Chemicals of Emerging Concern in the Great Lakes Basin: An Analysis of Environmental Exposures

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1 Introduction

Environmental analysis and monitoring have long been recognized as a means for assessing environmental quality. Within the Great Lakes watershed, the governments of the United States and Canada, together with collaborating agencies, have performed numerous surveys of environmental contaminants in the air, water, sediments, and biota. Environmental monitoring programs are necessary to develop

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comprehensive descriptions of environmental quality, including at spatial and temporal scales, and to provide a sound basis for effective measures, strategies, and policies to address environmental problems (Calamari et al. 2000). While an important use of monitoring data is to inform environmental risk assessment, information gained from environmental measurements is also important for priority setting in regard to addressing the potential hazards of chemical contaminants.

Over the past 10 years, the emphasis on monitoring has shifted from the analysis of the so-called legacy pollutants to a wide array of new chemicals that have been discovered in the environment. These newer pollutants are lumped collectively into a group referred to as "chemicals of emerging concern." While it has been known for over 20 years that compounds such as pesticides, detergents, personal care products, and pharmaceuticals enter the environment, the improvements in instrumentation and analytical methodology for detecting chemical substances in various environmental media (air, water, sediment, biota) have brought increased awareness and concern over the presence and potential risk that these chemicals may pose (Daughton 2001). Although thousands of chemicals are listed on chemical inventories in both the United States and Canada, very few are regulated as to their environmental release. The term "chemicals of emerging concern" increasingly is being used to characterize those chemicals used by society that are unregulated or inadequately regulated, and for which there is growing concern over the risk they may pose to the health of humans and ecosystems.

The topic of chemicals of emerging concern is not new to the International Joint Commission (IJC) and its advisory Boards. The Commission is an independent binational organization established by the governments of the United States and Canada under the Boundary Waters Treaty of 1909. Among the responsibilities of the Commission, under the Great Lakes Water Quality Agreement of 1978 and 1987 amendment, is the goal to restore and maintain the chemical, physical, and biological integrity of the Great Lakes Basin Ecosystem. Because the Great Lakes Water Quality Agreement focuses on a wide variety of water quality issues facing the Great Lakes Basin Ecosystem, the Commission created a priority-setting process to emphasize what it considers the most pressing issues. The Commission and its advisory bodies review and revise these priorities every 2 years as needed.

The topic of chemicals of emerging concern was addressed by the IJC Great Lakes Science Advisory Board with its *Expert Consultation on Emerging Issues of the Great Lakes in the 21st Century*, held February 5–7, 2003 at Wingspread, WI. Several papers in the IJC 2003–2005 Priorities Report dealt with this (chemicals of emerging concern) issue. Muir et al. (2006) summarized the various means for tracking, categorizing, and assessing chemicals in commerce and presented an overview of recent measurements of "new" chemicals in the Great Lakes. Walker (2006) addressed whether currently available tools, such as quantitative structure–activity relationships, can identify emerging pollutants that will threaten the Great Lakes ecosystem. Fox (2006) discussed the importance of monitoring programs in the context of meeting the requirements of the Great Lakes Water Quality Agreement.

In October 2007, the Commission began work on the 2007–2009 Nearshore Framework Priority. The purpose of this Priority is to assemble and report on the

latest scientific, policy, and governance information on the nearshore of the Great Lakes so as to assess the binational implications of nearshore conditions and stressors. Nearshore problems are pressing and have significant social, economic, and environmental impacts. Current nearshore water quality is being adversely impacted by increased human population and problems arising from the existence of impervious surfaces and fertilizer use. Nearshore water quality is also influenced by land-based discharges from urban and agricultural sources, sediment resuspension, habitat loss and degradation, and atmospheric deposition, as well as by offshore waters. As the population increases, sewage discharges to receiving waters increase and impinge on water quality in the nearshore. Water quality in the nearshore is important to fish, aquatic birds, amphibians, and reptiles, since nearly all fish species spawn, have nursery grounds, and feed in the nearshore at some time in their development. The link between land-based activities and the nearshore has become recognized as the key challenge to protecting and restoring the chemical, physical, and biological integrity of the waters of the Great Lakes Basin Ecosystem.

Within the context of the 2007–2009 Nearshore Framework Priority, a multi-board work group was assembled to address the Priority on Chemicals of Emerging Concern. This group was charged with reviewing the scientific and policy aspects related to identification, impact, and management of chemicals of emerging concern in the Great Lakes. As a first step, a review of the status of current scientific knowledge on the occurrence of chemicals of emerging concern in the Great Lakes watershed was performed.

The objectives of this report, prepared for the multi-board work group, were to review and compile all peer-reviewed scientific studies and reports that had emerged since 1997; the scope of the review was on chemicals of emerging concern that could pose threats to water quality in the Great Lakes watershed. Emphasis was placed on chemicals discharged to the Great Lakes nearshore waters from wastewater treatment plants, as well as from other point and non-point sources of rural and urban pollution. The concentrations of chemicals in various environmental media disclosed by the review were assembled into a database, which was statistically analyzed to develop a quantitative understanding of current environmental exposures. To develop an initial assessment of their potential ecological significance, the concentrations found were compared with currently available regulatory standards, guidelines, or criteria.

2 Methods: Data Identification and Analysis

2.1 Identification and Critical Evaluation of Studies

A literature search was conducted to identify recent environmental analysis studies (i.e., published between 1997 and 2008) which contained information on ecological exposures and the concentrations of chemicals of emerging concern in the Great Lakes Basin and watershed. The search terms were developed to capture as much

information as possible on a wide variety of potential contaminants, in relevant environmental media (surface waters, sediment, biota, etc.). Excluded from consideration was information on concentrations reported in the atmosphere, precipitation, groundwater, and wastewater treatment effluents and biosolids. In addition to the literature search, input from experts in the field of environmental measurements and data from existing databases (Environment Canada, US Environmental Protection Agency, US Geological Survey, etc.) were sought as sources of information.

Each study that was found was critically evaluated for reliability using the review process described by Klečka et al. (2007); this process is generally based on internationally recognized guidance for the evaluation of measured data to be used in risk assessment (Canadian Environmental Protection Act (CEPA) 1997; European Commission (EUC) 2003a). All of the studies found were determined to be acceptable for use in this investigation.

2.2 Description of the Database

A database was constructed from all acceptable data in Microsoft Excel and contained detailed information for each sample obtained in each study. Information on samples included in the database were as follows: location, source, date of sample collection, type of matrix, reported concentrations found, analytical methodology, method detection limits, quality assurance and quality control information, reliability rating for the study, references, and comments.

2.3 Statistical Treatment of Data

Summary statistics were developed for the various datasets, including the number of data points, frequency of detection, average concentrations, standard deviation, minimum and maximum concentrations, and 5th and 95th percentile values, using the calculation functions in Excel. A considerable portion of the analytical values in the database were reported as being below the detection limit of the analytical method. For the statistical analysis, a variety of methods were considered for dealing with censored (i.e., non-detect) data. For this investigation, all values reported as "non-detectable" were set at one-half the method detection limit or minimum residue level (depending on the information available), since this is a long-established technique, which has been accepted by the regulatory community.

Much of available data in the database consisted of concentration values for various analytes in individual samples. However, in several studies, only summary statistics were reported for measured concentrations (i.e., information was provided for the number of samples, frequency of detection, minimum and maximum concentrations, etc.). When such studies were encountered, the corresponding authors were contacted when appropriate, and in many cases, the raw data were obtained. When only summary data were available (e.g., min–max), the maximum reported concentrations were used in the present analysis. When a dataset for a contaminant

of interest consisted of a mixture of single-point and summary data, collections of related single-point data were initially analyzed to develop summary results, which were then combined in the statistical analysis of the remaining data.

3 Chemicals of Emerging Concern in the Great Lakes Basin

A total of 80 papers or reports, published between 1997 and 2008, were identified that contained environmental measurements for a variety of chemicals of emerging concern in the Great Lakes watershed. Although numerous papers were initially identified in the literature search, some studies were excluded because they were outside the cogent geographic boundaries or were published in the early 1990s. In addition, many other prospectively useful papers initially identified contained information on persistent organic pollutants or on other historical contaminants (e.g., DDT, polychlorinated biphenyls (PCBs).) that were considered to be outside the scope of this investigation. All of the papers relevant to this study were judged to be either reliable or very reliable. A summary of the assembled information on concentrations of chemicals of emerging concern in the Great Lakes Basin is shown in Table 1.

Table 1 Summary of available information on concentrations of chemicals of emerging concern in the Great Lakes Basin

Category	Number analytes	Data points by media	Sampling period
Current-use pesticides	88	Water = 12,471 Sediment = 296	1992–2006
Pharmaceuticals	60	Water = 980 Sediment = 20 Biota = 21	1999–2006
Organic wastewater contaminants; personal care products; steroids and hormones	66	Water = 267 Sediment = 69	1997–2006
Alkylphenol ethoxylates	24	Water = 385 Sediment = 361 Biota = 163	1994–2002
Synthetic musks	9	Water = 375 Sediment = 48 Biota = 42	1999–2006
Perfluorinated surfactants	31	Water = 241 Biota = 400	1998–2003
Polybrominated diphenyl ethers	28	Sediment = 45 Biota = 2,152	1979–2006
Other flame retardants	10	Water = 32 Sediment = 119 Biota = 509	1994–2006
Chlorinated paraffins	10	Water = 90 Sediment = 70 Biota = 455	1996–2004

From the 80 reviewed papers, a database was developed which contained a total of 19,611 data points, representing the results of the analysis of single samples or summary data (ranges, minimum–maximum). Concentrations in surface waters ($n = 14{,}841$) and biota ($n = 3{,}742$) represented the majority of the available data. Fewer values were reported for sediments ($n = 1{,}028$). Although the atmosphere is recognized as being an important medium for environmental transport of chemicals, and serves as a source for other environmental media, studies that focused on atmospheric concentrations (air, precipitation, etc.) were excluded from the present analysis.

The majority of the papers reviewed and used focused on a single category or group of chemicals, although one described the results of a nationwide reconnaissance program performed on the presence of organic wastewater contaminants in surface waters (Kolpin et al. 2002). In many of the papers, sampling locations were characterized as being downstream from municipal wastewater discharges, receiving waters for industrial facilities, areas susceptible to agricultural or urban contamination, or harbors or ports.

We divided the substances in the database into nine categories and will deal separately with each category. In each section below, we first provide a brief overview of the studies found that provided concentrations of various analytes within the category, and thereafter present the results of the statistical analysis on those values. To assess the potential ecological significance, exposure concentrations were then compared with the appropriate existing regulatory criteria. A compilation of the various standards, guidelines, and criteria is provided in Table 2. The various regulatory criteria that are summarized in Table 2 are ecologically based and are included in the report to provide a context or benchmark for comparison with environmental exposures to chemicals of emerging concern in the Great Lakes Basin.

