related to legacy contamination from closed tanneries in Aurora and Newmarket.

Sampling Period and Protocols

Tributary water samples were collected in 2015 on October 7 and 14 and November 13 and 19. Water was collected, unfiltered, using an extendable pole fitted with a 500-ml polyethylene (PET) bottle or, for chromium samples, a polypropylene (PPE) bottle provided by the analysis lab. Samples were kept chilled at 4°C until analysis. Sediment samples were collected on October 6-7 and October 13-14. Sampling for chromium occurred on October 16 and 20. Using a stainless steel Eckman Grab Sampler, the top 5-15 cm of sediment was collected at each site and scooped into a glass jar provided by the analysis lab. As with water samples, sediment was kept on ice at ~4°C for transport to the lab.

Lake surface water and sediment samples were collected on October 23, 26, 27, and November 3, 2015. Water was collected from a depth of 2 m (or 1 m for Holland River sites) below the surface using a Van Dorn Beta™ Horizontal Bottle Sampler (Wildco) and poured into PPE bottles supplied by the analysis lab. Sediment samples were collected at each site using a petite Ponar grab sampler (Wildco). As at tributary sites, sediment was placed in 500-ml glass jars. Both water and sediment samples were kept on ice at ~4°C for transport to the analysis lab.

Large pieces of organic debris (e.g., twigs, leaves, mussels) were removed from the sampled sediment. After the collection for each site, the dredge samplers were rinsed several times with source water, followed by rinses with distilled water.

Chemical analysis

Samples were analyzed for organic contaminants, heavy metals, and trace metals by Maxxam Analytics (Mississauga, ON). The detection limit mentioned in this document refers to the Reportable Detection Limit (RDL; Appendix C). Analyses were undertaken for petroleum hydrocarbons (PHCs), polycyclic aromatic hydrocarbons (PAHs), and metals (including chromium) for water and sediment samples; phenols (water samples only); and organochlorine pesticides (OCPs), neutral chlorinated compounds (NCCs), and polychlorinated biphenyls (PCBs) (sediment samples only).

Sediment and water quality guidelines

Results were compared to Provincial Water Quality Objectives (PWQOs; MECP, 2019a) and Canadian Water Quality Guidelines for the Protection of Aquatic Life (CWQGs; CCME, 2014). The PWQOs state a desirable level of water quality and were developed to protect and preserve aquatic life, and the recreational potential of surface waters within Ontario. The CWQGs were developed to protect aquatic species by establishing acceptable levels for substances, or conditions that affect water quality and are based on toxicity data for the most sensitive species of plants and animals found in Canadian waters.

Sediment results were compared to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CSeQGs; CCME, 2014) and the Table 1 Standards contained in the Soil, Groundwater and Sediment Standards for Use Under Part XV.1 of the Environmental Protection Act (MECP, 2019b). The CSeQGs protect aquatic organisms that live on or in lake or river. The Interim Sediment Quality Guidelines (ISQGs) and Probable Effects Levels (PELs) were used as comparative criteria. Sediment chemical concentrations below the ISQGs are not expected to result in any adverse biological effects. Concentrations above the PELs are expected to be frequently associated with adverse biological effects. Chemical concentrations between the ISQGs and PELs represent the range in which effects are occasionally observed. The use of these two values is a practical means of assessing potential toxic concerns at sites. For parameters where an ISQG or PEL guideline is not available the Table 1 Standards are utilized. The Table 1 Standards are adverse effects-based values that are within the range of measured background sediment and are considered to provide a level of ecosystem protection.

Results And Discussion

Petroleum hydrocarbons (PHCs)

PHCs, commonly known as fossil fuels, are found in numerous everyday products such as fuel (including gasoline and home heating) and for producing materials such as plastics, tires, fertilizers, and many other commonly used products (Petroleum.co.uk, 2015). Contamination from PHCs is one of the most common types of soil and groundwater pollution in Canada. Mixtures of PHCs can contain various constituents with a wide range of chemical structures and properties, which dictate their environmental impacts, including their distribution, bioavailability, toxicity and persistence. PHC mixtures typically have hundreds of components and it is impractical and impossible to measure each of these for toxic potential.

Analysis of PHCs separates results into “fractions” that are based on the number of carbons contained in different PHC compounds. These fractions have been identified by CCME (2001b) : Fraction 1 (6-10 carbon atoms, such as gasoline); Fraction 2 (10-16 carbons such as diesel, kerosene, and creosote; Fraction 3 (16-34 carbons, heavier diesel, lubricating oils, and polycyclic aromatic hydrocarbons (PAHs)); and Fractions 4 (34-50 carbons) and 4G (50+ carbon atoms) that include heavy lubricating and fuel oils and asphalt.

Fractions 2, 3, 4 and 4G were analyzed in this study. Fraction 2 is a semi-volatile group and can be soluble. Fraction 3 has PHCs of low volatility and solubility, and can contain PAHs. Fractions 4 and 4G are heavy with low solubility giving them a propensity to sink in water. Heavier PHCs have low volatility, don't degrade easily and bind with organic matter. With these characteristics, they tend to build-up in sediments.

Surface Water Results

PHCs were not above detectable levels in any water samples from the tributaries or lake in 2015 (see Appendix B: Table A-2a,b). In a previous study (LSRCA, 2006), PHCs (reported as Total Extractable Hydrocarbons (TEH), heavy diesel in fraction 3) were detected at Tannery Creek in Aurora (TS-9) during one rain event sample, with the source likely surface run-off.

Sediment Sample Results

Tributary sites:

In 2015, PHCs were detected in sediment from 14 of 27 tributary sites (Table 1a), mostly corresponding to urbanized or intensive agricultural land use areas. The highest levels of PHCs were found in Orillia and Newmarket, with other detections occurring in Barrie, Innisfil, and the vegetable polders. Most of the results (at eight of 14 sites) were for heavier fractions (F3 through F4G) of PHCs that are typical of non-point sources such as current and former industrial lands and the use of diesel fuel. One site that is downstream of a heavily industrialized area, Mill Creek in Orillia (TS-26), was the only site that had Fraction 2 PHCs (lighter hydrocarbons) above the detection limit.

Polder sites:

Four sites adjacent or downstream from polders had Fraction 3 PHCs only (TS-7, West Holland River; WH-6, Bradford Marsh; WH-8, Holland Marsh; and WH-10, Colbar Marsh). Fraction 3 are associated with heavier diesel, lubricating oils, as well as polycyclic aromatic hydrocarbons.

Comparison to 2004 samples:

The 2015 sample results had PHCs similar to the 2004 samples, although slightly lower. Differences between years could be due to heterogeneity of sediment at the sites, differences in detection limits between the two years and other laboratory quality controls (i.e., moisture content of the sample), or perhaps declining concentrations at some sites.

Lake sites:

Results for PHCs in sediment for the lake sites are listed in Table 1b and are summarized below. PHCs were detected in sediment from eight of 12 sites. The highest levels (including Fractions 3 to 4G), occurred at the two sites near Barrie (B-LITT-14 and K-38) and one site in the East Holland River (EH-1). There were lower concentrations, having only fraction 3 PHCs, at other sites in the Holland River, Cook’s Bay, and at Shannon and Shingle bays near Orillia. At EH-1, the higher concentrations compared to upstream samples (TS-8, Green Lane, and TS-23, Western Creek, both in Newmarket Table 2a), which are closer to potential urban sources indicate the source may be historical or PHCs migrated downstream and accumulated through time.

Sediment samples from the nearshore site B-LITT-14 had elevated levels of Fraction 4G that were much higher than those recorded in the contributing tributaries (TS-28, -29 and -30; Table 2a). There is the possibility that there may be a direct-to-lake source from the nearby shoreline as this area was a historic rail yard. Site K-38 is ~1 km offshore and at a greater depth (>30m compared to 8.8 m at B-LITT-14) that also had heavy fraction (4G) PHCs. These results may be due to offshore currents moving sediment PHCs down a steep slope from the nearshore to deeper depths in Kempenfelt Bay. Despite the high levels of PHCs recorded at Mill Creek in Orillia (TS-25, -26 and -27; Table 2a), the downstream lake sites (B-LITT-08 and N-32) had only low levels of Fraction 3 PHCs suggesting that the heavier hydrocarbons are not reaching the bay or may otherwise have become dissipated in the bay area. Lake sites adjacent to more naturalized areas (i.e., near the Oro Creek South Subwatershed and Thorah Island) did not have any PHCs detected.

PHC Sampling Summary:

PHCs were not detected in the surface water of tributary or lake sites in 2015, compared to one detection after a rain event in 2004. In sediment samples, PHCs were detected in 22 of 39 sites in 2015. The highest levels of PHCs in tributaries were at sites in Barrie, Innisfil, Newmarket and Orillia that are currently urbanized, or have a history of urban or industrial activity. At some polder sites, PHCs of Fraction 3 were recorded, which could be related to farming practices.

Although PHCs were not observed at high levels in the surface waters of the Lake Simcoe Watershed, they are present in some sediments and could be considered as a potential source of contamination to surface waters. Guidelines are not currently available for PHCs in sediment, but with high levels of PHCs in some areas there is a potential for adverse effects to aquatic systems and biological communities.

Table 1a. PHC concentrations (µg/g dry weight) from 2015 sediment sampling of the tributary sites and b) the lake sites.

a) Tributary sites (by subwatershed)	East Holland			Oro North			Barrie		Hewitts	Innisfil	West Holland and Polders			
PHC fraction	**TS-8**	**TS-22**	**TS-23**	**TS-25**	**TS-26**	**TS-27**	**TS-29**	**TS-30**	**TS-31**	**TS-33**	**TS-7**	**WH-6**	**WH-8**	**WH-10**
F2 (C10-C16 Hydrocarbons)					73									
F3 (C16-C34 Hydrocarbons)	83	80	120	140	2200	140	60	76	100	57	290	230	370	270
F4 (C34-C50 Hydrocarbons)	94		180	280	1000	100	62	94		86				
F4G-sg (Grav. Heavy Hydrocarbons)	860		1300	1700	4300	680	460	480		530				
Total PHCs	1037	80	1600	2120	7573	920	582	650	100	673	290	230	370	270
Blank = non detect														

Table 1b. PHC concentrations (µg/g dry weight) from 2015 sediment sampling of the lake sites.

b) Lake sites	**Holland River**			**Cook's**		**Kempenfelt**		**Shannon**	**Shingle**
PHC fraction	**WH-3**	**EH-1**	**HR-2**	**C-1**	**C-6**	**BLITT-14**	**K-38**	**BLITT-08**	**N-32**
F2 (C10-C16 Hydrocarbons)									
F3 (C16-C34 Hydrocarbons)	280	440	310	130	160	410	310	110	62
F4 (C34-C50 Hydrocarbons)		210				250	190		
F4G-sg (Grav. Heavy Hydrocarbons)		4000				6000	970		
Total PHCs	280	4650	310	130	160	6660	1470	110	62
Blank = non detect									

Polycyclic aromatic hydrocarbons (PAHs)

PAHs are multiple aromatic rings containing only carbon and hydrogen atoms. The sources of PAHs to the environment include combustion from gasoline and diesel engines, industrial emissions, as well as the burning of fossil fuels or organic material. The contamination of soils and sediment in Canada by PAHs is widespread because of the near ubiquitous nature of these major sources (CCME, 2010; CCME, 1999e). PAHs are relatively non-volatile, are poorly soluble, and are removed from the water column due to association with particulates. Through settling, PAHs can build up in the sediment over time.