3.1 Current-use Pesticides

Pesticides are widely used in both rural and urban applications to control or eliminate organisms that are considered damaging or harmful. Although often used to connote insecticides, the term pesticide actually includes herbicides, fungicides, and various other substances used to control a wide variety of pests. Unlike many of the other chemicals of emerging concern that are addressed in this report, pesticides are among the most stringently regulated substances in the United States and Canada. Before manufacturers can sell a pesticide, they must undergo a thorough scientific evaluation to determine if they can be safely used. Before sanctioning the use of a pesticide, thorough reviews of applications for registration are reviewed by scientific authorities in each government where it is to be used; the most critical evaluations address a variety of potential human health and environmental effects associated with use of the product or products. Potential registrants must generate voluminous scientific data to address many areas of potential concern, including the identity, composition, environmental fate, potential adverse effects and exposure to,

Table 2 Compilation of various regulatory standards, guidelines, and criteria for the substances examined in this study

US EPA		Environment Canada			European Union			
Substance	Water (μg/L)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	References[a]
Current-use pesticides								
2,4-D (2,4-dichloro-phenoxyacetic acid)		4.0						CCME (2007)
Atrazine		1.8						CCME (2007)
Azinphos-methyl	0.01							US EPA (1999)
Bromoxynil		5.0						CCME (2007)
Carbaryl		0.2						CCME (2007)
Carbofuran		1.8						CCME (2007)
Chlorpyrifos	0.041	0.02 0.002						US EPA (2006); CCME (2008)
Diazinon	0.17	0.08						US EPA (2006); IJC (1987)
Dicamba		10.0						CCME (2007)
Diclofop-methyl		6.1						CCME (2007)
Dimethoate		6.2						CCME (2007)
Glyphosate		65.0						CCME (2007)
Malathion	0.1							US EPA (2006)
MCPA (2-methyl-4-chlorophen-oxyacetic acid)		2.6						CCME (2007)
Methoprene		0.09						CCME (2007)
Metolachlor		7.8						CCME (2007)

Table 2 (continued)

US EPA		Environment Canada			European Union			
Substance	Water (μg/L)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	References[a]
Metribuzin		1.0						CCME (2007)
Parathion	0.013							US EPA (2006)
Picloram		29.0						CCME (2007)
Simazine		10.0						CCME (2007)
Triallate		0.24						CCME (2007)
Trifluralin		0.2						CCME (2007)
Organic wastewater contaminants and personal care products								
1,4-Dichloro-benzene		26.0			20.0	0.94		CCME (2007); EUC (2004)
Anthracene		0.012	0.0469		0.1	0.203		CCME (2007, 2002); EUC (2008e)
Benzo(*a*)pyrene		0.015	0.0319		0.022	1.73		CCME (2007, 2002); EUC (2008f)
Bis (2-ethylhexyl) phthalate		16.0			1.3	21.5		CCME (2007); EUC (2006a)
Bisphenol A		0.175	0.01 mg/L		1.5	0.024 mg/kg wwt 0.063 mg/kg dwt	2.67	EC and HC (2008); EUC (2008a)
Fluoranthene		0.04	0.111		0.01	0.071		CCME (2007, 2002); EUC (2008f)
Naphthalene		1.1	0.0346		2.0	0.373		CCME (2007, 2002); EUC (2003d, 2008f)

Table 2 (continued)

US EPA		Environment Canada			European Union			
Substance	Water (μg/L)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	References[a]
Phenanthrene		0.4	0.0419		1.3	2.71		CCME (2007, 2002); EUC (2008f)
Phenol		4.0			7.7	0.233		CCME (2007); EUC (2006b)
Pyrene		0.025	0.053		0.0046	0.032		CCME (2007, 2002); EUC (2008f)
Tetrachloroethylene		111.0			51.0	0.727		CCME (2007); EUC (2005d)
Alkylphenol ethoxylates								
Nonylphenol (NP)	6.6	1.0	1.4		0.33	0.039	10.0	CCME (2001); EUC (2002a); US EPA (2005)
Nonylphenol ethoxylates (NPEO)		TEQ[1]	TEQ					CCME (2001)
Nonylphenol ether carboxylates (NPEC)		TEQ	TEQ					CCME (2001)
Octylphenol (OP)		TEQ	TEQ		0.122	0.0074	10.0	CCME (2001); UKEA (2005)

Table 2 (continued)

US EPA		Environment Canada			European Union			
Substance	Water (μg/L)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	References[a]
Octylphenol ethoxylates (OPEO)		TEQ	TEQ					CCME (2001)
Octylphenol ether carboxylates (OPEC)		TEQ	TEQ					CCME (2001)
Synthetic musks								
Musk ketone					6.3	0.5	0.3	EUC (2005b)
Musk xylene					1.1	0.3	1.0	EUC (2005a)
Acetyl-hexamethyl tetralin (ANTN)					2.8	1.72	1.1	EUC (2008b)
Hexahydro-hexamethylcyclo-pentabenzopyran (HHCB)					4.4	2.0	3.33	EUC (2008c)
Perfluorinated surfactants								
Perfluorooctane sulfonic acid (PFOS)		ENEV[1] 0.491			2.5		0.0167	DEFRA (2004); EC (2006a)
Perfluorooctanoic acid (PFOA)					3.8			Hekster et al. (2002)

Table 2 (continued)

US EPA		Environment Canada			European Union			
Substance	Water (μg/L)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	Water (μg/L)	Sediment (mg/kg dwt)	2° Consumer (mg/kg food)	References[a]
Brominated flame retardants								
Penta-bromodiphenyl ether (BDE)		ENEV 0.053	ENEV 0.031	0.0084	0.53	0.31	1.0	EC (2006b); EUC (2001)
Octa-BDE		ENEV 0.017	ENEV 9.1	0.06	> 0.2	>49 wwt >127 dwt	6.7	EC (2006b); EUC (2003b)
Deca-BDE			ENEV 76.0	0.336	1.0 >0.2	>148 wwt >384 dwt	2,500	EC (2006b) EUC (2002b)
Hexabromocyclododecane (HBCD)					0.31	0.86 mg/kg dwt	15.3	EUC (2008g)
Chlorinated paraffins								
Short-chain chlorinated paraffins (C10–13) (SCCP)		0.89	3.55	10.0	0.5	0.88 wwt ~2.3 dwt	16.6	EC (2008); EUC (2008d)
Medium-chain chlorinated paraffins (C14–17) (MCCP)		1.8	27	0.42	1.0	5 wwt ~13 dwt	0.17	EC (2008); EUC (2005c)

[a] The following abbreviations are used in the table: *CCME* Canadian Council of Ministers of the Environment, *DEFRA* Department for Environment, Food, and Rural Affairs, *EC* Environment Canada, *EC* and *HC* Environment Canada and Health Canada, *ENEV* Estimated No Effect Value, *EUC* European Commission, *IJC* International Joint Commission, *TEQ* Toxic Equivalent, *UKEA* United Kingdom Environment Agency, *USEPA* United States Environmental Protection Agency

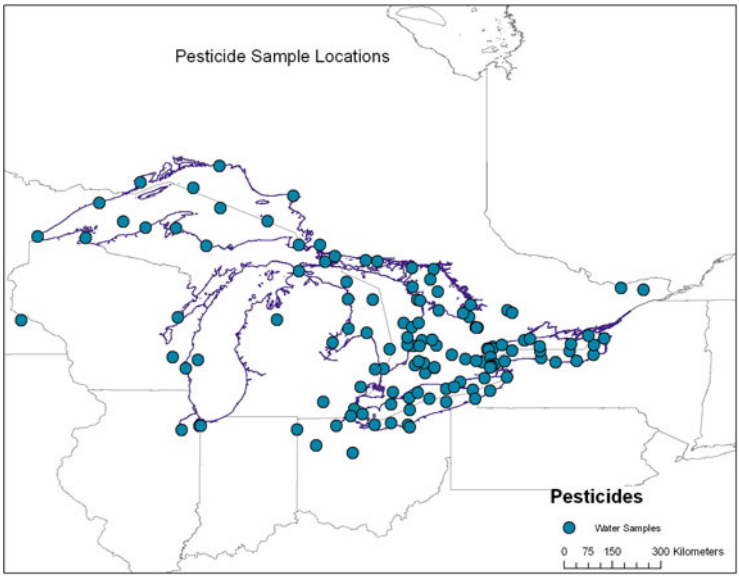
and potential risks associated with using the pesticide. These data allow government authorities to evaluate whether a pesticide has the potential to cause harmful effects in humans and ecosystems, including non-target organisms and endangered species. Government involvement does not end once a pesticide is registered and on the market. Both the registered products and how they are used are monitored through a series of education, compliance, surveillance, and enforcement programs. Pesticides are also periodically re-reviewed to determine if they continue to meet any updated government health and environmental standards, and whether the state of the science indicates they can continue to be used safely.

Concentrations of current-use pesticides in the Great Lakes Basin have been reported in seven studies (Gilliom et al. 2006; Kolpin et al. 2002; Struger and Fletcher 2007; Struger et al. 2004, 2007, 2008; Tertuliana et al. 2008). A number of surveys were conducted by Environment Canada to assess the concentration of pesticides in rural Canadian environments, as well as in the open waters of the Great Lakes. Gilliom et al. (2006) reported the results of an extensive analysis of pesticides in 51 water quality regions of the United States, of which 3 border on the Great Lakes. Kolpin et al. (2002) included the analysis of several pesticides in the recent nationwide reconnaissance of the presence of pharmaceuticals, hormones, and other organic wastewater contaminants in US surface waters. As shown in Fig. 1a and b, the sampling sites included those typical of agricultural and urban drainages, as well as open waters of the Great Lakes. When map coordinates were not provided by the authors, the locations of sampling sites were estimated from figures presented in the papers.

Our analysis focused only on those studies in which concentrations were reported in surface waters and sediments. However, several studies were identified in the literature search, in which analysis of current-use pesticide levels in air and precipitation were described (e.g., Carlson et al. 2004; James and Hites 1999; Miller et al. 2000; Tuduri et al. 2006). In several other studies, atmospheric concentrations and spatial and temporal trends were reported for several historically used organochlorine pesticides (Cortes et al. 1998; Sun et al. 2006a, b).

Struger et al. (2004) summarized the results of exploratory surveys conducted by Environment Canada on the concentrations of current-use pesticides in surface waters of the Laurentian Great Lakes. Large volume (20–50 L) samples were collected, during the period from 1994 to 2000, from Lakes Ontario, Erie, Huron, and Superior. Between 8 and 42 samples were collected each year, with a total of 220 samples collected over the entire investigation. The samples were analyzed for 39 different pesticides, including 15 neutral herbicides, 11 acid herbicides, and 13 organophosphorus insecticides. Because this sampling program was so extensive, the data in the report are presented as ranges (i.e., min–max concentrations). Six analytes, including Barban, diallate-2, triallate, phorate, phosmet, and disulfoton, were not detected in any of the samples. Atrazine, metolachlor, simazine, and 2,4-dichlorophenoxyacetic acid (2,4-D) were detected in greater than 50% of the samples; maximum concentrations reported were 1.04, 0.74, 0.28, and 0.08 μg/L, respectively. Both spatial and seasonal variations in concentrations of the herbicides were observed, which were related to their use patterns. The highest concentrations

A. Surface waters.



B. Sediments

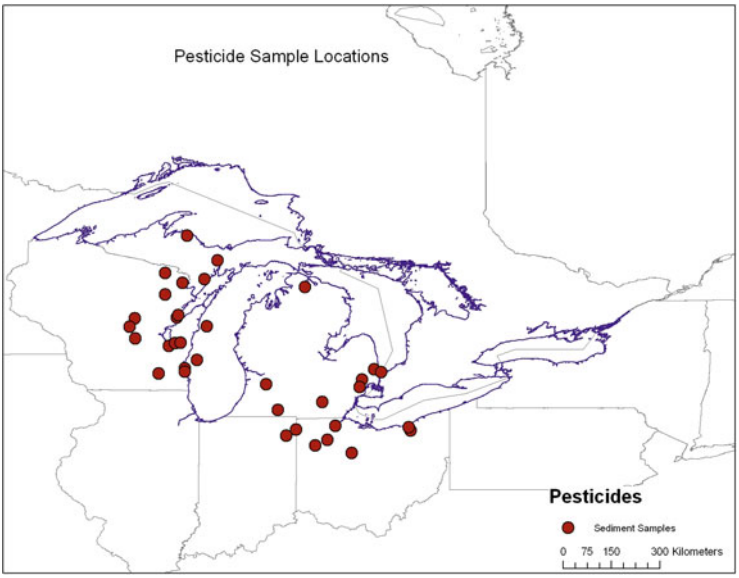


Fig. 1 Sampling locations for current-use pesticides. **a** Surface waters and **b** sediments

of atrazine, metolachlor, and 2,4-D were detected in samples from the western basin of Lake Erie, because of its close proximity to areas where these pesticides are applied in both agricultural and urban environments. The organophosphorus insecticides were also found primarily in Lake Erie. In general, an increasing concentration gradient from north to south was observed, with residues increasing as follows: Superior < Huron < Ontario < Erie. The authors reported that, although there was evidence of nearfield and farfield influences resulting from use of the various pesticides, all surface water samples met existing water quality guidelines or criteria for the protection of aquatic life.

Struger and Fletcher (2007) presented the results of an extensive monitoring program for lawn care and agricultural pesticides in the Don River and Humber River watersheds, which are tributaries of Lake Ontario in the vicinity of Toronto, ON (Ontario). During the period from 1998 to 2002, a total of 262 samples were collected from the study site. Samples were collected both during base-flow conditions ($n = 139$) and following rainfall events ($n = 123$). The samples were analyzed for a group of 152 pesticide-active ingredients. Because of the extensive amount of data included in the report, only summary data (frequency of detection and maximum concentrations) were available for our analysis. Although 11 different pesticidal ingredients were detected in the two rivers (2,4-D, atrazine, bromacil, carbofuran, chlorpyrifos, cypermethrin, diazinon, dicamba, mecoprop (MCPP), metolachlor, and metribuzin), 72% of the surface water samples contained residues of at least 1 pesticide. Aside from atrazine, which was detected more frequently and at higher concentrations, the study could not statistically distinguish between urban and agricultural pesticide inputs to the watersheds. Concentrations of four pesticides exceeded federal or provincial water quality criteria, in some of the samples. Diazinon exceeded the provincial criteria in 28% of the samples taken. For the other three (atrazine, carbofuran, and chlorpyrifos), the concentrations exceeded the criteria in less than 1% of the samples.

As a result of mosquito control programs implemented because of the increased incidence of the mosquito-borne West Nile Virus, Environment Canada and the Ontario Ministry of the Environment initiated a monitoring program in 2003 to investigate the occurrence and fate of methoprene and its metabolites in source areas and receiving bodies (Struger et al. 2007). Water samples were collected from two tributaries of Hamilton Harbor, four sites in open water areas of Hamilton Harbor, several sites in Cootes Paradise marsh at the western end of Hamilton Harbor, and six sites from a stream near Ottawa, ON. Methoprene was detected in 1 of 37 samples collected in the Hamilton area (0.1 μg/L), and in 1 of the 14 samples collected from the Ottawa stream (0.65 μg/L). Of the 51 samples collected, one exceeded the draft Interim Provincial Water Quality Objective (0.2 μg/L).

Struger et al. (2008) recently reported on the presence of glyphosate in surface waters of southern Ontario. Samples ($n = 502$) were collected from April to December over a 2-year period from 2004 to 2005. The sampling sites selected for the study were typical of agricultural and urban drainages in southern Ontario where glyphosate is commonly used. Because of the extensive information collected, only summary data were presented in the paper. Of the 203 samples collected in 2004

from 26 different field sites, 11 exceeded the detection limit (17 μg/L). When detected, the mean glyphosate concentrations were reported to be in the low μg/L range, with maximum concentrations as high as 40.8 μg/L. Similar results were reported for 2005. Of the 299 samples obtained from 58 different sites, 6 contained glyphosate concentrations above the detection limit. None of the samples collected during the 2-year period exceeded the Canadian Water Quality Guideline (65 μg/L).

In addition to the extensive pesticide monitoring performed throughout Canada and the Great Lakes, Kolpin et al. (2002) analyzed samples from tributaries of Lake Michigan as part of a nationwide reconnaissance program for surface waters in the United States. Samples from seven sites located in Illinois, Michigan, and Wisconsin were collected in 1999–2002 and analyzed for a series of pesticides that included carbaryl, chlordane, chlorpyrifos, diazinon, dieldrin, lindane, and methyl parathion. Of the various analytes, diazinon was detected in a single sample; all other values were reported as being below the detection limit. The concentration of diazinon detected in the sample (0.28 μg/L) exceeded the US Environmental Protection Agency Water Quality Guideline (0.17 μg/L).

Gilliom et al. (2006) presented results of the National Water Quality Assessment Program's first decade of water quality assessments, which included the analysis of 51 major hydrologic systems (study units) across the United States, during the period from 1992 to 2001. Nationally, water samples for pesticide analysis were collected from 186 stream sites. The sampling sites were selected to represent a mixture of agricultural, urban, undeveloped, and mixed-land-use settings. Of the 51 study units included in the analysis, 3 bordered on the Great Lakes. Water samples were analyzed for 75 pesticides and 8 pesticide degradates. In addition, 32 organochlorine pesticide compounds were analyzed in bed sediment samples collected from 1,052 sampling locations across the country. A screening level perspective on the potential significance of pesticide concentrations in streams indicated that 57% of the agricultural streams had concentrations of at least one pesticide that exceeded aquatic life benchmarks at least one time during the year. For urban settings and mixed-land-use settings, 83 and 42% of the streams had concentrations of at least one pesticide that exceeded aquatic life benchmarks at least one time during the year. Pesticides most frequently detected in stream water included five agricultural herbicides (atrazine, metolachlor, cyanazine, alachlor and acetochlor), five urban-use herbicides (simazine, prometon, tebuthiuron, 2,4-D, and diuron), and three widely used insecticides (diazinon, chlorpyrifos, and carbaryl).

Tertuliana et al. (2008) examined the occurrence and distribution of a broad range of organic compounds, including a number of current-use pesticides, in the Tinkers Creek watershed in northeastern Ohio. Sediment samples were collected during May–June of 2006 from 18 locations situated upstream and downstream from wastewater treatment plant discharges to the mainstream and tributaries of Tinkers Creek. Of the six current-use pesticides included in the analysis (atrazine, bromacil, metolachlor, prometon, chlorpyrifos, and diazinon), none were present in the sediment samples above a detection limit of 25 ng/g dry weight (dwt).

Based on the results of 7 studies conducted during the period from 1992 to 2006, a dataset was created containing information on surface water and sediment

concentrations for 88 different pesticides. Because of differences in these data, the database was divided and analyzed in two separate sections. Information available from Environment Canada for the concentration of current-use pesticides in Canadian surface waters and the waters of the Great Lakes were provided as summary data (minimum–maximum ranges) in the publications. The database contained 245 summary values reflecting the results for 47 analytes from 4,109 determinations. In contrast, individual data points for single samples were available for all of the United States Geological Survey (USGS; Gilliom et al. 2006) surface water data, representing the results for 74 current-use pesticides and metabolites for 12,226 determinations. The majority of the USGS data covered the sampling period from 1993 to 1997.

Summary statistics for the concentrations of the various analytes in Canadian surface waters and waters from the Great Lakes are presented in Table 3 and are illustrated in Fig. 2. When means and weighted means are given, they refer to the

Table 3 Summary statistics for current-use pesticides in Canadian waters and the Great Lakes

Analyte	*n*	Freq det (%)	Mean (μg/L)	Wt Mean (μg/L)	Min (μg/L)	Max (μg/L)
Neutral herbicides						
Atrazine	358	56.3	0.7893	0.7482	0.0047	3.6000
Barban	36	0.0	0.0038	0.0038	0.0038	0.0038
Benzoylprop-ethyl	46	2.2	0.0005	0.0004	0.0001	0.0011
Bromacil	84	14.3	0.9650	0.6500	0.2300	1.7000
Butylate	10	20.0	0.0019	0.0015	0.0002	0.0035
D-Atrazine	10	100.0	0.0098	0.0086	0.0039	0.0157
Deethylatrazine (DEA)	86	1.2	0.5125	0.7166	0.0250	1.0000
Diallate total isomer	36	11.1	0.0066	0.0104	0.0033	0.0132
Diallate-1	10	100.0	0.0027	0.0027	0.0025	0.0029
Diallate-2	10	0.0	0.0001	0.0001	0.0001	0.0001
Diclofop-methyl	46	17.4	0.0008	0.0014	0.0001	0.0020
D-Simazine	4	100.0	0.2810	0.2810	0.2810	0.2810
Glyphosate metabolite (AMPA)	410	3.9	31.9625	32.5890	8.5000	66.0000
Glyphosate	415	46.3	12.2537	15.0730	1.1700	40.8000
Metolachlor	393	50.4	0.6702	0.7174	0.0007	1.6000
Metribuzin	96	20.6	0.0560	0.0861	0.0002	0.1200
Simazine	46	93.5	0.0230	0.0302	0.0020	0.0431
Triallate	46	0.0	0.0001	0.0000	0.0000	0.0004
Trifluralin	46	10.9	0.0003	0.0006	0.0000	0.0009
Acid herbicides						
2,3,6-Trichloro-benzoic acid (2,3,6-TBA)	58	34.5	0.0168	0.0158	0.0002	0.0511

Table 3 (continued)

Analyte	*n*	Freq det (%)	Mean (μg/L)	Wt Mean (μg/L)	Min (μg/L)	Max (μg/L)
2,4,5-Trichloro-phenoxyacetic acid (2,4,5-T)	58	20.7	0.0012	0.0010	0.0002	0.0024
2,4,5-Trichloro-phenoxyproprionic acid (2,4,5-TP)	58	27.6	0.0044	0.0049	0.0002	0.0108
2,4-D	228	32.6	0.6629	1.0424	0.0014	1.6000
2,4-Dichloro-phenoxybutanoic acid (2,4-DB)	58	25.9	0.0072	0.0133	0.0009	0.0243
2,4-Dichloro-phenoxyproprionic acid (2,4-DP)	58	6.9	0.0029	0.0044	0.0002	0.0064
Bromoxynil	58	22.4	0.0015	0.0014	0.0002	0.0027
Dicamba	228	21.6	0.4511	0.5954	0.0002	2.2000
MCPA	58	17.2	0.0026	0.0029	0.0002	0.0054
Methylchloro-phenoxybutanoic acid (MCPB)	58	1.7	0.0003	0.0003	0.0002	0.0007
Methylchloro-phenoxypropionic acid (MCPP)	170	50.6	1.6500	1.8165	1.1000	2.4000
Picloram	58	12.1	0.0023	0.0038	0.0003	0.0061
Insecticides						
Azinphos-methyl	24	16.7	0.0155	0.0210	0.0006	0.0452
Carbofuran	86	1.2	0.5250	0.7238	0.0500	1.0000
Chlorpyrifos	108	6.8	0.1370	0.1299	0.0002	0.5200
Cypermethrin	84	1.2	0.2025	0.2786	0.0250	0.3800
Diazinon	194	39.6	0.3038	0.6169	0.0003	1.0000
Dibrom	24	8.3	0.0035	0.0032	0.0003	0.0078
Dimethoate	24	8.3	0.0117	0.0159	0.0003	0.0344
Disulfoton	24	0.0	0.0002	0.0002	0.0002	0.0002
Ethion	24	4.2	0.0007	0.0010	0.0002	0.0019
Fonofos	24	4.2	0.0010	0.0014	0.0001	0.0028
Malathion	24	8.3	0.0070	0.0096	0.0001	0.0208
Methoprene	37	2.7	0.0250	0.0162	0.0000	0.1000
Parathion	24	8.3	0.0014	0.0019	0.0003	0.0038
Phorate	24	0.0	0.0001	0.0001	0.0001	0.0001
Phosmet	24	0.0	0.0006	0.0006	0.0006	0.0006
Terbufos	24	8.3	0.0048	0.0066	0.0001	0.0143

analysis of maximum concentration values reported by the authors. The neutral herbicides atrazine, diallate, metolachlor, and simazine were detected in 50–100% of the samples. Other herbicides frequently detected were glyphosate (46.3%) and several of the phenoxy acid or benzoic acid herbicides, including 2,3,6-trichlorobenzoic acid (2,3,6-TBA; 34.5%), 2,4-D (32.6%), dicamba (21.6%), and