In 2015, and the 2004 study, various PAH constituents were observed in the surface waters and sediments of Lake Simcoe and its tributaries, mostly associated with urbanized areas. Due to their low solubility, PAHs tend to be more often found in sediment, but they can be present in surface water.

Surface Water Results

PAHs were found in the surface water of 4 of 34 sample sites in 2015. Of the 19 PAH constituents analyzed, only Benzo(a)pyrene had detectable concentrations and was present at two tributary (TS-26, Mill Creek at James St. West in Orillia at 0.014 μg/L; and TS-29, Bunkers Creek in Barrie at 0.011 μg/L) and two lake sites (EH-1, lower East Holland River at 0.013 μg/L and B-LITT-08, Shannon Bay near Orillia at 0.011 μg/L). Despite being at detectable levels, the concentrations recorded for Benzo(a)pyrene were below the EC guideline (0.015 ug/L).

Site TS-1 (Mill Creek, Orillia) had PAH constituents detected in 2004, and in 2015 at TS-26, a nearby site on Mill Creek. Tannery Creek in Aurora (T-9) had PAH constituents detected in 2004, but not 2015, at levels that were above guidelines, but this sample was collected during a rain event. PAH constituents recorded at TS-9 in 2004 were benzo(b/j)fluoranthene, benzo(g,h,i)perylene, chrysene, fluoranthene, indeno(1,2,3-cd)pyrene and pyrene. For the majority of PAH constituents, the 2004 laboratory detection limits were lower than in 2015, which influenced some direct comparison between the two studies.

Sediment Sample Results

Tributary sites:

Of the 27 tributary sites sampled for sediment, 24 had PAHs detected (Table 2). The majority of sites (70%) had at least one PAH constituent that exceeded available guidelines. The constituents that most commonly exceeded the guidelines in the tributary sites were 2-methylnaphthalene, benzo(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene, phenanthrene and pyrene. Although there is no guideline for benzo(b/j)fluoranthene, it occurred in most of the sites. The highest levels of PAHs were found at Mill Creek (TS-26) in Orillia and at sites in the East Holland River (TS-8 and TS-23), the West Holland River (TS-7), Innisfil (TS-33) and Barrie (TS-29 and TS-30). Most of these sites have a significant area of urban or industrial land uses. Almost every PAH constituent was found in samples from TS-26, TS-7 and TS-8, often exceeding guideline concentrations that are associated with adverse biological effects.

Polder sites:

All sites in and around the polders had some PAHs recorded. One of these, Bradford Marsh (WH-6), had the highest content of PAHs among polders with the majority of the PAH constituents exceeding ISQG guidelines. The Inner Canal sites of the Holland Marsh (WH-5, WH-7, WH-8, WH-9) and outer canal (North Canal, WH-4) had varying amounts of total PAHs, with a variety of PAH constituents present and several exceedances of the ISQG guidelines. It is interesting to note that TS-7, just downstream of both the Holland and Bradford Marsh outlets, had much higher PAH content than these polder sites. 2-methylnaphthalene was above the ISQG guideline at all of the “WH” sites, with a level greater than the PEL at Colbar Marsh (WH-10).

Note about PAHs and PHCs:

The levels of total PAHs generally correspond with total PHCs for the sampled sediment, likely due to both contaminants having similar sources (fossil fuels, lubricant oils, etc.). All sites followed this pattern to some extent, except for TS-7 (having very high PAHs but only moderate PHCs) and TS-25 (having substantial PHCs but only moderate PAHs). These different patterns may be due to the two sites having different sources of PHCs and PAHs.

Comparison to 2004 samples:

Of the 2015 sample sites, nine were sampled in 2004. Two of these sites, TS-7 (West Holland River) and TS-8 (East Holland River), had very high PAH content in 2004, although almost every PAH constituent was higher in 2015. There were more total PAHs and more constituents recorded at the polder sites in 2015 as compared to 2004, particularly the North Canal (WH-4) of Holland Marsh. Hawkestone Creek (TS-2) and Maskinonge River (TS-10) had no PAHs reported in 2004 but had several guideline exceedances in 2015. Conversely, Tannery Creek (TS-9) had more above guideline PAH concentrations in 2004 than in 2015, and the Beaver River (TS-17) had some above guideline concentrations in 2004, but no PAHs recorded at a downstream site (TS-24) in 2015.

Other studies of PAHs in the region:

In a study of sediment PAH concentrations across southern Ontario in 2008-9, Chaudhuri et al. (2017) found that elevated concentrations of total PAHs occurred in areas of higher population density and urban activity. Our highest (2015) level at TS-26 in Orillia (20,570 µg/kg) would have ranked fourth highest in comparison to the southern Ontario reports (Chaudhuri et al., 2017b; unpublished dataset). From 17 sites in the Lake Simcoe Watershed sampled by Chaudhuri et al. (2017), which included a suite of land uses (natural, agricultural and urban), the highest levels of PAHs in the watershed were found in the East Holland River and Uxbridge Brook (2,522 and 1,960 µg/kg, respectively). In comparison our East Holland tributary results ranged from 150-5,564 µg/kg of total PAHs, and 837-1,017 µg/kg north of the confluence of the East and West branches of the Holland River.

Lake sites:

Ten of 12 lake sites had exceedances of guideline concentrations for PAHs (Table 2). The highest levels were found near Barrie in Kempenfelt Bay (B-LITT-14, K-38) where all 18 PAH constituents were present at concentrations above the relevant guideline. Although the levels of PAHs in nearby tributaries draining into Kempenfelt Bay were almost as high, the situation could be similar to PHCs in this area, where lake currents / sediment transport likely moved contaminants into the deeper offshore basin.

Other records above guideline values were reported at sites in the Holland River (EH-1, HR-2, HR-6, WH-3), that are downriver from urban and intensive agriculture areas (including Newmarket, Aurora, Bradford and the vegetable polders), which had moderate to high levels of PAHs in tributary samples. As in the tributary samples, there was a correspondence of PAH and PHC levels of the sediment samples, with the more naturalized areas, such as B-LITT-09 in Oro-South having the lower levels of these contaminants than sites near urban areas, such as K-38 in Kempenfelt Bay. The constituents that most commonly exceeded the guidelines in the lake sites were 2-methlnaphthalene, benzo(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene and pyrene, similar to the tributary sediments.

PAH Sampling Summary:

In surface water samples PAHs were detected at levels that could potentially cause adverse effects on aquatic ecosystems. From our 2004 and 2015 sampling, PAHs in surface waters were observed mostly in association with urbanized areas (Aurora, Barrie, Newmarket, Orillia), and some intensively agricultural areas. In sediment samples, PAHs were detected at most lake and tributary sites sampled in 2015 (36 out of 39 sites in total). The highest levels of PAHs observed in the tributaries were in Barrie, Innisfil, Newmarket and Orillia. Not only are these areas of current intensive urbanization but some have been historically active centres as well. Sites associated with the vegetable polders had PAHs at levels exceeding guidelines.

Table 2a. PAH concentrations (µg/kg dry weight) from 2015 sediment sampling of the tributary sites

a) TRIBUTARY SITES	**ISQG**	**PEL**	**Table 1**	Hawke.	Mask.	East Holland				Oro North			Barrie			Hewitts	Innisfil
PAH constituent	**(µg/kg)**	**(µg/kg)**	**(µg/kg)**	**TS-2**	**TS-10**	**TS-8**	**TS-9**	**TS-22**	**TS-23**	**TS-25**	**TS-26**	**TS-27**	**TS-28**	**TS-29**	**TS-30**	**TS-31**	**TS-33**
1-Methylnaphthalene						7					130						
2-Methylnaphthalene	**20.2**	**201**				8					220	16				12	
Acenaphthene	**6.71**	**89**		13		33					230	14		8	28		8
Acenaphthylene	**5.87**	**128**				14	10										
Anthracene	**46.9**	**245**	**220**	13		66	6				220	27		44	59		42
Benzo(a)anthracene	**31.7**	**385**	**320**	46	19	390	29	11	230	36	1300	63	6	270	250		170
Benzo(a)pyrene	**31.9**	**782**	**370**	42	16	410	42	14	290	38	2300	63	8	290	260		180
Benzo(b/j)fluoranthene				58	20	570	61	19	400	46	3400	90	10	400	350	16	240
Benzo(g,h,i)perylene			**170**	22	10	250	30	11	180		2300	48	8	200	170	11	120
Benzo(k)fluoranthene			**240**	23	7	210	22	8	150		1000	32		150	110		77
Chrysene	**57.1**	**862**	**340**	48	15	410	35	11	230	30	1200	70	7	310	240	11	160
Dibenz(a,h)anthracene	**6.22**	**135**	**60**	6		65	7				520			39	33		24
Fluoranthene	**111**	**2355**	**750**	140	34	1300	81	29	420	77	2100	180	20	900	770	24	480
Fluorene	**21.2**	**144**	**190**	13		41					170	17		16	26		14
Indeno(1,2,3-cd)pyrene			**200**	27	13	300	35	12	220		2500	52	7	230	200		130
Naphthalene	**34.6**	**391**									180	11					
Phenanthrene	**41.9**	**515**	**560**	120	6	600	39	11	57		1000	130	7	380	400		260
Pyrene	**53**	**875**	**490**	100	26	910	64	24	350	71	1800	140	16	650	590	18	360
Total PAHs				**671**	**166**	**5584**	**460**	**150**	**2527**	**298**	**20570**	**953**	**89**	**3887**	**3486**	**92**	**2265**

Blank = non detect

> ISQG or Table 1

>PEL

Table 2b. PAH concentrations (µg/kg dry weight) from 2015 sediment sampling of the lake sites.