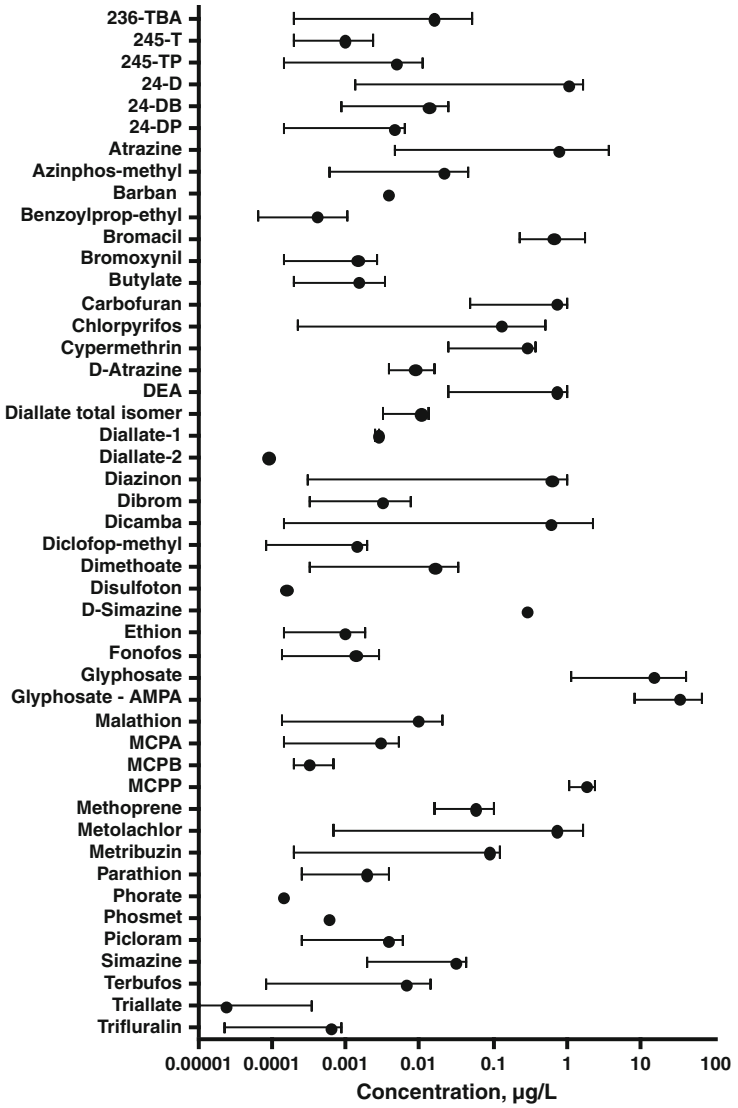


Fig. 2 Minimum, weighted mean, and maximum concentrations reported for current-use pesticides in surface waters, Canadian streams, and Great Lakes

MCPP (mecoprop; 50.6%). For these herbicides, the maximum concentrations were generally in the low microgram per liter range (0.01–3.6 µg/L), with the exception of glyphosate, in which a maximum concentration of 40.8 µg/L was reported for a single sample. The remaining herbicides were all detected at lower frequencies and at concentrations less than 1 µg/L. When compared with current water quality guidelines or criteria (Table 2), atrazine exceeded the standards in some samples (<1%).

Of the insecticides detected in Canadian surface waters and waters of the Great Lakes, azinphos-methyl and diazinon were among those most frequently detected (16.7 and 39.6%) with maximum concentrations ranging from 0.045 to 1.0 μg/L (Table 3). The remaining insecticides were detected less frequently (<10%) and at maximum concentrations less than 1.0 μg/L. Disulfoton, phorate, and phosmet were not detected in any of the samples. As summarized previously (Struger and Fletcher 2007), diazinon exceeded current regulatory criteria in 28% of the samples taken, whereas azinphos-methyl, carbofuran, chlorpyrifos, and methoprene seldom (<1%) exceeded the standard, and when they did so, it was usually in a single sample.

Summary statistics for the concentrations of the various pesticides in surface waters from three US water quality units that border the Great Lakes are presented in Table 4. Of the neutral herbicides, the highest maximum concentrations (4.7–85.20 μg/L) were reported for acetochlor, alachlor, atrazine, bentazon, cyanazine, fluometuron, metolachlor, metribuzin, propham, and simazine. Maximum concentrations ranging from 3.05 to 37.3 μg/L were also observed for several phenoxy acid herbicides. In contrast, the 95th percentile concentrations for all of the herbicides were less than 1.0 μg/L, with the exception of atrazine (2.77 μg/L) and 2,4-D (1.178 μg/L). Maximum concentrations, ranging from 2.57 to 22.5 μg/L, were reported for several insecticides (chlorpyrifos, diazinon, malathion, methiocarb, and oxamyl), although the 95th percentile concentrations for these insecticides were less than 1.0 μg/L. For the remaining fungicides and parasiticides, all of the reported concentrations were below 1.0 μg/L.

When the concentrations of current-use pesticides in US surface waters were compared to current water quality guidelines or criteria (Table 2), the reported concentrations for bromoxynil, carbaryl, carbofuran, dicamba, picloram, simazine, triallate, and trifluralin were all within the regulatory criteria. With 2,4-D, malathion, 2-methyl-4-chlorophenoxyacetic acid (MCPA), metolachlor, and metribuzin, the 95th percentile concentrations were below the regulatory guidelines, but exceedances were noted for the maximum reported concentrations. Concentrations of atrazine, azinphos-methyl, chlorpyrifos, diazinon, and parathion exceeded the regulatory standards in 6–32% of the samples.

As summarized in Table 5, limited data were available for the concentrations of current-use pesticides in sediments; the concentrations reported by Gilliom et al. (2006) and Tertuliana et al. (2008) are presented in this same table. Of the 11 current-use pesticides that have been analyzed, 5 were detected in 18–27% of the samples ($n = 38$) at concentrations ranging from 0.5 to 13.0 ng/g dwt.

3.2 Pharmaceuticals

Prescription and non-prescription drugs are extensively used to treat diseases in humans and domestic animals. In urban environments, these compounds make their way to wastewater treatment plants where they may be ultimately discharged to the environment in effluents or through application onto agricultural land as biosolids.

Table 4 Summary statistics for current-use pesticides in US streams

Analyte	*n*	Freq det (%)	50th percentile (μg/L)	95th percentile (μg/L)	Min (μg/L)	Max (μg/L)
Neutral herbicides						
Acetochlor	165	100	0.030	0.142	0.001	10.60
Alachlor	165	100	0.008	0.176	0.001	6.70
Atrazine	165	100	0.041	2.770	0.001	85.20
Benfluralin	165	76	0.005	0.011	0.001	0.016
Bentazon	165	100	0.030	0.130	0.003	7.32
Bromacil	164	100	0.040	0.120	0.001	1.63
Butylate	165	100	0.001	0.040	0.001	0.100
Cyanazine	165	100	0.011	0.777	0.001	9.97
Deethylatrazine (DEA)	164	99	0.022	0.393	0.001	3.87
Dichlobenil	165	95	0.040	0.066	0.003	0.210
Dichlorprop	165	96	0.050	0.070	0.003	0.600
Dinoseb	165	97	0.040	0.060	0.001	0.210
Diuron	165	98	0.040	0.060	0.001	0.180
Ethyldipropyl-thiocarbamate (EPTC)	165	76	0.002	0.020	0.001	0.020
Ethalfluralin	165	76	0.005	0.017	0.001	0.018
Fenuron	165	99	0.030	0.130	0.001	0.210
Fluometuron	165	100	0.030	0.085	0.002	5.00
Linuron	165	76	0.003	0.018	0.001	0.394
Metolachlor	165	100	0.012	0.774	0.001	77.60
Metribuzin	165	76	0.003	0.163	0.002	4.92
Molinate	165	76	0.002	0.009	0.001	0.010
Napropamide	164	77	0.007	0.020	0.001	0.056
Neburon	165	99	0.030	0.240	0.001	0.240
Norflurazon	165	99	0.021	0.130	0.001	0.240
Pebulate	165	76	0.005	0.008	0.001	0.091
Pendimethalin	164	77	0.003	0.011	0.001	0.113
Prometon	165	99	0.013	0.093	0.001	0.681
Pronamide	165	76	0.009	0.011	0.001	0.021
Propachlor	166	99	0.005	0.034	0.001	0.170
Propanil	165	76	0.005	0.021	0.001	0.080
Propham	165	100	0.110	0.110	0.001	5.61
Simazine	161	94	0.018	0.996	0.001	4.70
Tebuthiuron	165	76	0.002	0.011	0.001	0.024
Terbacil	165	76	0.017	0.018	0.001	0.106
Thiobencarb	164	76	0.002	0.011	0.001	0.011
Triallate	165	76	0.002	0.005	0.001	0.021
Trifluralin	165	76	0.005	0.050	0.001	0.050
Acid herbicides						
2,4,5-T	165	100	0.040	0.040	0.001	0.210
2,4,5-TP	165	100	0.030	0.110	0.001	3.050
2,4-D	165	100	0.080	1.178	0.001	6.140
2,4-DB	165	100	0.130	0.260	0.003	28.60

Table 4 (continued)

Analyte	*n*	Freq det (%)	50th percentile (μg/L)	95th percentile (μg/L)	Min (μg/L)	Max (μg/L)
Acifluorfen	165	76	0.040	0.240	0.003	0.240
Bromoxynil	165	76	0.100	0.275	0.016	0.275
Chloramben methyl	165	76	0.005	0.110	0.002	3.50
Clopyralid	165	92	0.070	0.240	0.003	0.240
Dacthal	164	76	0.002	0.020	0.001	0.144
Dicamba	165	100	0.050	0.100	0.001	0.635
MCPA	165	100	0.100	0.130	0.002	37.30
MCPB	165	100	0.130	0.510	0.002	19.00
Picloram	165	100	0.040	0.140	0.001	0.240
Triclopyr	165	100	0.040	0.140	0.001	0.850
Insecticides						
Aldicarb	165	76	0.100	0.600	0.040	0.600
Azinphos-methyl	164	73	0.003	0.020	0.001	0.124
Carbaryl	172	73	0.002	0.021	0.001	0.030
Carbofuran	165	76	0.009	0.010	0.001	0.011
Chlorpyrifos	172	96	0.003	0.339	0.002	10.00
Diazinon	172	97	0.006	0.186	0.001	22.50
Disulfoton	165	76	0.001	0.011	0.001	0.021
Ethoprop	165	76	0.002	0.009	0.001	0.010
Fonofos	165	100	0.001	0.050	0.001	0.843
Malathion	165	100	0.014	0.078	0.001	6.40
Methiocarb	165	100	0.030	0.130	0.003	2.57
Methomyl	165	99	0.030	0.240	0.001	0.240
Methyl parathion	172	73	0.002	0.030	0.001	0.330
Oxamyl	165	100	0.080	0.080	0.002	3.70
Parathion	165	100	0.005	0.056	0.001	0.080
cis-Permethrin	164	43	0.004	0.040	0.001	0.177
Phorate	165	76	0.006	0.018	0.001	0.510
Propargite	164	77	0.011	0.020	0.001	0.056
Propoxur	165	100	0.060	0.060	0.003	0.595
Terbufos	165	76	0.002	0.020	0.001	0.020
Fungicides						
Chlorothalonil	165	81	0.070	0.100	0.003	0.240
Dinitro-*ortho*-cresol (DNOC)	165	98	0.060	0.130	0.002	0.190
Parasiticide						
Oryzalin	165	100	0.021	0.140	0.001	0.140

Table 5 Summary statistics for current-use pesticides in US sediments

Analyte	*n*	Freq det (%)	Mean (ng/g dwt)	Min (ng/g dwt)	Max (ng/g dwt)
Neutral herbicides					
Atrazine	18	0	12.5	12.5	12.5
Bromacil	18	0	12.5	12.5	12.5
Metolachlor	18	0	12.5	12.5	12.5
Prometon	18	0	12.5	12.5	12.5
Acid herbicides					
Dacthal	38	18	4.2	2.5	13.0
Insecticides					
Chlorpyrifos	18	0	12.5	12.5	12.5
Diazinon	18	0	12.5	12.5	12.5
Endosulfan	37	22	1.0	0.5	5.0
cis-Permethrin	38	18	0.8	0.5	2.5
trans-Permethrin	37	27	4.7	2.5	13.0
Fungicides					
Chloroneb	38	18	4.2	2.5	13.0

In rural environments, the drugs that are used by humans or administered to livestock and poultry have the potential to enter the aquatic environment through runoff into surface water or through contamination of groundwater.

The detection of pharmaceutical compounds in the aquatic environment has received considerable attention in the technical literature and in the popular press. Prescription and non-prescription drugs have been detected in rivers and streams in both North America and Europe, and several recent reviews have addressed the occurrence and fate of pharmaceuticals in the environment (e.g., Monteiro and Boxall 2010; Walraven and Laane 2008). Wastewater treatment plants and agricultural operations are important sources of these contaminants to surface waters, but limited data exist on the spatial distribution of drugs in receiving waters near such sources. Concentrations of pharmaceuticals in surface waters from the Great Lakes Basin have been reported in 11 studies. The locations of the sampling sites for pharmaceuticals are shown in Fig. 3.