b) LAKE SITES	**ISQG**	**PEL**	**Table 1**	Holland River				Cook's		Kempenfelt		Main (W)	Shannon	Shingle	Main (E)
PAH constituent	**(µg/kg)**	**(µg/kg)**	**(µg/kg)**	**EH-1**	**HR-2**	**HR-6**	**WH-3**	**C-1**	**C-6**	**BLITT-14**	**K-38**	**BLITT-09**	**BLITT-08**	**N-32**	**BLITT-05A**
1-Methylnaphthalene										33	20				
2-Methylnaphthalene	**20.2**	**201**		64	120	140	110	40	48	80	60	6	22	21	11
Acenaphthene	**6.71**	**89**					17			26	22				
Acenaphthylene	**5.87**	**128**								100	95				
Anthracene	**46.9**	**245**	**220**	19			68			130	110				
Benzo(a)anthracene	**31.7**	**385**	**320**	72	44	34	150		30	440	380		25	10	
Benzo(a)pyrene	**31.9**	**782**	**370**	110	77	59	130		52	630	580		40	19	
Benzo(b/j)fluoranthene				210	140	110	200	17	100	830	800		60	31	
Benzo(g,h,i)perylene			**170**	150	100	82	97	13	78	530	550		39	21	
Benzo(k)fluoranthene			**240**	72	43	32	79		32	280	260		17		
Chrysene	**57.1**	**862**	**340**	110	65	48	170		37	410	340		39	19	
Dibenz(a,h)anthracene	**6.22**	**135**	**60**	21			19			110	100				
Fluoranthene	**111**	**2355**	**750**	200	140	110	310	21	90	830	770		43	20	
Fluorene	**21.2**	**144**	**190**				23			33	32				
Indeno(1,2,3-cd)pyrene			**200**	140	93	73	100	13	85	540	550		47	25	
Naphthalene	**34.6**	**391**								40	25				
Phenanthrene	**41.9**	**515**	**560**	51	35	29	190		30	330	280		13		
Pyrene	**53**	**875**	**490**	190	160	120	270	18	75	800	740		37	19	
Total PAHs				**1409**	**1017**	**837**	**1933**	**122**	**657**	**6172**	**5714**	**6**	**382**	**185**	**11**

Blank = non detect

> ISQG or Table 1

>PEL

Phenols

Phenols are organic compounds composed of benzene rings with various configurations and numbers of hydroxyl groups. Phenols are commonly used to produce resins that are used in the construction, automotive, and appliance industries; but are also found in automobile exhaust, pesticides and household disinfectants. Phenols do not tend to persist or accumulate in the environment. They are most dangerous and concerning when found in large quantities (such as from industrial spills) or if there is a constant source. They are highly soluble in water, where they are leaching from soils and sediment. Thus, phenols sampling focused on surface water in 2015. The analytical method used (4AAP Phenols) gives the minimum phenol content of the sample. The results from this method, together with the PWQO (that is based on this same method) are meant to be used as a screening tool.

Phenols were detected in 2015 at one tributary site (WH-10; Colbar Marsh) and one lake site (K-38; Kempenfelt Bay). The level of phenols at the roadside ditch beside a farm within Colbar Marsh (3.1 µg/L) was greater than the PWQO guideline (1.0 µg/L) and the phenol concentration at the lake site was equal to the guideline.

In the 2004 study, phenols were present at eight of 21 sample sites, with seven of these sites in urbanized areas (Aurora, Barrie, Cannington, Newmarket, Orillia, Uxbridge). Five of these eight sites were sampled in the 2015 study, with an additional two sites in close proximity to 2004 sites. In 2015, phenols were not reported at any of these common sites.

Organochlorine Pesticides (OCPs)

Organochlorine pesticides are synthetic chemical compounds used as herbicides, insecticides, and fungicides because of their potent toxicity to pests. Various OCP compounds were used extensively in Canada starting in the 1940s or 1950s, but were later banned or highly restricted. Their residues in soils and sediment from historical use still contribute to “legacy” contamination. Most OCPs have an affinity for organic matter and are hydrophobic, typically accumulating in sediments of aquatic systems. Because of this affinity for sediments, and difficulty sampling OCPs from water, only sediment samples were collected for this part of our investigation. Twelve tributary sites and nine lake sites were sampled for OCPs, targeting areas of intensive agriculture including the vegetable polders with their downstream river and lake areas (Figure A-4).

Tributary sites:

At all eight sites that were within, adjacent to, or downstream of the vegetable polders, the following OCPs were recorded at levels above sediment guidelines: aldrin, eldrin, endosulfan compounds, and DDT and metabolites (Table 3).

Aldrin and dieldrin

Aldrin and dieldrin were observed at all polder sites (WH-5 to WH-10) at concentrations exceeding the Table 1 guidelines (MECP, 2019b). In the case of dieldrin, its concentration exceeded the PEL by over four times the limit at one site (WH-5), which also had aldrin and dieldrin in the 2004 study. Outside of the Holland Marsh, these pesticides were below the detection limit at downstream sites TS-7 and WH-3. In a study by Chaudhuri et al. (2017), sediment samples collected in 2008-9 from the Holland Marsh contained the highest level of ∑Drin (sum of aldrin, dieldrin and endrin; 31.5 µg/kg) in the province, with a level similar to those observed by LSRCA in the 2015 sampling.

Endosulfan compounds

Endosulfan I and/or II were present at Colbar Marsh (WH-10) and Inner Canal sites of the Holland Marsh (WH-7, WH-8 and WH-9) although not at the outlet site (Bradford Pumping Station #2; WH-5). Endosulfan sulfate was observed at all polder sites (WH-5 to WH-10). In 2004, endosulfan I and II (but not endosulfan sulfate) were present at WH-5, opposite to 2015. At North Schomberg (WH-1), endosulfan sulfate was present in 2004, but not 2015. The endosulfan compounds measured in the ditch beside Colbar Marsh (WH-10) yielded concentrations higher (333 µg/kg) than any found in Ontario by Chaudhuri et al. (2017).

DDD, DDE and DDT

DDT and/or its metabolites (DDD and DDE) were found at all polder sites (WH-5 to WH-10), as well as at the North Canal (WH-4) and West Holland River (TS-7) downstream of the Holland Marsh. The total sum of DDT isomers (o,p'- and p,p' -DDT) exceeded the PEL guideline at all of these sites except for WH-4 which did not indicate any DDT specific isomers. The site at Colbar Marsh had the highest level of total DDT (1200 µg/kg), almost seven times higher than the average found in the Holland Marsh (146 µg/kg). The lowest concentration (11 µg/kg) was found downstream of Holland Marsh polder (TS-7) although this still exceeds guidelines. All polder sites (TS-7 and WH4 to WH-10) had high levels of total DDD and total DDE that exceeded the PELs. The DDD concentration measured at Colbar Marsh (2600 µg/kg) was over 300 times the PEL (8.51 µg/kg), with DDE also extremely high (2800 µg/kg) at 560 times the PEL (6.75 µg/kg). The Inner Canal sites of the Holland Marsh also returned very high DDD and DDE concentrations although slightly lower than at the Colbar Marsh.

Comparing the 2004 and 2015 studies, some signs of possible DDT degradation were observed in the 11 year period although these differences could also be attributed to heterogeneity of the sediments. The West Holland site (TS-7) did not have any DDD detected in 2004 whereas concentrations in 2015 were above the PEL. At the outlet of the Holland Marsh (Bradford Pumping Station #2; WH-5) levels of DDT and its metabolites were higher in 2015, implying a movement from the Inner Canal. DDT was observed in 2004, but not in 2015, at WH-4, which may be due to the cleanout, construction, and relocation of the North Canal between these sampling periods (HMDSJMSB, 2017). Alternatively, this result could imply the breakdown of DDT to its metabolites, as DDD and DDE were observed in both 2004 and 2015.

Notes about DDT in the Holland Marsh

Historically, DDT use in the Holland Marsh was reported as two to four DDT sprays per year occurring for 10-15 years, ending with the ban in 1970 (Miles and Harris, 1978). Concentrations of DDT, DDD, and DDE recorded in the polders are considered very high according to measurements from other agricultural areas in the U.S. and Canada (Chaudhuri et al., 2017; CCME, 1999d). Break down of DDT and its metabolites may be slower in the Holland Marsh compared to other impacted sites because the muck soils may sequester DDT, inhibiting biodegradation (Aigner et al., 1998). Lembcke et al. (2011) concluded that fish at higher trophic levels may be taking up enough DDT in the vicinity of the Holland Marsh to exceed Canadian consumption guidelines for wildlife of fish tissues (CCME, 1999g; Lembcke, 2011), thus posing a risk to piscivorous birds and mammals. In most cases, DDT slowly breaks downs into DDE and DDD (ATSDR, 2002a). As most of the total DDT in the Holland Marsh is composed of DDE and DDD (94-98%), these results suggest that this DDT is likely from historical use. The Colbar Marsh site had very high levels of DDT and the proportion of other metabolites was slightly lower (82%), suggesting either a more recent use of DDT, or slower degradation to metabolites due to the specific soil conditions, less movement of sediment through runoff events because of the ditch system, and/or higher original concentrations.

In the Holland Marsh and the other polders, DDT and metabolites are bound to sediments and can be transported during flow events that mobilize sediment. The majority of movement of DDT and its metabolites through the Holland River system is likely due to sediment being transported during polder pump-off events or other agricultural runoff. The concentrations of DDD and DDE downstream of the polders are much lower than sites within the polders, though still in exceedance of the guidelines. Lower levels of DDE were detected further downstream in Cook’s Bay of Lake Simcoe, implying that the degradation products of DDT are being slowly transported through the system. Atmospheric deposition is likely not a significant source of DDT to the Lake Simcoe Watershed, as DDT was not recorded in the watershed except in and around the polders, where historic spraying application of DDT is known to have occurred.

Chlordane compounds:

Chlordanes were not detected in 2015 at any sites. In 2004, Chlordane (as a-Chlordane) was only found at the Holland Marsh outlet (WH-5). Chaudhuri et al. (2017) found higher levels of chlordanes in the Lake Simcoe watershed, often exceeding the ISQG guidelines in more urbanized areas (e.g. Aurora and Uxbridge). They noted that this was common throughout the province, where chlordane, unlike other OCPs, was higher in areas of higher population density rather than agricultural areas.

Lake sites:

Nine lake sites were sampled for OCPs, including areas downstream of the vegetable polders (Holland River and Cook's Bay), and also Kempenfelt Bay and one site in the main basin of Lake Simcoe. Aldrin, dieldrin and endosulfan were not detected at lake sites.

DDD, DDE and DDT

DDE and/or DDD were detected at five sites in Cook's Bay and the Holland River (Table 3). The West Holland River site (WH-3) closest to the Marsh outlet had the highest levels of DDE (150 µg/kg) and DDD (95 µg/kg, which were similar to the results from TS-7, a site 200m upstream. Further downstream at HR-2 (200 m downstream of the confluence of the East and West Holland rivers) and HR-6 (at the outlet of the Holland River into Cook's Bay) the levels were lower (DDE = 33 µg/kg; DDD = 18 µg/kg and DDE = 34 µg/kg; DDD = 16 µg/kg, respectively) but above the PEL. In Cook's Bay, concentrations were lower (C-1 DDE = 6 µg/kg; C-6 DDE = 10 µg/kg), but still above guidelines, and only the p,p-DDE isomer was detected. At lake sites, DDE concentrations were consistently higher than DDD.

OCP Sampling Summary

In this study, the OCPs detected were likely from historic use, and slow degradation in organic soils has led to legacy contamination. Aldrin, eldrin, endosulfan compounds, as well as DDT and its metabolites, were found in sediments associated with vegetable polder sites (i.e. Holland, Bradford, and Colbar marshes). The two breakdown products of DDT (DDD and DDE) were also found downstream of the polders in the Holland River and Cook's Bay, suggesting legacy contaminants are being slowly transported through the system in mobilized sediments. The concentrations of OCPs at tributary and lake sites exceeded guidelines, often much greater than the Probable Effects Levels (PELs), indicating there is a higher potential for adverse effects within these aquatic systems. In comparison to the results in a study by Chaudhuri et al. (2017), some OCPs found in this study had concentrations that were among or above the highest recorded in Ontario. Long-term monitoring of OCPs in and downstream of the vegetable polders is important to identify declines in concentrations and to track their movement in the watershed.

Table 3a. Organochlorine Pesticide concentrations (µg/kg dry weight) from 2015 sediment samples of the tributary sites.

a) TRIBUTARY SITES	**ISQG**	**PEL**	**Table 1**	W. Holland	Polders and canals						
OC pesticides	**(µg/kg)**	**(µg/kg)**	**(µg/kg)**	**TS-7**	**WH-4**	**WH-5**	**WH-6**	**WH-7**	**WH-8**	**WH-9**	**WH-10**
Aldrin			2.00			16	25	17	10	21	12
Dieldrin	2.85	6.67	2.00			27	19	21	13	18	19
Aldrin + Dieldrin						43	43	38	23	39	31
Endosulfan I (alpha)	n/a								26		10
Endosulfan II (beta)								15	40	11	83
Total Endosulfan								15	66	11	93
Endosulfan sulfate						9	18	8	22	18	240
o,p-DDD				23	9	370	87	320	230	500	840
p,p-DDD				75	31	1100	160	900	670	1300	1800
Total DDD (o,p-DDD + p,p-DDD)	3.54	8.51	8.00	99	40	1500	240	1200	900	1800	2600
o,p-DDE								46			58
p,p-DDE				120	22	1000	340	750	570	1600	2700
Total DDE (o,p-DDE + p,p-DDE)	1.42	6.75	5.00	120	22	1000	340	800	570	1600	2800
o,p-DDT						31	16	17	9	24	220
p,p-DDT				11		150	68	82	44	220	1000
Total DDT (o,p-DDT + p,p-DDT)	1.19	4.77	7.00	11		180	83	100	53	250	1200
Total DDT+ Metabolites				220	62	2600	660	2100	1500	3600	6600

Blank = non detect
> ISQG or Table 1
>PEL

Table 3b. Organochlorine Pesticide concentrations (µg/kg dry weight) from 2015 sediment samples of the lake sites.

b) LAKE SITES	**ISQG**	**PEL**	**Table 1**	Holland River			Cook's Bay	
OC pesticides	**(ug/kg)**	**(ug/kg)**	**(ug/kg)**	**HR-2**	**HR-6**	**WH-3**	**C-1**	**C-6**
o,p-DDD								
p,p-DDD				18	16	95		
Total DDD (o,p-DDD + p,p-DDD)	3.54	8.51	8.00	18	16	95		
o,p-DDE								
p,p-DDE				33	34	150	6	10
Total DDE (o,p-DDE + p,p-DDE)	1.42	6.75	5.00	33	34	150	6	10
Total Metabolites				51	51	250	6	10

Blank = Non Detect

> ISQG or Table 1

>PEL

Neutral chlorinated compounds (NCC)

NCCs are a large group of chlorinated organic contaminants that includes hexachlorobenzene, octachlorostyrene, hexachlorobutadiene, pentachlorobenzene and others. Hexachlorobenzene (HCB) is produced as a by-product in the manufacture of other regulated organic chemicals (e.g. rubber, dyes, and wood preservatives) and is also a contaminant in the production of some pesticides. Major releases of HCB to the environment occur as a by-product of chemical manufacture, from pesticide applications, or in treated wastewater from non-ferrous metal manufacturing. HCB is a very persistent environmental chemical due to its chemical stability and resistance to break down by microbes. HCB has a tendency to bioccumulate in fish and mammals and has been listed as a dangerous substance in the environment because of inherent toxicity to aquatic organisms. Sediment samples from tributary and lake sites that were tested for OCPs were tested also for NCCs (hexachlorobenzene and octachlorostyrene), but no NCCs were present in 2015, as was found in the 2004 study.

Polychlorinated Biphenyls (PCBs)

PCBs are a group of synthetic chlorinated organic compounds used historically for hundreds of industrial and commercial purposes. A number of complex mixtures were produced for commercial use and were marketed under the trade name Aroclor. Some uses of PCBs include: dielectric and coolant fluids in electrical equipment (such as powerline transformers); and as plasticizers in paint, dyes, and carbonless copy paper. Bans and restrictions were placed on PCBs in the late 1970s in North America but environmental problems continue because of their persistent and toxic nature. Most PCBs that enter into the aquatic environment eventually end up in the sediment, where aquatic biota can be exposed to them.

The sediment of 12 tributary sites and nine lake sites were analyzed for PCBs, samples also tested for OCPs and NCCs, above. A total PCB guideline exceedance occurred at one lake site near Barrie in Kempenfelt Bay (B-LITT-14 at 160 µg/kg), and for Aroclor 1254, a constituent of total PCBs, at one tributary site (Beaver River; TS-24; 54 µg/kg; total PCBs guideline = 34.1 µg/kg). In 2004, no PCBs were detected in sediments from 13 sample sites, six of which were used in this 2015 study. In another study, Helm et al. (2011) reported PCBs, including one exceedance of the total PCB guideline in Kempenfelt Bay sediment collected in 2008, which they attributed to historical uses. Lower concentrations were reported in Cook's Bay and the Main Basin that were attributed to atmospheric deposition from regional air masses. Chaudhuri et al. (2017), in an Ontario-wide study, investigated PCBs in the sediment of some Lake Simcoe tributaries in 2008/2009 and found that Tannery Creek (in Aurora) had PCB levels that exceeded the ISQG guideline, noting that PCBs tended to be elevated in association with higher population density and urbanization.

Metals

Trace and heavy metals can occur naturally, with many being essential elements for organisms, however anthropogenic activities have contributed increased concentrations to aquatic ecosystems that may cause adverse effects to aquatic biota. Contamination of surface waters and sediments with metals can occur from anthropogenic activities such as mining, smelting and industrial wastes; as well as long-range atmospheric transport from distant industrialised regions. The fate of metals in surface waters is dependent on several factors, including the properties of a given metal, the chemistry of the water, and the association with particulate matter.

Sediment at 27 tributary sites and 12 lake sites were sampled for metals, targeting urbanized areas, agricultural areas including the vegetable polders and naturalized areas.

Tributary sites:

Metals were detected at all 27 tributary sites sampled but exceeded guideline concentrations at eight sites. The most exceedances were reported at Mill Creek, downstream of industrialized areas in Orillia (TS-26), that had concentrations of cadmium, chromium, copper, lead, nickel, and zinc above guidelines (Table 4). Within the polders, six of seven sites had copper concentrations above guidelines, with two sites also having exceedances in lead (WH-6, Bradford Marsh) and arsenic (WH-10, Colbar Marsh). Elevated concentrations of copper in association with agriculture are not uncommon as copper is often used as a soil treatment and the use of pesticides also likely raised levels of copper (Czuba and Hutchinson, 1980). In the East Holland River, TS-8 (downstream of Aurora and Newmarket) had concentrations of chromium above guideline. In addition to this study, routine water samples are analyzed for key metals through the Provincial Water Quality Monitoring Program Network (PWQMN). LSRCA and Kawartha Conservation (2016) found that copper had not often exceeded the guideline in the West Holland River (site TS-7 in this study; downstream of the Holland Marsh) even though there was substantial copper in the sediment of Holland Marsh samples upstream.

Among sites sampled in both the 2004 and 2015 studies, TS-8 had an exceedance in chromium, and WH-5 had copper higher than guideline; although concentrations at both sites were lower in 2015. Additionally, in 2004, site TS-8 had an exceedance in lead and TS-9 had chromium above guideline, but this was not recorded in 2015.

Lake sites:

As with the tributary samples, metals were reported at all lake and lower Holland River sites, however only six of the 12 sites had concentrations above guideline values (Table 4). All six of these sites had exceedances in the amount of chromium, likely washing in from the surrounding catchment or by airborne transport. Two of the lower Holland River sites (EH-1 at Holland Landing and HR-2 at the confluence of the East and West Holland rivers) also had copper concentrations above guidelines, with EH-1 also having an exceedance in zinc. Three of the six lake sites had exceedances in metals: C-6 in Cook’s Bay (chromium, cadmium, and lead), as well as the two sites near Barrie, BLitt-14 (cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc) and K-38 (cadmium, chromium, lead, mercury, nickel, and silver).

Table 4a. Metal concentrations (µg/g dry weight) from sediment samples of the tributary sites.

a) TRIBUTARY SITES	**ISQG**	**PEL**	**Table 1**	Hawke.	Mask.	Beaver	East Holland				Oro North			Lovers	Barrie			Hewitts
Total metals	**(µg/kg)**	**(µg/kg)**	**(µg/kg)**	**TS-2**	**TS-10**	**TS-24**	**TS-8**	**TS-9**	**TS-22**	**TS-23**	**TS-25**	**TS-26**	**TS-27**	**TS-4**	**TS-28**	**TS-29**	**TS-30**	**TS-31**
Acid Extractable Antimony (Sb)												0.9	0.3					
Acid Extractable Arsenic (As)	5.9	170	6									2	2					
Acid Extractable Barium (Ba)				17	24	34	16	16	20	18	31	120	69	17	7	13	16	74
Acid Extractable Beryllium (Be)												0.3						0.2
Acid Extractable Boron (B)												6						
Acid Extractable Cadmium (Cd)	0.6	3.5	0.6									0.9	0.4					
Acid Extractable Chromium (Cr)			26	3	5	7	50	10	8	11	6	27	14	5	18	3	6	12
Acid Extractable Cobalt (Co)			50	1	1	2	2	2	2	2	2	6	3	1	2	1	1	4
Acid Extractable Copper (Cu)	35.7	197	16	1	3	3	13	15	7	24	3	55	10	2	2	3	5	8
Acid Extractable Lead (Pb)	35.0	91.3	31	1	2	4	10	4	3	8	5	**93**	11	1	3	8	6	5
Acid Extractable Mercury (Hg)	0.170	0.486	0.2									0.1						
Acid Extractable Molybdenum (Mo)												1.1			0.5			
Acid Extractable Nickel (Ni)			16	2	2	4	3	3	3	4	3	18	6	2	3	2	3	6
Acid Extractable Selenium (Se)												0.6						
Acid Extractable Silver (Ag)			0.5									0.4						
Acid Extractable Thallium (Tl)												0.1	0.1					0.1
Acid Extractable Uranium (U)				0.2	0.3	0.3	0.3	0.2	0.4	0.2	0.2	0.6	0.4	0.2	0.3	0.1	0.2	0.4
Acid Extractable Vanadium (V)				8	11	14	9	7	21	8	13	20	26	13	27		11	22
Acid Extractable Zinc (Zn)	123	315	120	9	13	26	32	24	20	52	22	**340**	69	8	14	22	34	48