Kolpin et al. (2002) reported the results of a nationwide reconnaissance study of the occurrence of pharmaceuticals, hormones, and other organic wastewater contaminants in water resources. Samples were collected during 1999 and 2000 from a network of 139 streams across 30 states, of which 19 sites were located within the Lake Michigan drainage basin. The selection of the sampling sites was biased toward areas considered to be susceptible to contamination from human, industrial, and agricultural sources (i.e., downstream from urbanization, livestock production, etc.). Of the 95 organic wastewater contaminants included in the study, 41 represented different pharmaceuticals, including veterinary care products and human prescription and non-prescription drugs. In general, the human and veterinary antibiotics were detected less frequently (14 of 31 were non-detected in all samples) than

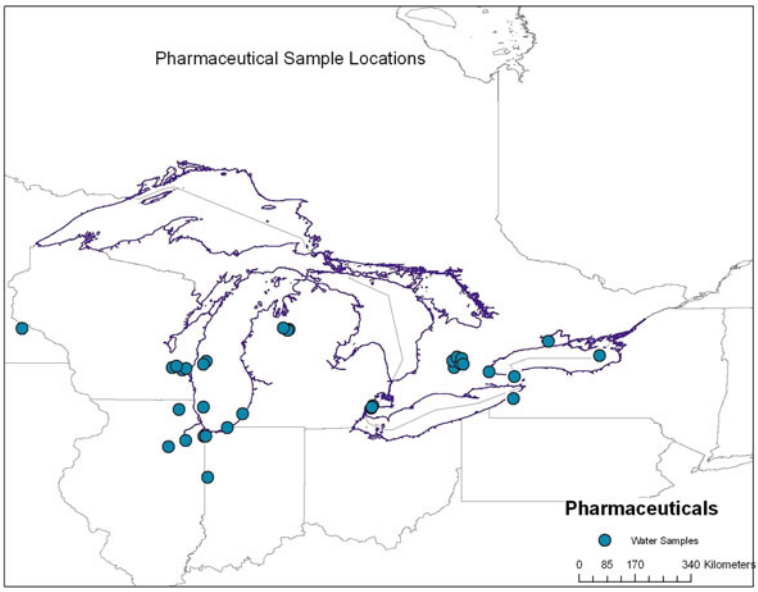


Fig. 3 Sampling locations for pharmaceutical compounds

were the other prescription drugs (5 of 15 were non-detected). Detection limits for the various analytes ranged from 0.001 to 0.26 μg/L (mean ± SD; 0.065 ± 0.054). Non-prescription drugs (including caffeine and cotinine) were generally detected at higher frequencies, than were other pharmaceuticals, which may be at least partially a result of their greater annual use.

Metcalfe et al. (2003) analyzed for the presence of 18 pharmaceuticals in surface waters from the lower Great Lakes. Samples were collected in the summer and fall of 2000 at open water sites in Lake Erie and Lake Ontario. Additional samples were collected in 2000 and 2002 from sites in the Detroit River and Hamilton Harbor in the vicinity of discharges from wastewater treatment plants for the cities of Windsor and Hamilton, Ontario. A variety of drugs were detected at nanogram per liter concentrations from sites that were up to 500 m downstream from the discharges of the wastewater treatment plants. The highest concentrations were noted for ibuprofen (0.79 μg/L), naproxen (0.55 μg/L) and carbamazepine (0.65 μg/L). Caffeine and cotinine (nicotine metabolite) were generally present in the receiving waters and are considered markers for human excretion. Pharmaceutical compounds were not detected (<1 to <10 ng/L) at open water locations in western Lake Erie or in the Niagara River near the municipality of Niagara-on-the-Lake. However, clofibric acid, ketoprofen, fenoprofen, and carbamazepine were detected at low levels (0.02–0.06 μg/L) in samples collected in 2000 from Lake Ontario and at sites on the Niagara River near Fort Erie that were relatively remote from wastewater discharges.

Jones-Lepp (2006) addressed the utility of analyzing for chemical markers of human waste contamination in surface waters and the development of analytical methods for detecting urobilin, a by-product of hemoglobin degradation. Surface water samples were collected in 2004 from various sites in the United States, including two samples from recreational beaches on the Lake Michigan shoreline that were near wastewater treatment plant effluent outfalls. The samples were analyzed for urobilin and azithromycin, an antibiotic widely prescribed for human use. Neither analyte was present in the samples above the detection limit (<1 ng/L).

Lissemore et al. (2006) described the geographical and temporal distribution of pharmaceuticals detected within seven tributaries of the Grand River watershed in southern Ontario. Related work, which summarized the analytical methods and their application to samples from the same locations, was reported by Hao et al. (2006). Samples were collected in May–November of 2003 and March–April of 2004 from seven agricultural and one urban location. The rural sampling sites were previously identified as having had a high risk for agricultural runoff. Of 28 pharmaceuticals surveyed, 14 were detected in the stream samples ($n = 125$) at nanogram per liter concentrations. The five most frequently detected analytes were lincomycin (91.2%), monensin (75.2%), carbamazepine (48.8%), sulfamethazine (32.8%), and trimethoprim (20%); median and maximum concentrations for these analytes ranged from 1 to 44 ng/L and from 15 to 1,172 ng/L, respectively. The highest concentrations were reported for monensin and sulfamethazine; these are used strictly for livestock production, which is consistent with the selection of sampling sites in areas suspected of agricultural contamination. With the exception of carbamazepine (0.16–24 ng/L), prescription drugs with strictly human uses were not detected in the samples.

Servos et al. (2007) examined the presence of eight pharmaceuticals and the antimicrobial, triclosan, in drinking water sources used in Southern Ontario. Samples were collected during the fall of 2002 from facilities located near Burlington, ON. Of the facilities included in the study, 4 used river waters and 11 used lake waters as source waters. Most of the river water sampling sites were situated downstream from one or more municipal wastewater treatment plants, whereas the lake sites were more remote from any direct discharges. River water samples showed the highest levels of naproxen and ibuprofen, with concentrations ranging as high as 176 and 150 ng/L, respectively. Low levels of gemfibrozil (19.2 ng/L), diclofenac (15 ng/L), and indomethacin (6 ng/L) were also detected in river water. In contrast, the concentrations of the various pharmaceuticals in lake water samples were less than 5 ng/L.

Chu and Metcalfe (2007) described the development of sensitive analytical methods and their application to the analysis of several selective serotonin re-uptake inhibitors that are widely used to treat depression. Fish ($n = 7$) were collected in 2002 from Hamilton Harbor. Paroxetine, fluoxetine, and norfluoxetine were detected in 54–86% of the fish with maximum concentrations ranging from 0.58 to 1.08 ng/g wet weight (wwt).

Tertuliana et al. (2008) examined the occurrence and distribution of 151 pharmaceutical and organic wastewater compounds in the Tinkers Creek watershed in

northeastern Ohio. Tinkers Creek is the largest tributary leading into the Cuyahoga River. The study included an evaluation of passive samplers, such as polar organic chemical integrative samplers (POCIS) and semi-permeable membrane devices (SPMD) for providing time-weighted measures of concentration in the streams over the exposure period. Additional sediment samples were also collected at each of the stations where the passive samplers were deployed. The samples were collected during May–June of 2006 from 18 locations situated upstream and downstream from wastewater treatment plant discharges to the mainstream and tributaries of Tinkers Creek. Because of variations in site-specific factors (temperature and water velocity) and the strong sorptive capacity, the concentrations of the various analytes were reported in units of nanograms per POCIS disk and could not be adjusted for variations in sampling rates. For this reason, results of the water analysis provided qualitative indications of the presence/absence of the various analytes at the sampling locations. Of the 52 pharmaceuticals included in the analysis, a total of 12 antibiotics and 20 prescription and non-prescription drugs were detected in water at one or more of the sites. The detections were generally higher in passive samplers located downstream of outfalls as compared to those deployed upstream of outfalls or at reference locations. Additionally, eight pharmaceuticals were detected in streambed sediments at all sites in the Tinkers Creek watershed. Median and maximum concentrations for the various pharmaceutical compounds in sediment ranged from 2 to 13 ng/g dwt and from 3.3 to 75 ng/g dwt, respectively. Non-prescription drugs including diphenhydramine, caffeine, and miconazole were detected at higher frequencies (28–50%) in the sediments at concentrations ranging from 0.3 to 75 ng/g dwt.

Three additional studies have reported concentrations for a few pharmaceuticals in a limited number of samples taken from the Detroit River. The sampling sites ranged from locations downstream of the Little River Wastewater Treatment Plant (Windsor, ON) to further downstream near the intake site for the A.H. Weeks Water Treatment Plant, which furnishes drinking water to the city of Windsor, ON. Boyd et al. (2003) reported concentrations for clofibric acid (103 ng/L), ibuprofen (<2.6 ng/L), fluoxetine (<25.4 ng/L), and naproxen (63 ng/L) in samples of raw intake water taken in 2002. Hua et al. (2006a) reported trace levels of carbamazepine (0.3–3.8 ng/L), caffeine (2.3–24 ng/L), and cotinine (0.1–1.6 ng/L) in raw intake water samples collected in 2003. The primary focus of these investigations was on the effectiveness of water treatment technologies for the removal of trace contaminants. In a follow-up study, Hua et al. (2006b) reported on the spatial distribution and the influence of seasonal changes on the concentration of a variety of acidic and neutral pharmaceuticals in samples from the Detroit River. Ten of 17 compounds were detected downstream of the wastewater treatment plant at the confluence of the Little River and the Detroit River at concentrations of less than 100 ng/L, on average. In spite of the large dilution, three compounds (carbamazepine, caffeine, and cotinine) were detectable at low nanogram per liter concentrations at shoreline sites several kilometers downstream.

Based on the available information, a database was created containing 1,021 data points (either single values, means, or ranges) for 60 pharmaceutical compounds

analyzed in surface water, sediments, and biota from the Great Lakes Basin. As summarized in Table 6, the number of surface water samples analyzed for each of the substances varies from 2 to 303. The frequency with which the various compounds have been detected varies from 0 to as high as 84%. Detection limits among the compounds varied from 0.001 to 0.26 μg/L. In general, higher detection limits were reported by Kolpin et al. (2002), which may derive from the analytical methods employed being designed to detect multiple analytes at the sacrifice of some sensitivity.