Blank = Non Detect

> ISQG or Table 1

>PEL

a cont'd) TRIBUTARY SITES	ISQG	PEL	Table 1	Innisfil		West Holland			Polder and canals						
Total metals	(µg/kg)	(µg/kg)	(µg/kg)	TS-32	TS-33	TS-7	WH-1	WH-2	WH-4	WH-5	WH-6	WH-7	WH-8	WH-9	WH-10
Acid Extractable Antimony (Sb)					0.2	0.2	0.3	0.3			0.5	0.2			0.4
Acid Extractable Arsenic (As)	5.9	170	6			2	2	2	1	5	5	4	3	3	12
Acid Extractable Barium (Ba)				11	12	83	80	100	55	65	63	72	64	97	69
Acid Extractable Beryllium (Be)						0.4	0.5	0.4	0.3	0.4	0.3	0.2	0.2	0.3	0.4
Acid Extractable Boron (B)						7		5		26	18	18	15	11	27
Acid Extractable Cadmium (Cd)	0.6	3.5	0.6			0.3	0.1	0.3		0.3	0.3	0.3	0.2	0.2	0.4
Acid Extractable Chromium (Cr)			26	3	9	17	20	18	13	13	12	10	9	11	16
Acid Extractable Cobalt (Co)			50	1	1	6	7	6	5	6	4	3	3	4	6
Acid Extractable Copper (Cu)	35.7	197	16	1	4	29	15	16	14	52	55	69	53	89	150
Acid Extractable Lead (Pb)	35.0	91.3	31	1	1	13	10	14	8	14	54	25	14	12	14
Acid Extractable Mercury (Hg)	0.170	0.486	0.2							0.1	0.1	0.1			0.1
Acid Extractable Molybdenum (Mo)										1.6	1.2	0.6	0.8		1.2
Acid Extractable Nickel (Ni)			16	1	2	13	12	12	10	13	9	8	7	9	14
Acid Extractable Selenium (Se)										0.5					0.5
Acid Extractable Silver (Ag)			0.5												
Acid Extractable Thallium (Tl)						0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Acid Extractable Uranium (U)				0.1	0.2	0.5	0.4	0.4	0.4	1.0	1.0	1.0	0.6	0.5	1.4
Acid Extractable Vanadium (V)				8	6	23	25	25	22	20	19	13	14	17	22
Acid Extractable Zinc (Zn)	123	315	120	9	28	74	67	79	37	68	80	71	73	71	120

Blank = Non Detect

> ISQG or Table 1

>PEL

Table 4b. Metal concentrations (µg/g dry weight) from sediment samples of the lake sites.

b) LAKE SITES	**ISQG**	**PEL**	**Table 1**	Holland River				Cook's		Kempenfelt		Main (W)	Shannon	Shingle	Main (E)
Total metals	**(µg/kg)**	**(µg/kg)**	**(µg/kg)**	**EH-1**	**HR-2**	**HR-6**	**WH-3**	**C-1**	**C-6**	**BLITT-14**	**K-38**	**BLITT-09**	**BLITT-08**	**N-32**	**BLITT-05A**
Acid Extractable Antimony (Sb)				0.4	0.3				0.4	1.3	1.0				
Acid Extractable Arsenic (As)	5.9	170	6	5	4	3	4	1	4	4	5				
Acid Extractable Barium (Ba)				98	100	97	110	140	130	110	130	11	34	34	17
Acid Extractable Beryllium (Be)				0.4	0.4	0.3	0.5		0.4	0.4	0.5				
Acid Extractable Boron (B)				8	11	5	10		8	8	12				
Acid Extractable Cadmium (Cd)	0.6	3.5	0.6	0.4	0.4	0.4	0.4	0.1	0.7	1.9	0.9		0.2	0.2	
Acid Extractable Chromium (Cr)			26	110	67	49	19	12	63	480	240	5	4	5	4
Acid Extractable Cobalt (Co)			50	6	5	4	7	2	5	5	6	2	2	2	2
Acid Extractable Copper (Cu)	35.7	197	16	62	37	24	32	35	17	58	27	1	4	4	2
Acid Extractable Lead (Pb)	35.0	91.3	31	27	23	16	20	5	39	100	75	2	5	6	2
Acid Extractable Mercury (Hg)	0.170	0.486	0.2	0.1	0.1	0.1	0.1		0.1	0.5	0.6				
Acid Extractable Molybdenum (Mo)					0.6	0.6	0.6		0.5	0.8	0.7				
Acid Extractable Nickel (Ni)			16	13	13	10	12	3	16	27	18	2	3	4	2
Acid Extractable Selenium (Se)				0.6	0.8	0.6	0.7		1.0	1.0	1.1				
Acid Extractable Silver (Ag)			0.5							1.0	0.6				
Acid Extractable Thallium (Tl)				0.2	0.1	0.1	0.1	0.1	0.2	0.3	0.2	0.1		0.1	
Acid Extractable Uranium (U)				0.4	0.5	0.6	0.6	0.4	0.7	0.7	0.8	0.3	0.3	0.3	0.3
Acid Extractable Vanadium (V)				22	21	16	25	5	20	24	26	11	6	7	8
Acid Extractable Zinc (Zn)	123	315	120	140	110	90	98	26	77	170	120	12	21	20	10

Blank = Non Detect
> ISQG or Table 1
>PEL

Chromium in the East Holland River system

Chromium exists in two states in aquatic systems: trivalent (Cr^{3+}), an essential element for humans that is from both natural and anthropogenic sources and considered non-toxic; and hexavalent (Cr^{6+}) that occurs only from anthropogenic sources and is both toxic and a carcinogen. As stated in the above metals section, chromium was detected in the Lake Simcoe Watershed particularly in the East Holland Watershed. Thus, we undertook a targeted study of 20 sites in the East Holland River to investigate the distribution and potential toxicity of chromium. Chromium-based compounds were traditionally used in tanneries to stabilize leather. Historically environmental pollution has been associated with these facilities, and chromium (including hexavalent Cr^{6+}) can be found at high concentrations in aquatic systems adjacent to or downstream of tannery sites, even long after these tanneries have ceased operation. Legacy contamination of other metals in aquatic systems can be attributed to the leather-making process as well. There are two historic tanneries on the East Holland River, Collis Leather in Aurora (active 1910 to 1988) and Davis Leather Tannery in Newmarket (active from 1905 to 1962).

In addition to the samples reported previously, 20 water and sediment samples were taken in the East Holland River targeting areas upstream and downstream of the two former tanning facilities and analyzed for chromium as well as other metals.

Water samples

In water samples, total chromium, including the trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) forms were not detected in the East Holland River. Among other metals, only aluminum (11 sites), copper (1 site), and iron (14 sites) exceeded guideline concentrations (Table 5).

Sediment samples

Total and trivalent chromium were detected in sediment samples from all 20 sites, although only nine sites had concentrations exceeding the guideline: Tannery Creek in Aurora adjacent to the former Collis Leather (CR-4 and CR-5), Fairy Lake in Newmarket (CR-10), at five sites of the East Holland River downstream from the former Davis Tannery between Davis Drive and Green Lane (CR-14, -15, -17, -18, -19), and at the most downstream site of the study in Holland Landing (CR-20). Hexavalent chromium was detected at three sites in this study: at Collis Leather (CR-5); north of Davis Drive, downstream of Davis Tannery, at the inlet of Western Creek (CR-13), and at Green Lane (CR-19) (Table 6).

In 2004, two sites (CR-9 and CR-19) on the East Holland River recorded chromium in exceedance of the guideline, and higher than concentrations recorded at these sites in 2015.

Another study (Earth Tech Canada, Inc. reported in the Aurora Banner, 2011), made note of elevated chromium levels in sediments downstream of the Collis Leather site and attributed this to legacy contamination from leather tanning.

Additional metals were analyzed at 19 of the 20 sites along the East Holland River. Although all samples contained metals, only two sites had concentrations above guidelines. The Collis Leather site (CR-4) in Aurora had exceedances in arsenic and zinc, and the George Richardson Pond (CR-16) had an exceedance in zinc (Table 6).

Chromium Summary:

Although chromium was not found in surface water samples, other metals did exceed guidelines at some sites, which may be a result of industrial activities in the area, possibly of a historical nature. In sediment samples, there were levels of chromium that exceeded the guidelines at locations downstream of discontinued tanneries. The majority of this chromium was the trivalent form, although the toxic hexavalent form was present at both tannery sites and in one downstream site.

Trivalent chromium has very low solubility and associates more with particulates that can settle and accumulate in sediment (Rifkin et al., 2004). Hexavalent chromium is more soluble and more mobile in aquatic systems, but can speciate to the trivalent form by microbial processes. These factors may contribute to the lack of chromium in the surface water of the 2015 sampling study, and the dominance of trivalent chromium in the sediment. In this study, it was found that much of the chromium recorded was bound to the sediment in the trivalent form, moving downstream over time in sediments mobilized by river flow.

The suite of different metals, including chromium, occurring at sampling sites adjacent to the two tannery sites, with exceedances of arsenic and zinc, have the potential to cause adverse effects to aquatic biota. The levels of metals in our study sites, likely due in large part to the leather-making industry, are an example of legacy contamination that continues to pose a threat to aquatic ecosystems long after the original discharge.

Table 5. Chromium and other metal concentrations (µg/L) in water samples from the East Holland River system.

CHROMIUM SITES	**PWQO**	Tannery Creek									Fairy Lake	East Holland River					George Richardson			
Total metals	**(µg/L)**	**CR-1**	**CR-2**	**CR-3**	**CR-4**	**CR-5**	**CR-6**	**CR-7**	**CR-8**	**CR-9**	**CR-10**	**CR-11**	**CR-12**	**CR-13**	**CR-14**	**CR-15**	**CR-16**	**CR-17**	**CR-18**	**CR-19**
Aluminum (Al)	75	27	75	68	39	53	19	46	73	85	120	120	110	140	110	110	100	130	230	140
Antimony (Sb)	20														1					1
Arsenic (As)	100		1	1	1	1														
Barium (Ba)		110	110	110	100	100	89	78	72	64	74	71	71	69	70	70	62	69	70	66
Boron (B)	200	10					18	18	20	25	26	30	29	28	32	30	54	27	33	30
Calcium (Ca)		87000	76000	78000	76000	76000	94000	82000	78000	69000	96000	91000	90000	86000	90000	91000	54000	85000	89000	82000
Copper (Cu)	5		2	1	1	1	2	2	3	3	1	2	1	4	2	1	3	3	4	5
Iron (Fe)	300	230	510	460	340	380	170	240	250	250	340	350	350	370	350	340	320	390	610	420
Lead (Pb)	25		0.8	0.7		0.5								0.6		0.5	0.7	0.8	1.4	0.7
Lithium (Li)		5	5	5	5	5		8	10	9	8	7	8	6	7	7	9	7	6	6
Magnesium (Mg)		17000	16000	17000	17000	17000	16000	15000	14000	13000	17000	16000	16000	16000	16000	17000	12000	15000	16000	15000
Manganese (Mn)		27	35	33	27	28	18	29	34	39	53	54	51	51	52	51	72	53	70	53
Molybdenum (Mo)	40	0.6	0.7	0.6	0.7	0.6	0.7	0.6	0.6	0.6	0.6	0.5	0.6	0.7	0.6		0.9	0.5	0.5	0.6
Nickel (Ni)	25									1									1	
Potassium (K)		1900	2100	2200	2200	2100	2400	3100	3700	3900	3100	3400	3300	3700	3500	3400	3200	3500	3600	3600
Silicon (Si)		7000	7000	7200	6800	6900	4900	5600	4700	4200	4800	4700	4600	4200	4500	4600	4100	4300	4700	4300
Sodium (Na)		47000	36000	38000	38000	37000	76000	60000	65000	60000	80000	85000	82000	110000	92000	87000	89000	86000	86000	80000
Strontium (Sr)		230	210	220	210	210	270	240	230	210	280	280	270	270	280	280	260	270	280	260
Titanium (Ti)				6							6	5	5	8	6	5	5	6	12	6
Uranium (U)	5	0.7	0.5	0.5	0.5	0.5	0.8	0.6	0.5	0.4	0.6	0.5	0.5	0.5	0.6	0.5	0.2	0.5	0.5	0.5
Vanadium (V)	6								0.6	0.7	0.9	0.9	0.8	1.0	0.9	0.9	0.8	1.0	1.2	1.0
Zinc (Zn)	30	6	10	8	7	6	5		7	8				6			10	6	11	8

Blank = Non Detect
>PWQO

Table 6. Detections (µg/g dry weight) of a) chromium, and b) other metals in sediment samples from the East Holland River system.

a) CHROMIUM SITES	**Table 1**	Tannery Creek									Fairy Lake
Chromium species	(µg/g)	**CR-1**	**CR-2**	**CR-3**	**CR-4**	**CR-5**	**CR-6**	**CR-7**	**CR-8**	**CR-9**	**CR-10**
Acid Extractable Chromium (Cr)	26	11	10	23	220	120	6	16	10	24	58
Chromium (+3)		11	9	23	220	120	6	16	10	24	58
Chromium (VI)						0.2					

CHROMIUM SITES	**Table 1**	East Holland River					George Richardson				Holland Landing
Chromium species	(µg/g)	**CR-11**	**CR-12**	**CR-13**	**CR-14**	**CR-15**	**CR-16**	**CR-17**	**CR-18**	**CR-19**	**CR-20**
Acid Extractable Chromium (Cr)	26	20	8	12	28	130	24	81	270	58	120
Chromium (+3)		20	8	11	28	130	24	81	270	57	120
Chromium (VI)				1.2						0.4	
Blank = Non Detect											
>Table 1											

b) CHROMIUM SITES	**ISQG**	**PEL**	**Table 1**	Tannery Creek			East Holland River				Green Lane
Total metals	(µg/g)	(µg/g)	(µg/g)	**CR-1**	**CR-4**	**CR-7**	**CR-11**	**CR-14**	**CR-16**	**CR-17**	**CR-19**
Acid Extractable Antimony (Sb)					0.7			0.2	1.2	0.4	
Acid Extractable Arsenic (As)	5.9	170	6	3	31	2		1	2	1	
Acid Extractable Barium (Ba)				43	79	12	14	33	71	33	24
Acid Extractable Beryllium (Be)				0.2	0.3				0.3		

b) CHROMIUM SITES	ISQG	PEL	Table 1	Tannery Creek			East Holland River				Green Lane
Total metals	(µg/g)	(µg/g)	(µg/g)	**CR-1**	**CR-4**	**CR-7**	**CR-11**	**CR-14**	**CR-16**	**CR-17**	**CR-19**
Acid Extractable Cadmium (Cd)	0.6	3.5	0.6	0.1	0.5				0.3		0.1
Acid Extractable Cobalt (Co)			50	3	4	2	2	2	5	2	2
Acid Extractable Copper (Cu)	35.7	197	16	7	22	5	7	7	34	14	8
Acid Extractable Lead (Pb)	35.0	91.3	31	15	29	7	7	11	28	15	12
Acid Extractable Mercury (Hg)	0.170	0.486	0.2	0.1							
Acid Extractable Molybdenum (Mo)					0.5				0.7		
Acid Extractable Nickel (Ni)			16	6	9	3	5	4	10	5	4
Acid Extractable Thallium (Tl)				0.1	0.1				0.1		
Acid Extractable Uranium (U)				0.4	0.4	0.2	0.4	0.3	0.4	0.4	0.2
Acid Extractable Vanadium (V)				16	16	10	28	14	19	14	9
Acid Extractable Zinc (Zn)	123	315	120	42	130	34	28	49	190	60	42

Blank = Non Detect

> ISQG or Table 1

Conclusions

The Lake Simcoe Watershed has long been the setting for anthropogenic activity including industry (e.g., tanneries), urban development, intensive agriculture and also recreational pursuits. However, our human activities can introduce contaminants to aquatic systems of the watershed. In some cases, these contaminants are found at levels that could cause adverse effects on aquatic organisms. The purpose of this study was to investigate likely contaminants in the watershed, identify areas of potentially high concentrations (e.g. urban centres, current and former industrial lands, and intensive agricultural areas), and compare contaminant locations and concentrations with a study carried out in 2004 by LSRCA.

In terms of PHCs, no guideline values currently exist but Mill Creek in Orillia has the highest concentration (7,573 µg/g) in sediment; or 11 times higher than the average (686 µg/g) of other tributary sites. The lake had high PHC amounts in the lower East Holland River (4,650 µg/g) and in shallow water sediment off Barrie (6,660 µg/g). These high concentrations were related to PHC Fraction 4G, which made up of creosotes and other large chain hydrocarbons. PAHs did not exceed guideline values in surface water tested, but high results were found in sediments at Mill Creek in Orillia (20,570 µg/g), the outlet of the Holland Marsh (13,066 µg/g) and the East Holland River at Green Lane, below Aurora and Newmarket (5,584 µg/g). Higher concentrations were also found in Lake Simcoe in the shallow and deeper water near Barrie (6,172 µg/g and 5,714 µg/g, respectively). Although no NCCs were detected at our study sites, phenols exceeded guideline values (1.0 µg/L) at Colbar Marsh (3.1 µg/L) and the deepwater lake site near Barrie (1.0 µg/L). PCBs exceeded guidelines at the shallow water site off Barrie.

Of greater concern from this study were the presence of OCPs and metals in the Lake Simcoe Watershed. OCPs were mostly found in, and downstream of, areas of intense agricultural use (e.g. Holland Marsh and other polders) where they were used extensively as pesticides in the mid-20th century. Most concerning was the presence of DDT, and its metabolites DDD and DDE, that had some of the highest concentrations recorded in Ontario, are very persistent, and can have large impacts to foodwebs, especially in top-level predators. Heavy metals (esp. cadmium, copper, arsenic, and zinc) were found in areas with heavy industrial uses (particularly Mill Creek in Orillia), but the presence of chromium is of special concern in the East Holland River, linked to the locations of former leather tanneries in Aurora and Newmarket.

Generally, the contaminants recorded in the Lake Simcoe Watershed are mostly the result of non-point anthropogenic sources (e.g. automobile exhaust, fossil fuel combustion) and specific areas of industrial, urban, and agricultural land-use activities (e.g., pesticides). Although some contaminants may be linked to current uses (e.g. PHCs, PAHs, phenols), others are likely legacy contaminants (i.e. DDT and chromium) from historical activities. Overall, it is recommended that regular monitoring of specific contaminants (e.g. DDT and metabolites, chromium, heavy metals) be undertaken more frequently as trends in chemical contaminants are difficult to ascertain from two sampling events, spaced 11 years apart. Routine sampling should target areas of guideline exceedances such as urban centres (Aurora, Barrie, and Newmarket) and intensive agricultural areas (Holland Marsh and other polders). More frequent and targeted sampling will aid in better evaluating our understanding of changes in chemical contaminants, including decreases or increases in concentration, movement through the watershed, and the potential risks to aquatic organisms or human health.

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Appendix A. - Sites sampled in the Lake Simcoe watershed in 2015.

Table A-1a. List of sites and locations for tributary samples.

Subwatershed	Site-ID	Easting	Northing	Site Description
Hawkestone Creek subwatershed	TS-2	621797	4928204	Hawkestone Creek (EC flow gauge station)
Maskinonge River subwatershed	TS-10	626088	4897958	Maskinonge River (PWQMN/LSPP site)
Beaver River subwatershed	TS-24	653635	4917772	Beaver River at Conc. 2 (EC flow gauge station)
East Holland River subwatershed	TS-8 **	623727	4881810	East Holland River at Green Lane, East Gwillimbury GO Train Station
East Holland River subwatershed	TS-9 **	622339	4875444	Tannery Creek (PWQMN site), Aurora
East Holland River subwatershed	TS-22	626781	4872085	East Holland River at Vandorf Sideroad (LSRCA flow gauge station), Aurora
East Holland River subwatershed	TS-23	623176	4879673	Western Creek (LSPP site), Newmarket
Oro Creeks North subwatershed	TS-25	622354	4937861	Mill Creek, Old Barrie Road and Line 15N, Orillia
Oro Creeks North subwatershed	TS-26	625514	4939223	Mill Creek, James St. West, Orillia
Oro Creeks North subwatershed	TS-27	625088	4938749	Mill Creek, Memorial Drive and Hwy 12, Orillia
Lovers Creek subwatershed	TS-4	607457	4914162	Lovers Creek (PWQMN/LSPP site), Barrie
Barrie Creeks subwatershed	TS-28	603604	4915683	Kidds Creek (LSPP site), Barrie
	TS-29	603768	4915232	Bunkers Creek (LSPP site), Barrie
	TS-30	604078	4914367	Hotchkiss Creek (LSPP site), Barrie
Hewitts Creek subwatershed	TS-31	608949	4913770	Hewitts Creek (LSPP site), Barrie
Innisfil Creeks subwatershed	TS-32	616223	4909232	Leonards Creek (LSPP site), Alcona

Subwatershed	Site-ID	Easting	Northing	Site Description
	TS-33	616437	4908198	Bon Secours Creek, 25th Sideroad and Innisfill Beach Road, Alcona
West Holland River subwatershed	TS-7	616364	4885477	West Holland River, bridge at Hwy 11 (PWQMN/LSPP site)
	WH-1	609486	4880914	North Schomberg River (LSPP site)
	WH-2	607547	4875011	Upper Schomberg River at Leonard Rd.
Vegetable Polders and Canals	WH-4	614776	4882782	North Canal at Simcoe St.
	WH-5	616362	4885150	Inner Canal, Bradford Pumping Station #2, Holland Marsh
	WH-6	616224	4885371	Professor Day Pumphouse, ditch alongside Bradford Marsh
	WH-7	615009	4880997	Inner Canal, end of Keele Lane, Holland Marsh
	WH-8	613301	4879257	Inner Canal, Wanda and Devald, Holland Marsh
Vegetable Polders and Canals	WH-9	610546	4875874	Inner Canal, River Road, Holland Marsh
	WH-10	617559	4888892	Colbar Marsh, ditch along Bathurst St.
** same location for tributary sampling and chromium sampling				