Table 6 Summary statistics for pharmaceutical compounds in surface waters

Analyte	*n*	Freq det (%)	Mean (μg/L)	Wt Mean (μg/L)	Min (μg/L)	Max (μg/L)
Veterinary and human antibiotics						
Azithromycin	16	0	0.0005	0.0005	0.0005	0.0005
Carbadox	143	0	0.0260	0.0196	0.0100	0.0500
Chloramphenicol	125	0	0.0025	0.0025	0.0025	0.0025
Chlortetracycline	159	1	0.1247	0.1632	0.0250	0.1920
Ciprofloxacin	18	0	0.0158	0.0158	0.0100	0.0250
Doxycycline	143	3	0.0556	0.0689	0.0250	0.0730
Enrofloxacin	18	0	0.0256	0.0256	0.0100	0.0500
Erythromycin	231	29	0.0504	0.0396	0.0001	0.2800
Lincomycin	231	84	0.0613	0.2060	0.0140	0.3550
Monensin	213	80	0.2328	0.7355	0.0200	1.1720
Norfloxacin	18	0	0.0158	0.0158	0.0100	0.0250
Oxytetracycline	159	0	0.0332	0.0159	0.0030	0.1000
Roxithromycin	143	6	0.0103	0.0041	0.0020	0.0250
Sarafloxacin	18	0	0.0100	0.0100	0.0100	0.0100
Sulfachloropyridazine	229	15	0.0542	0.0301	0.0070	0.0700
Sulfadimethoxine	159	8	0.0405	0.0494	0.0250	0.0560
Sulfamerazine	159	0	0.0126	0.0055	0.0002	0.0250
Sulfamethazine	247	43	0.0569	0.2169	0.0005	0.4100
Sulfamethizole	18	0	0.0500	0.0500	0.0500	0.0500
Sulfamethoxazole	150	6	0.0260	0.0147	0.0090	0.0990
Sulfathiazole	159	3	0.0271	0.0208	0.0160	0.0500
Tetracycline	159	0	0.0437	0.0358	0.0250	0.1000
Trimethoprim	253	41	0.0161	0.0128	0.0002	0.1340
Tylosin	143	3	0.0150	0.0075	0.0050	0.0300
Virginiamycin	143	0	0.0325	0.0194	0.0150	0.0500
Prescription drugs						
Albuterol	7	0	0.0145	0.0145	0.0145	0.0145
Atorvastatin	12	50	0.0088	0.0088	0.0050	0.0150
Bezafibrate	189	13	0.0423	0.0210	0.0010	0.2000
Carbamazepine	290	70	0.0724	0.0596	0.00003	0.6600
Cimetidine	7	29	0.0118	0.0118	0.0035	0.0530
Clofibric acid	204	19	0.0285	0.0213	0.0005	0.1750
Codeine	9	0	0.0527	0.0527	0.0120	0.1000
Cyclophosphamide	15	20	0.0029	0.0040	0.0002	0.0050
Dehydronifedipine	7	14	0.0059	0.0059	0.0050	0.0110
Diclofenac	208	17	0.0331	0.0253	0.0002	0.1940

Table 6 (continued)

Analyte	*n*	Freq det (%)	Mean (μg/L)	Wt Mean (μg/L)	Min (μg/L)	Max (μg/L)
Digoxin	2	0	0.1300	0.1300	0.1300	0.1300
Digoxigenin	7	0	0.0040	0.0040	0.0040	0.0040
Diltiazem	7	14	0.0084	0.0084	0.0060	0.0230
Enalaprilat	7	0	0.0760	0.0760	0.0760	0.0760
Fenoprofen	78	36	0.0335	0.0359	0.0002	0.1420
Fluoxetine	23	26	0.0142	0.0139	0.0050	0.0460
Gemfibrozil	303	26	0.0157	0.0122	0.0010	0.1120
Indomethacin	159	16	0.0047	0.0048	0.0002	0.0180
Meclocycline sulfosalicylate	125	0	0.0025	0.0025	0.0025	0.0025
Metformin	7	14	0.0213	0.0213	0.0015	0.1400
Norfluoxetine	15	0	0.0048	0.0049	0.0045	0.0050
Paroxetine metabolite	7	0	0.1300	0.1300	0.1300	0.1300
Pentoxifylline	15	40	0.0039	0.0054	0.0001	0.0090
Ranitidine	7	0	0.0050	0.0050	0.0050	0.0050
Warfarin	7	0	0.0005	0.0005	0.0005	0.0005
Non-prescription drugs						
Acetaminophen	7	0	0.0045	0.0045	0.0045	0.0045
Caffeine	46	68	0.0316	0.0448	0.0005	0.3000
Cotinine	43	72	0.0074	0.0106	0.0001	0.0500
1,7-Dimethylxanthine	7	0	0.0090	0.0090	0.0090	0.0090
Ibuprofen	211	16	0.0729	0.0688	0.0013	0.7900
Ketoprofen	83	33	0.0140	0.0227	0.0001	0.0500
Naproxen	297	26	0.0630	0.0712	0.0025	0.5510

Of the 57 different compounds analyzed in the water samples, 24 were not detected in any of the samples. With respect to the 980 data points for water, detectable concentrations of the various pharmaceutical compounds were reported for 330 samples (34%). Veterinary and human antibiotics were generally the least-often detected pharmaceutical compounds. Of those that were detected, the most frequent include erythromycin (29%), lincomycin (84%), monensin (80%), sulfamethazine (43%), and trimethoprim (41%); mean and maximum reported concentrations for these analytes ranged from 0.02 to 0.24 μg/L and from 0.13 to 1.17 μg/L, respectively. The prevalence and maximum concentrations for these analytes likely reflect the large amount of data contributed by the studies of Hao et al. (2006) and Lissemore et al. (2006); these authors studied pharmaceutical concentrations in surface waters downstream from agricultural operations. The other antibiotics were detected at lower frequencies and at maximum concentrations less than 0.2 μg/L.

Prescription and non-prescription drugs were frequently detected in surface waters. The range of concentrations reported for each of the pharmaceutical compounds is illustrated in Fig. 4. Carbamazepine (antiepileptic), ibuprofen

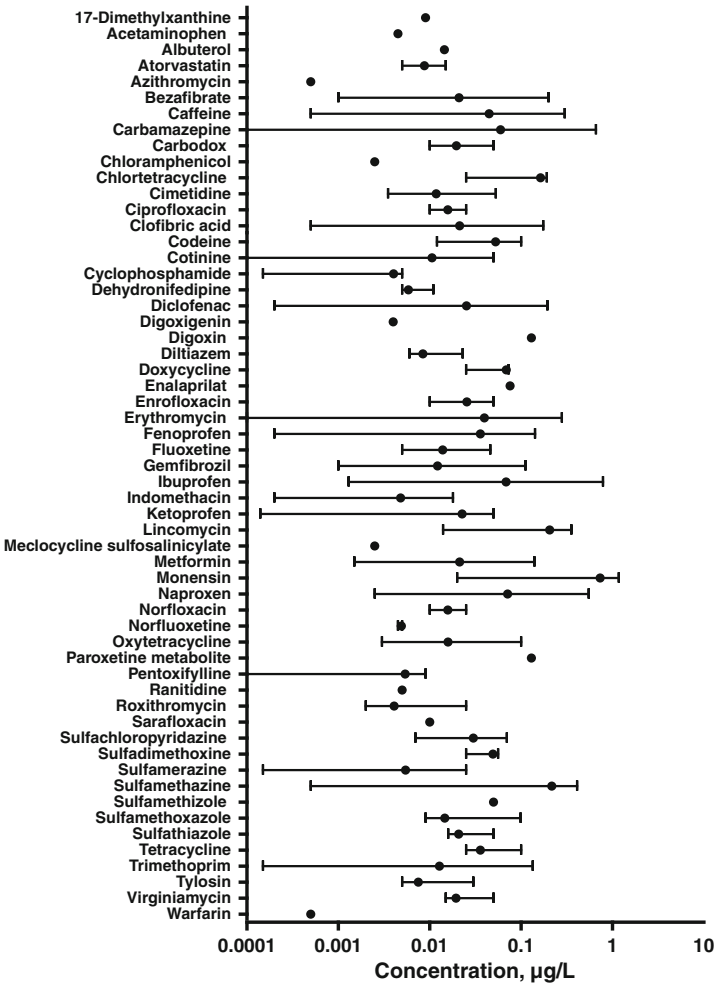


Fig. 4 Minimum, weighted mean, and maximum concentrations reported for pharmaceutical compounds in surface waters

(analgesic/anti-inflammatory), and naproxen (analgesic/anti-inflammatory) were detected at the highest concentrations (0.55–0.79 µg/L); the frequency with which they were present in the samples ranged from 16 to 70% (Table 6). Caffeine and cotinine were among the substances most frequently detected (68–72%) and are generally considered biomarkers of human excretion. Of the prescription drugs, atorvastatin (lipid regulator), cimetidine (antacid), fenoprofen (anti-inflammatory), fluoxetine (anti-depressant), gemfibrozil (anti-hyperlipidemic), and pentoxifylline (vasodilator) were detected at frequencies greater than 25% with maximum concentrations ranging from 0.009 to 0.142 µg/L. Other prescription drugs (bezafibrate,

Table 7 Summary statistics for pharmaceutical compounds in sediments

Analyte	*n*	Freq det (%)	Median (ng/g dwt)	Min (ng/g dwt)	Max (ng/g dwt)
Veterinary and human antibiotics					
Azithromycin	18	0	0.5	0.5	0.5
Erythromycin	18	11	4.4	0.5	8.2
Sulfamethoxazole	18	22	2.0	1.8	3.3
Thiabendazole	18	0	0.5	0.5	0.5
Trimethoprim	18	11	3.8	0.3	7.4
Prescription drugs					
Albuterol	18	0	0.5	0.5	0.5
Carbamazepine	18	0	0.5	0.5	0.5
Cimetidine	18	0	0.5	0.5	0.5
Codeine	18	0	0.5	0.5	0.5
Dehydronifedipine	18	6	12.0	12.0	12.0
Diltiazem	18	11	13.0	0.8	25.0
Fluoxetine	18	0	0.5	0.5	0.5
Ranitidine	18	0	0.5	0.5	0.5
Warfarin	18	0	0.5	0.5	0.5
Non-prescription drugs					
Acetaminophen	18	0	0.5	0.5	0.5
Caffeine	18	28	7.7	1.5	12.0
Cotinine	18	0	0.5	0.5	0.5
1,7-Dimethylxanthine	18	0	0.5	0.5	0.5
Diphenhydramine	18	50	12	0.3	75.0
Miconazole	18	28	7.7	6.1	11.0

clofibric acid, cyclophosphamide, diclofenac, diltiazem, indomethacin, and metformin) were detected at frequencies less than 25%, and their maximum concentrations were generally less than 0.2 μg/L.

As summarized in Table 7, limited data are available for the concentrations of pharmaceutical compounds in sediments. Of the 20 compounds that have been analyzed, 8 were detected. Diphenhydramine was most frequently detected at median and maximum concentrations of 12 and 75 ng/g dwt, respectively. Caffeine, miconazole, and sulfamethoxazole were detected at frequencies greater than 20% at maximum concentrations ranging from 3.3 to 12 ng/g dwt. The other compounds were detected at lower frequencies and at maximum concentrations less than 25 ng/g dwt.

In summary, the available data suggest that pharmaceutical compounds may occur at nanogram to low microgram per liter concentrations in surface water samples. At present, there are no standards, guidelines, or criteria with which to compare the concentrations. Pharmaceutical compounds are most frequently detected near the point of discharge from wastewater treatment plants or agricultural operations, especially in locations where hydrologic conditions result in minimal dilution. Collectively, the frequency with which pharmaceutical compounds have

been detected in surface waters of the Great Lakes Basin is low; detectable concentrations have been reported for 34% of the 980 data points. However, as noted by Metcalfe et al. (2003), detectable concentrations of some drugs, including clofibric acid, ketoprofen, fenoprofen, and carbamazepine, may be present at low nanogram per liter levels in surface waters taken from open waters or from sites that are relatively remote from the influence of wastewater discharges.

3.3 Organic Wastewater Contaminants, Hormones, and Steroids

A variety of chemicals have been detected in surface waters downstream from wastewater treatment plants. The organic wastewater contaminants discussed in this section include a variety of industrial chemicals and personal care products not addressed in other sections of this report. Available information on concentrations of human and animal hormones and steroids is also addressed.

Much of the available information on the concentration and distribution of organic wastewater contaminants in the Great Lakes Basin were from Kolpin et al. (2002). As previously noted, surface water samples were collected during 1999 and 2000 as part of a nationwide reconnaissance program from a network of 139 streams across 30 states, of which 19 sites were located within the Lake Michigan drainage basin (sampling locations not illustrated). The selection of the sampling sites was biased toward areas considered to be susceptible to contamination from human, industrial, and agricultural wastewaters. Of the 95 organic wastewater contaminants included in the study, 40 represented a variety of industrial chemicals (anti-corrosives, antioxidants, plastics monomers, plasticizers, solvents, etc.), personal care products (deodorizers, fragrances, disinfectants, insect repellant), polycyclic aromatic hydrocarbons (PAHs), as well as human and animal hormones and steroids.

Tertuliana et al. (2008) examined the occurrence and distribution of a broad range of pharmaceutical and organic wastewater compounds in the Tinkers Creek watershed in northeastern Ohio. In addition to using passive samplers, sediment samples were collected at each of the sampling stations. The samples were collected during May–June of 2006 from 18 locations situated upstream and downstream from wastewater treatment plant discharges to the mainstream and tributaries of Tinkers Creek. Of the 57 organic wastewater compounds included in the analysis, a total of 33 organic wastewater compounds and 4 steroids were detected in sediment at one or more of the sites.

Based on the available literature, a database was developed containing 336 reported values for the 66 compounds analyzed in surface waters and sediments from the Great Lakes Basin. As summarized in Table 8, between 4 and 29 surface water samples were analyzed for each of the contaminants. The frequencies with which the various compounds were detected in water ranged from 0 to as high as 90%. Reported detection limits for the compounds ranged from 0.005 to 2.0 μg/L. The concentrations of organic wastewater contaminants detected in sediment are

Table 8 Summary statistics for organic wastewater constituents in surface waters

Analyte	*n*	Freq det (%)	Min (μg/L)	Max (μg/L)
Anti-corrosives/antioxidants				
Butylated hydroxy toluene	7	14.3	< 0.08	0.1
3-*tert*-Butyl-4-hydroxy anisole	7	0.0	< 0.12	
2,6-Di-*tert-p*-benzoquinone	7	14.3	< 0.07	0.06
2,6-Di-*tert*-butyl-phenol	7	14.3	< 0.08	0.1
5-Methyl-1*H*-benzotriazole	4	75.0	< 0.15	0.55
Deodorizer/fragrances				
Acetophenone	7	14.3	< 0.1	0.1
1,4-Dichlorobenzene	7	28.6	< 0.03	0.17
Disinfectants				
4-Methyl phenol	7	42.9	< 0.04	0.07
Phenol	7	28.6	< 0.08	0.6
Triclosan	29	89.7	< 0.004	0.3
Insect repellant				
N,*N*-Diethyltoluamide	4	75.0	< 0.08	0.24
Plasticizers/plastics manufacture				
Bis(2-ethylhexyl)adipate	7	0.0	< 1.5	
Bis(2-ethylhexyl)phthalate	7	14.3	< 2.0	20
Bisphenol A	7	57.1	< 0.09	0.8
Diethyl phthalate	4	25.0	< 0.25	0.2
Ethanol, 2-butoxy phosphate	7	42.9	< 0.07	0.82
Phthalic anhydride	7	42.9	< 0.15	0.9
Triphenyl phosphate	7	0.0	< 0.1	
Polycyclic aromatic hydrocarbons				
Anthracene	7	14.3	< 0.05	0.05
Benzo(*a*)pyrene	7	28.6	< 0.05	0.11
Fluoranthene	7	42.9	< 0.03	0.2
Naphthalene	7	14.3	< 0.02	0.02
Phenanthrene	7	42.9	< 0.05	0.06
Pyrene	7	57.1	< 0.03	0.27
Solvents				
Tetrachloroethylene	7	14.3	< 0.03	0.2
Steroids/hormones				
cis-Androsterone	5	20.0	< 0.005	0.031
Cholesterol	12	66.7	< 1.5	2.38
Coprostanol	12	50.0	< 0.6	0.73
Equilenin	5	0.0	< 0.005	
Equilin	5	0.0	< 0.005	
17α-Estradiol	5	20.0	< 0.005	0.001
17α-Ethynyl estradiol	5	0.0	< 0.005	
17β-Estradiol	12	0.0	< 0.005	
Estriol	5	20.0	< 0.005	0.02
Estrone	5	0.0	< 0.005	

Table 8 (continued)

Analyte	*n*	Freq det (%)	Min (μg/L)	Max (μg/L)
Mestranol	5	0.0	< 0.005	
19-Norethisterone	5	0.0	< 0.005	
Progesterone	5	0.0	< 0.005	
Stigmastanol	4	0.0	< 2.0	
Testosterone	5	0.0	< 0.005	

summarized in Table 9. The frequencies with which the various compounds were detected varied from 0 to 100%. As noted in the table, between 5 and 73 sediment samples were analyzed for the various contaminants. When available, the concentrations reported in Great Lakes Basin were compared to US Environmental Protection Agency (US EPA), Environment Canada (EC), and European Union (EU) regulatory criteria and guidelines (Table 2).

Table 9 Summary statistics for organic wastewater constituents in sediments

Analyte	*n*	Freq det (%)	Median (ng/g dwt)	Min (ng/g dwt)	Max (ng/g dwt)
Anti-corrosives/antioxidants					
3-*tert*-Butyl-4-hydroxy anisole	18	6	12.5	12.5	12.5
Deodorizer/fragrances					
Acetophenone	18	89	35	10	90
AHTN	18	56	30	10	80
Camphor	18	0	12.5	12.5	12.5
1,4-Dichlorobenzene	18	17	16	16	16
HHCB	18	50	60	20	390
Indole	18	100	55	30	1,100
Isoborneol	18	0	12.5	12.5	12.5
Isoquinoline	18	0	12.5	12.5	12.5
D-Limolene	18	11	10	10	10
Menthol	18	0	12.5	12.5	12.5
3-Methyl indole	18	100	30	10	150
Disinfectants/preservatives					
4-Methyl phenol	18	89	35	10	260
Phenol	18	83	70	20	220
Triclosan	18	17	36	30	56
Insect repellant					
N,*N*-Diethyltoluamide	18	0	12.5	12.5	12.5
Chemicals/plastics manufacture					
Anthraquinone	18	100	70	20	240
Benzophenone	18	0	12.5	12.5	12.5
Benzylbutylphthalate	5	0	150	150	150
Bis (2-ethylhexyl)phthalate	23	97	4,030	30	29,700
Bis(isononyl)phthalate	5	0	150	150	150

Table 9 (continued)

Analyte	*n*	Freq det (%)	Median (ng/g dwt)	Min (ng/g dwt)	Max (ng/g dwt)
Bisphenol A	73	38	21.6	0.075	60
Carbazole	18	100	50	20	130
4-Cumylphenol	18	0	12.5	12.5	12.5
Dibutyl phthalate	5	0	150	150	150
Diethyl phthalate	33	11	80	10	150
Isopropylbenzene	18	6	12.5	12.5	12.5
2,2,4,4-Tetrabromodiphenylether	18	0	12.5	12.5	12.5
Tributylphosphate	18	0	12.5	12.5	12.5
Triphenyl phosphate	18	0	12.5	12.5	12.5
Tris(2-butoxyethyl) phosphate	18	39	30	20	70
Tris(dichloroisopropyl)phosphate	18	0	12.5	12.5	12.5
Polycyclic aromatic hydrocarbons					
Anthracene	18	94	50	10	110
Benzo(*a*)pyrene	18	100	140	30	390
2,6-Dimethylnaphthalene	18	100	25	10	60
Fluoranthene	18	100	540	80	1,400
1-Methylnaphthalene	18	89	20	10	40
2-Methylnaphthalene	18	100	20	10	50
Naphthalene	18	100	20	10	40
Phenanthrene	18	94	250	60	720
Pyrene	18	100	400	60	1,100
Solvents					
Isophorone	18	0	12.5	12.5	12.5
Steroids/hormones/natural products					
Cholesterol	18	100	560	260	2,800
Coprostanol	18	83	80	20	300
β-Sitosterol	18	100	620	210	2,500
β-Stigmastanol	18	83	140	30	1,100

A variety of industrial chemicals (anti-corrosives/antioxidants, substances used in chemicals or plastics manufacture, solvents, etc.) were detected in both surface waters and sediments. Of the industrial chemicals detected in water (Table 8), the anti-corrosive agent, 5-methyl-1*H*-benzotriazole was detected in 75% of the samples at concentrations as high as 0.55 μg/L. This frequency of detection was higher than found in the nationwide survey (31.5%; Kolpin et al. 2002), although a higher maximum concentration (2.4 μg/L) was reported elsewhere in the United States. Several compounds related to plastics manufacture, including the monomers bisphenol A (BPA) and phthalic anhydride, and a plasticizer (ethanol-2-butoxy phosphate), were also among those xenobiotics that were frequently detected in Great Lakes surface waters. The other chemicals, including antioxidants, plasticizers, and solvents, were detected less frequently, ranging from their absence to being present in 25% of the samples. The concentrations of most of the industrial chemicals in water were low

(<1 μg/L), with the exception of bis(2-ethylhexyl)phthalate (DEHP), which was detected in a single sample at 20 μg/L. This value exceeds the EC Interim Water Quality Guideline (16.0 μg/L) and the EU predicted no effect value (1.3 μg/L).

Of the industrial chemicals detected in sediment (Table 9), bis(2-ethylhexyl)phthalate was detected in 97% of the samples at median and maximum concentrations of 4,030 and 29,700 ng/g dwt, respectively. The highest concentration, which exceeds the EU PNEC (predicted no-effect concentration) for sediment (21,500 ng/g dwt), was reported by McDowell and Metcalfe (2001) in samples taken in the vicinity of the wastewater treatment plant discharge in Hamilton Harbor, ON. In contrast, bis(2-ethylhexyl)phthalate concentrations detected in Tinkers Creek downstream from wastewater discharges ranged from 30 to 120 ng/g dwt (Tertuliana et al. 2008). Anthraquinone and carbazole were also frequently detected (100%) in sediment at concentrations ranging from 20 to 240 ng/g dwt. The other chemicals, including various antioxidants, plasticizers, and solvents, were detected less frequently and at concentrations less than 100 ng/g dwt.

BPA, a monomer used in the manufacture of epoxy resins and polycarbonate plastics, was detected in 57.1% of the surface water samples at concentrations ranging from below the detection limit to as high as 0.8 μg/L (Table 8). These results are somewhat higher than those of a recent statistical analysis of BPA exposures in North American aquatic environments (Klečka et al. 2009). Based on the analysis of 1,068 weighted observations for North American surface waters, BPA has been reported at concentrations above the detection limit in 20% of analyzed samples. Median and 95th percentile concentrations for North American waters were 0.081 μg/L and 0.47 μg/L, respectively. As summarized in Table 9, BPA has also been detected in 38% of the sediment samples at concentrations ranging from below the detection limit to 60 ng/g dwt. Chu et al. (2005) reported that BPA was detected in 65% of sediment samples from Lake Erie ($n = 55$) at concentrations ranging up to 6.1 ng/g dwt. Tertuliana et al. (2008) detected BPA in 11% of the samples from Tinkers Creek, with estimated concentrations ranging from 20 to 60 ng/g dwt.

Risk assessments for BPA have been conducted by several regulatory authorities around the world (Advanced Industrial Science and Technology (AIST) 2007; Environment Canada and Health Canada (EC and HC) 2008; European Commission (EUC) 2008a). The European Chemicals Bureau of the EUC (EUC 2008a) has recently completed a comprehensive risk assessment for BPA and has defined PNECs for water and sediment of 1.5 μg/L and 63 μg/kg dwt, respectively. The PNEC for water was derived using a species sensitivity distribution approach, based on chronic data for 16 different species across a wide range of trophic levels. Environment Canada (EC and HC 2008) has also recently finalized a screening assessment for BPA. The PNEC values for water and sediment are 0.175 μg/L and 0.01 mg/L, respectively. Note that the PNEC value for sediment was derived from a water-only exposure study. Considering the available data for BPA in the Great Lakes, the maximum concentrations for water and sediment are below the European PNEC values. However, the maximum concentration exceeds the Canadian PNEC for water, but is below the PNEC for sediment organisms.

Among the personal care products (deodorizers/fragrances, disinfectants, insect repellants, etc.), triclosan and *N*,*N*-diethyltoluamide were among those most frequently detected (>75%) in Great Lakes waters (Table 8). The substances 1,4-dichlorobenzene, phenol, and 4-methylphenol were detected less frequently and at concentrations below 1 μg/L. Many of these substances were also present in sediment (Table 9). Among those most frequently detected were a number of natural products used commercially, including acetophenone, indole, 3-methyl indole, 4-methyl phenol, and phenol; concentrations in sediment ranged from 10 to 1,100 ng/g dwt. The maximum concentrations for 1,4-dichlorobenzene and phenol in water and sediment are below EC and EU criteria (Table 2).