Table A-1b. List of sites and location for lake samples

(b) LAKE PROGRAM	Site-ID	Easting	Northing	Site Description
Holland River	WH-3	616377	4885702	West Holland River, at Hwy 11, downstream of bridge, north of marina. Mud / peat material bottom, 2.2 m deep
	EH-1	618695	4888523	East Holland River, downstream of Queensville Sideroad West, mud bottom, 1.8 m deep
	HR-2	618608	4891553	Holland River, just downstream of confluence of East and West Holland River sites, mud bottom, 2.7 m deep
	HR-6	618298	4894887	Holland River, mouth at green buoy, mud bottom, 2.4 m deep
Cook's Bay	C-1	618798	4896450	Cook's Bay, south, at entrance to Holland River. Mud bottom, abundant plant growth, 3.1 m deep

	C-6	618770	4901560	Cook's Bay, north, east of DeGrassi Pt. Mud and mussel shell bottom, 15 m deep
Kempenfelt Bay	B-Litt-14	604591	4914854	Kempenfelt Bay, littoral zone, off Centennial Beach in Barrie, north of Hotchkiss Creek outlet. Mud bottom 10 m deep
	K-38	605460	4915160	Kempenfelt Bay, east of drop off, mud bottom. 20.1 m deep
Main Basin (W)	B-Litt-09	620661	4924787	Main Basin (west), littoral zone, mud/ cobble bottom, 7 m deep. Parkside Beach Oro-Medonte, west of 9 Line S
Shannon Bay	B-Litt-08	627183	4938367	Shannon Bay, littoral zone, 4.2 m deep. Mud bottom, abundant plant growth
Shingle Bay	N-32	626640	4937530	Shingle Bay, in line with Victoria Point, mud bottom, 6.4 m deep
Main Basin (E)	B-Litt-05A	643936	4923951	Main Basin (east), between Trent Canal and Thorah Island, littoral zone, 7.1 m deep, sand bottom with sparse plant growth

Table A-1c. List of sites and location for chromium samples in the East Holland Subwatershed

Site-ID	Easting	Northing	Site Description
CR-1	622835	4872038	Tannery Creek, downstream of Golf Links Drive
CR-2	622716	4872368	Tannery Creek, end of Reuban St.
CR-3	622721	4872598	Tannery Creek, Collis Leather, south end parking lot
CR-4	622720	4872602	Tannery Creek, Collis Leather, about halfway up parking lot, just downstream of culvert
CR-5	622732	4872634	Tannery Creek, Collis Leather, towards north end of parking lot
CR-6	622753	4872731	Tannery Creek, downstream side of Tyler St. culvert
CR-7	622602	4873121	Tannery Creek, downstream from Wellington St., upstream of walking bridge
CR-8	622473	4874581	Tannery Creek, St. Andrew's College (LSRCA flow gauge station)
CR-9 **	622453	4874572	Tannery Creek (PWQMN/LSPP site; same location TS-9)
CR-10	623722	4878557	Fairy Lake, concrete dock
CR-11	623546	4879464	East Holland River, south side of Davis Drive, about 20 m downstream of concrete structure
CR-12	623467	4879785	East Holland River, Tannery Mall, under walking bridge
CR-13	623348	4879960	East Holland River, Tannery Mall, just downstream of Western Creek inlet

CR-14	623333	4880127	East Holland River, Tannery Mall, north end of parking lot
CR-15	623445	4880398	East Holland River, Madsen's Greenhouse
CR-16	623684	4880614	George Richardson Stormwater Pond
CR-17	623672	4880907	East Holland River, beside south end of Global Pet Foods (GPF) Dog Park
CR-18	623751	4881034	East Holland River, beside north end of GPF dog park, about 15 m upstream of weir
CR-19 **	623723	4881794	East Holland River, East Gwillimbury GO Train Station (same location as TS-8)
CR-20	620968	4883554	East Holland River, Holland Landing (PWQMN/LSPP site)

** same location for tributary sampling and chromium sampling

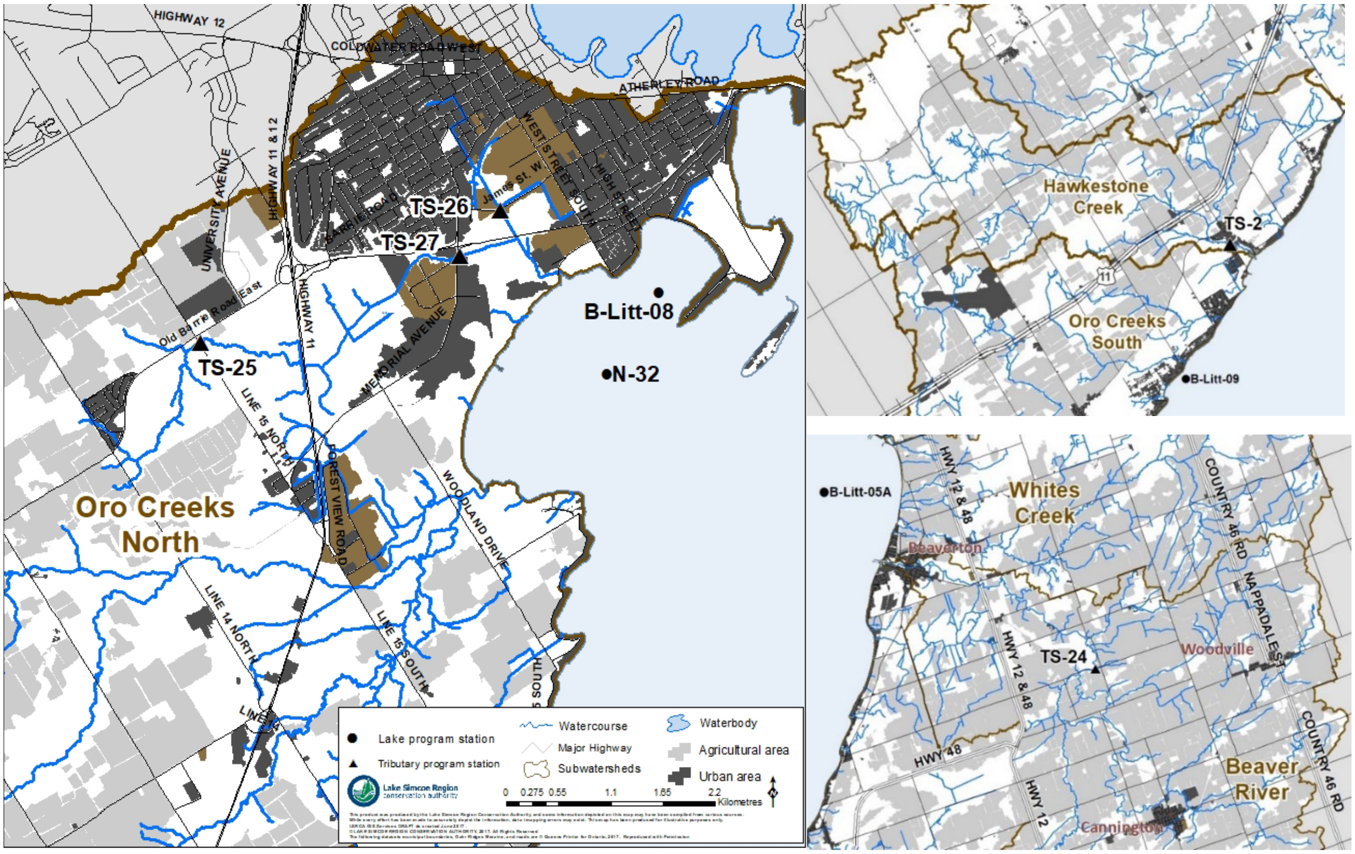

Figure A1 - Closer view of tributary sites sampled in Oro Creeks North subwatershed (left; TS-25, -26, -27), Hawkestone Creek subwatershed (top right; TS-2) and Beaverton River subwatershed (bottom right; TS-24)

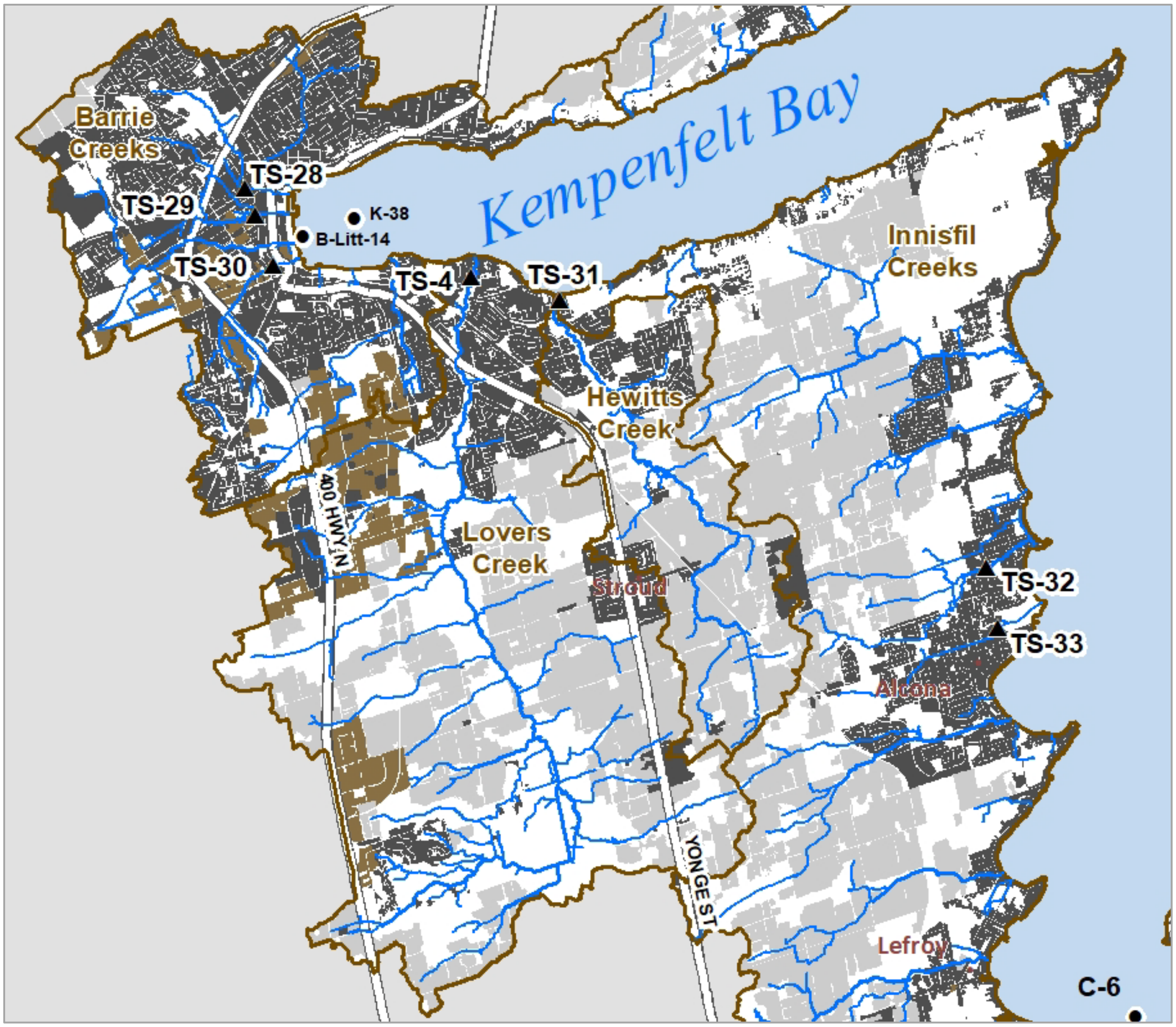

Figure A-2. Closer view of tributary sites sampled in Innisfil Creeks (TS-32, -33), Hewitts Creek (TS-31), Lovers Creek (TS-4) and Barrie Creeks (TS-28, -29, -30) subwatersheds. Note that industrialized areas are illustrated by solid brown polygons.

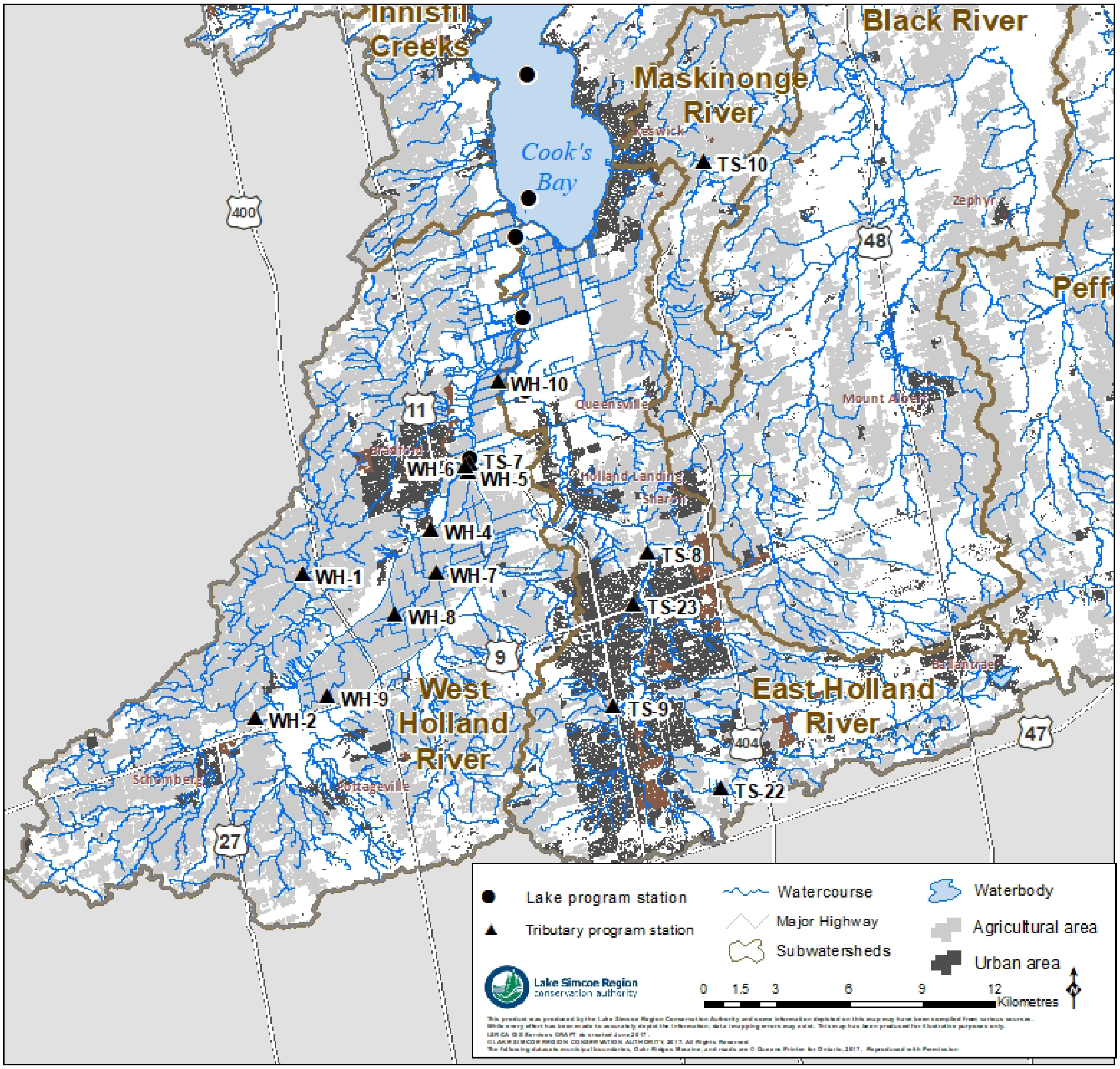

Figure A-3. Closer view of tributary sites sampled in West Holland River (TS-7, WH-1 to -10), East Holland River (TS-8, -9, -22, -23) and Maskinonge River (TS-10) subwatersheds. Note that industrialized areas are illustrated by solid brown polygons.

Figure A-4. Closer view of lake sites sampled.

Appendix B. Dates of sample collections.

Table A-2a. Sample collection date for tributary samples

Site-ID	PHC	PAH	Phenols	PHC	PAH	Metals	OCPs	NCCs	PCBs
	SW	SW	SW	SD	SD	SD	SD	SD	SD
TS-2	13-Nov	13-Nov	13-Nov	13-Oct	13-Oct	13-Oct			
TS-10	13-Nov	13-Nov	13-Nov	07-Oct	07-Oct	07-Oct	07-Oct	07-Oct	07-Oct
TS-24	07-Oct, 13-Nov	07-Oct, 13-Nov	07-Oct, 13-Nov	07-Oct	07-Oct	07-Oct	07-Oct	07-Oct	07-Oct
TS-8 **				06-Oct	06-Oct	06-Oct			
TS-9 **	19-Nov	19-Nov	19-Nov	06-Oct	06-Oct	06-Oct			
TS-22				06-Oct	06-Oct	06-Oct			
TS-23	19-Nov	19-Nov	19-Nov	06-Oct	06-Oct	06-Oct			
TS-25	19-Nov	19-Nov	19-Nov	13-Oct	13-Oct	13-Oct			
TS-26	19-Nov	19-Nov	19-Nov	13-Oct	13-Oct	13-Oct			
TS-27	19-Nov	19-Nov	19-Nov	13-Oct	13-Oct	13-Oct			
TS-4	13-Nov	13-Nov	13-Nov	13-Oct	13-Oct	13-Oct			
TS-28	19-Nov	19-Nov	19-Nov	13-Oct	13-Oct	13-Oct			
TS-29	19-Nov	19-Nov	19-Nov	13-Oct	13-Oct	13-Oct			
TS-30	19-Nov	19-Nov	19-Nov	13-Oct	13-Oct	13-Oct			
TS-31	13-Nov	13-Nov	13-Nov	13-Oct	13-Oct	13-Oct			
TS-32	19-Nov	19-Nov	19-Nov	13-Oct	13-Oct	13-Oct			
TS-33	19-Nov	19-Nov	19-Nov	13-Oct	13-Oct	13-Oct			
TS-7	19-Nov	19-Nov	19-Nov	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct

Site-ID	PHC	PAH	Phenols	PHC	PAH	Metals	OCPs	NCCs	PCBs
	SW	SW	SW	SD	SD	SD	SD	SD	SD
WH-1	19-Nov	19-Nov	19-Nov	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct
WH-2	19-Nov	19-Nov	19-Nov	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct
WH-4	19-Nov	19-Nov	19-Nov	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct
WH-5				14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct
WH-6				14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct
WH-7				14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct
WH-8	19-Nov	19-Nov	19-Nov	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct
WH-9	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct
WH-10	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct	14-Oct

SW = surface water sample; SD = sediment sample

** same location for tributary sampling and chromium sampling

Site and chemical sampled in 2004 also

Table A-2b. Sample collection date for lake samples

Site-ID	**PHC**	**PAH**	**Phenols**	**PHC**	**PAH**	**Metals**	**OCPs**	**NCCs**	**PCBs**
	SW	**SW**	**SW**	**SD**	**SD**	**SD**	**SD**	**SD**	**SD**
WH-3	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct
EH-1	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct
HR-2	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct
HR-6	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct
C-1	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct
C-6	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct	23-Oct
B-Litt-14	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct
K-38	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct	27-Oct
B-Litt-09	26-Oct	26-Oct	26-Oct	26-Oct	26-Oct	26-Oct			
B-Litt-08	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov			
N-32	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov			
B-Litt-05A	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov	03-Nov

SW = surface water sample; SD = sediment sample

Table A-2b. Sample collection date for chromium samples

SW = surface water sample; SD = sediment samples

** = same location for tributary and chromium sampling

Site-ID	Cr III	Cr VI	Metals	Metals
	SW, SD	SW, SD	SW	SD
CR-1	16-Oct	16-Oct	16-Oct	16-Oct
CR-2	16-Oct	16-Oct	16-Oct	
CR-3	16-Oct	16-Oct	16-Oct	
CR-4	16-Oct	16-Oct	16-Oct	16-Oct
CR-5	16-Oct	16-Oct	16-Oct	
CR-6	16-Oct	16-Oct	16-Oct	
CR-7	16-Oct	16-Oct	16-Oct	16-Oct
CR-8	16-Oct	16-Oct	16-Oct	
CR-9 **	16-Oct	16-Oct	16-Oct	
CR-10	16-Oct	16-Oct	16-Oct	
CR-11	16-Oct	16-Oct	16-Oct	16-Oct
CR-12	16-Oct	16-Oct	16-Oct	
CR-13	16-Oct	16-Oct	16-Oct	
CR-14	16-Oct	16-Oct	16-Oct	16-Oct
CR-15	16-Oct	16-Oct	16-Oct	
CR-16	16-Oct	16-Oct	16-Oct	16-Oct
CR-17	16-Oct	16-Oct	16-Oct	16-Oct
CR-18	16-Oct	16-Oct	16-Oct	
CR-19 **	16-Oct	16-Oct	16-Oct	16-Oct
CR-20	20-Oct	20-Oct	20-Oct	

Appendix C. **Laboratory detection limits.**

Method Detection Limit (MDL) is the measured response at which there is a stated probability of 99% that the analyte is present. The MDL is determined by statistical analysis of replicate results of analysis of low-level samples or low-level spikes. The statistical determination of the MDL will result in the establishment of a level at which the probability of reporting a false positive or false negative is at a defined level, for example at 1-5%.

Please note that the MDL can vary slightly from day to day, the experience level of the analyst, instrument fluctuations, slight temperature differences, etc. This can lead to different limits for the sample analytical method, from sample to sample, form analytical batch to batch, between sample duplicates, and/or between instruments. Therefore, we use Reportable Detection Limit (RDL) to allow for a consistent detection limit to be reported by eliminating the fluctuations normally encountered with a MDL. RDLs are equal to or greater (anywhere between 2-10x) than MDLs and greatly reduce the variability encountered when measuring near the extreme low-end range of the instrument's performance.