Triclosan was frequently detected in the surface water samples from the Great Lakes Basin (89.7%) and had concentrations ranging from below the detection limit to as high as 0.3 μg/L. In contrast, triclosan was infrequently detected (17%) in sediment and had maximum concentrations less than 100 ng/g dwt. Triclosan is an antimicrobial disinfectant agent used for over 30 years in a wide array of personal care and consumer products. Triclosan was detected less frequently in water in the nationwide reconnaissance study (57.6%; Kolpin et al. 2002), although the maximum reported concentration was higher (2.3 μg/L) elsewhere in the United States. Hua et al. (2005) reported low triclosan concentrations, ranging from 4 to 8 ng/L in surface water samples taken from two sites along the Detroit River shoreline, downstream of the Little River Wastewater Treatment Plant (Windsor, ON). Servos et al. (2007) reported low levels of triclosan (34 ng/L) in river water samples collected in southern Ontario.

Valters et al. (2005) reported the presence of triclosan and methyl-triclosan in the blood plasma of pelagic and benthic fish (13 species) that were collected from the Detroit River during 2001 and 2002. Concentrations of triclosan in plasma of pelagic fish ranged from 1.87 to 10.27 ng/g wwt. Similar concentrations were reported in plasma from benthic fish (0.76–5.53 ng/g wwt). The levels of methyl-triclosan were lower, ranging from 0.0004 to 0.013 ng/g wwt. The source of methyl-triclosan was attributed to biological methylation during wastewater treatment (Balmer et al. 2004; Lindstrom et al. 2002). The authors noted that anthropogenic sources of triclosan in the Detroit River system contribute to the concentrations detected in the fish; however, when compared to the levels of other organohalogen compounds measured in the plasma, the concentrations of triclosan were comparable to those for total polybrominated diphenyl ethers (PBDEs; 0.16–21.07 ng/g wwt), but considerably lower than the total PCB concentrations detected in the same fish (10.4–909.1 ng/g wwt).

The insect repellant *N*,*N*-diethyltoluamide (DEET) was frequently detected (75%) in water but not in sediment samples from the Great Lakes Basin. According to the US EPA (1998), approximately 30% of the US population uses DEET annually as an insect repellant. With the spread of the West Nile virus, there have been frequent official recommendations that residents in affected areas use products containing DEET. Concentrations in the Great Lakes Basin ranged from below the detection limit (0.08 μg/L) to as high as 0.24 μg/L. These results are consistent

with those of Sandstrom et al. (2005) who reported that DEET was detected at levels of 0.02 μg/L or greater in 73% of the 56 stream sites sampled in the United States during the year 2000. Although DEET was frequently detected at all sites, the median concentration was low (0.05 μg/L). The highest concentrations (maximum of 1.1 μg/L) were found in samples collected from urban areas.

A variety of PAHs were also measured in water and sediment samples from the Great Lakes Basin (Tables 8 and 9). Combustion by-products, including pyrene, phenanthrene, fluoranthene, and benzo(a) pyrene, were among the most frequently detected compounds, and they displayed maximum concentrations ranging from 0.06 to 0.27 μg/L in water and from 390 to 1,400 ng/g dwt in sediment. Although anthracene and naphthalene were detected less frequently in water, they were generally found in all sediment samples. Several other PAHs that are components of petroleum hydrocarbon fuels (gasoline, diesel fuel) were also detected in sediments. When the maximum concentrations are compared to regulatory criteria developed by the EC and EU, naphthalene and phenanthrene concentrations in water are below the guidelines for water and sediment, but many of the other PAH compounds exceed those limits (Table 2).

Lopes and Furlong (2001) reported the occurrence of 65 semi-volatile organic contaminants (SVOCs) in streambed samples collected between 1992 and 1995 from 536 sites representing 20 major river basins. Although the details of the investigation were not available for our study, it is apparent that some of the samples were collected in eastern Wisconsin from the Western Lake Michigan drainage basin. From the summary information provided in the paper, the highest SVOC concentrations, which included a variety of PAHs, phthalates, and phenols, were detected in samples collected from the northeastern United States and Great Lakes Basins. PAH and phthalate concentrations were 10 times higher in areas influenced by urban activities (high population densities and large metropolitan areas) than at sites with other land uses. The highest total PAH (170,000 μg/kg) and total phenol (4,900 μg/kg) concentrations were measured near Milwaukee, WI. The authors reported that on the basis of sediment quality guidelines, adverse effects are probable at 7.5% and are possible at 16.2% of the sites. High PAH concentrations contributed the greatest potential for adverse effects on aquatic ecosystems.

A variety of human, animal, and plant hormones and steroids were also detected in water and sediment samples from the Great Lakes Basin (Tables 8 and 9). Cholesterol (plant and animal steroid) and coprostanol (fecal steroid) were present in more than half of the water, and nearly all of the sediment samples. Two plant steroids (sitosterol and stigmastanol) were also frequently detected in sediment. *cis*-Androsterone (urinary steroid), 17α-estradiol (hormone), and estriol (hormone) were also detected in 20% of the water samples. Detection frequencies for the latter compounds, in waters of the Great Lakes, are comparable to those reported by Kolpin et al. (2002), although generally higher concentrations were found elsewhere in the United States. Higher detection frequencies and maximum concentrations were also reported by Kolpin et al. (2002) for many other hormones and steroids that were not detected in the Great Lakes Basin. For example, 17α-ethynyl estradiol and 17β-estradiol were present in 10–16% of the samples nationwide at

maximum concentrations from 0.009 to 0.073 μg/L. As noted by Kolpin et al. (2002), when potency and aquatic toxicity are considered, measured concentrations of reproductive hormones may have greater implications for the health of aquatic organisms than measured concentrations of the other emerging contaminants. Previous research (Baronti et al. 2000; Purdom et al. 1994; Routledge et al. 1998) has shown that even low-level exposure (<0.001 μg/L) to select hormones can illicit adverse effects in aquatic species.

In summary, a variety of organic wastewater contaminants have been detected in the Great Lakes Basin, representing a wide range of residential, industrial, and agricultural origins. Of those addressed here, the most frequently detected in water included 5-methyl-1*H*-benzotriazole, triclosan, *N*,*N*-diethyltoluamide, BPA, and several PAHs. Measured concentrations for Great Lakes waters were generally low (<1 μg/L) and generally were below regulatory guidelines or criteria, other than as noted above. Many of the compounds, however, do not have such guidelines established. Concentrations of many other organic wastewater contaminants that were detected in the nationwide reconnaissance, including current-use pesticides, pharmaceuticals, alkylphenol ethoxylates, synthetic musks, and flame retardants, are discussed in other sections of this report.

3.4 Alkylphenol Ethoxylates

Alkylphenol ethoxylates (APEO) have been used as surfactants for more than 50 years. APEO in use today include nonylphenol ethoxylates (NPEO), comprising about 80% of the market, whereas octylphenol ethoxylates (OPEO) comprise about 20% of the market. These compounds have been the subject of considerable regulatory attention, primarily from concerns about their aquatic toxicity and weak endocrine activity. Risk assessments have been conducted by regulatory authorities around the world (EC and HC 2001; EUC 2002a; United Kingdom Environment Agency; UK EA 2005; US EPA 1996), and risk management strategies have been implemented, which include their use reduction and/or elimination in certain applications, along with voluntary reductions in their use in several countries. Today, NPEO are primarily used for industrial applications that include pulp and paper production, textile manufacturing, and use in the formulation of crop protection chemicals. They are also used in industrial and institutional cleaners and detergents. Although nonylphenol (NP) is used primarily in the manufacture of NPEO, some is also used in the production of resins and plastics stabilizers. In contrast, octylphenol (OP) is produced in significantly lower volumes and is used primarily as a chemical intermediate in the production of phenolic resins. Because of their use patterns, most of the spent APEO are discharged into wastewater treatment systems, which have been shown to be effective in reducing loads entering the environment (Melcer et al. 2007). Although most APEO are removed during wastewater treatment, metabolites consisting of alkylphenols (AP), low mole APEO, and alkylphenol ether carboxylates (APEC) have been reported in effluents, streams, and rivers across North America.

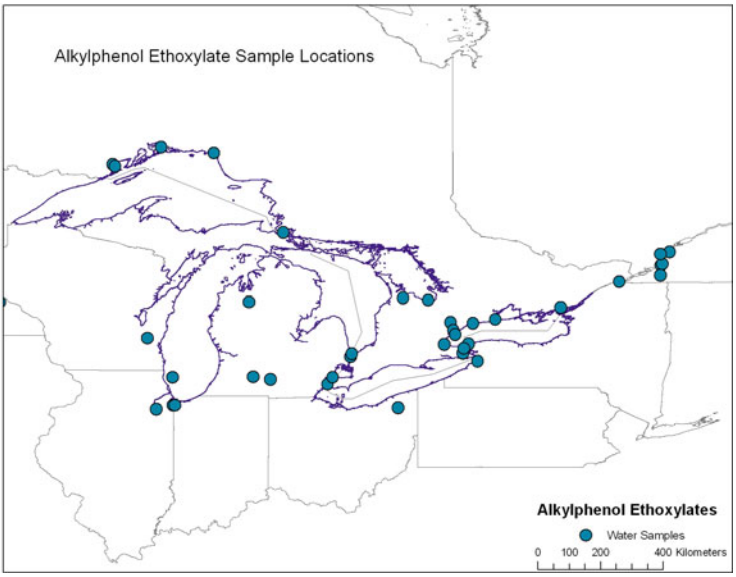
Concentrations of APEO and their metabolites have been reported in environmental samples by numerous investigators over the past 15 years. As discussed below, the concentrations of APEO in the Great Lakes Basin, including levels in surface water, sediment, and biota, have been reported in 10 studies. The geographic distribution of the sampling sites is shown in Fig. 5a and b.

Bennie et al. (1997) reported on the occurrence of AP and low mole APEO in waters of the Great Lakes Basin and the upper St. Lawrence River. Surface water samples collected during 1994 and 1995 from 35 sites showed measurable quantities of NP and OP in 24% of the samples at concentrations ranging from below the detection limit to 0.92 μg/L. Low mole NP1EO and NP2EO were present in 32–58% of the water samples at levels as high as 10 μg/L. Sediment samples from all nine heavily industrialized sites had detectable levels of NP at concentrations ranging from 0.17 to 72 μg/g dwt. OP was detected in 89% of the samples at lower concentrations (<0.01–1.8 μg/g dwt). NP1EO and NP2EO were present in 66% of the samples; the maximum concentrations ranged from 6 to 38 μg/g dwt. The authors noted that the highest concentrations were all below acute toxicity thresholds, but were sufficient to raise concern with regard to long-term effects on fish.

Bennett and Metcalfe (1998) analyzed for NP and OP in 28 sediment samples collected from both industrialized and pristine regions throughout Lakes Huron, Erie, and Ontario. The results indicated that the AP are widely distributed in sediments from the lower Great Lakes. NP and OP concentrations were generally low (<1 μg/g dwt) except in sediments collected near urban and industrial centers. In the vicinity of wastewater treatment discharges, NP and OP concentrations as high as 37.8 μg/g dwt and 23.7 μg/g dwt were reported. In a follow-up study, Bennett and Metcalfe (2000) examined the spatial distribution of APEO and their degradation products in receiving waters near sewage treatment plant discharges in Hamilton Harbor and in the Detroit River. The investigators collected sediment samples, deployed semi-permeable membrane devices, and caged freshwater mussels at 24 locations in the summer of 1996. NP concentrations were elevated (>20 μg/g dwt) in the Detroit River downstream of both the Windsor and Detroit wastewater treatment plant discharges, but rapidly declined to less than 1 μg/g dwt downstream. Among the reported NP concentrations in Great Lakes sediments, the highest (110 μg/g) was that detected in the vicinity of the outflow of the Burlington wastewater treatment plant in Hamilton Harbor. Analysis of the spatial data for Hamilton Harbor indicated that the concentrations of NP and the low mole NPEO decreased by a factor of 2 over distances of 30–50 m. The authors concluded that the environmental distribution of APEO is expected to be localized in areas close to the point of discharge and are likely to decline at sites a few hundred meters from the source.

Kannan et al. (2001) analyzed sediments from the upper Detroit and lower Rouge Rivers in Detroit, MI as well as samples from a non-point source location in Lake Michigan (near Muskegon, MI). Several industrial facilities and combined sewer overflows located along the two rivers have historically impacted the levels of sediment contaminants. Thirty four samples were collected in June 1998 and analyzed for NP, OP, and a variety of chlorinated aromatic compounds. The distribution of

A. Surface waters



B. Sediments

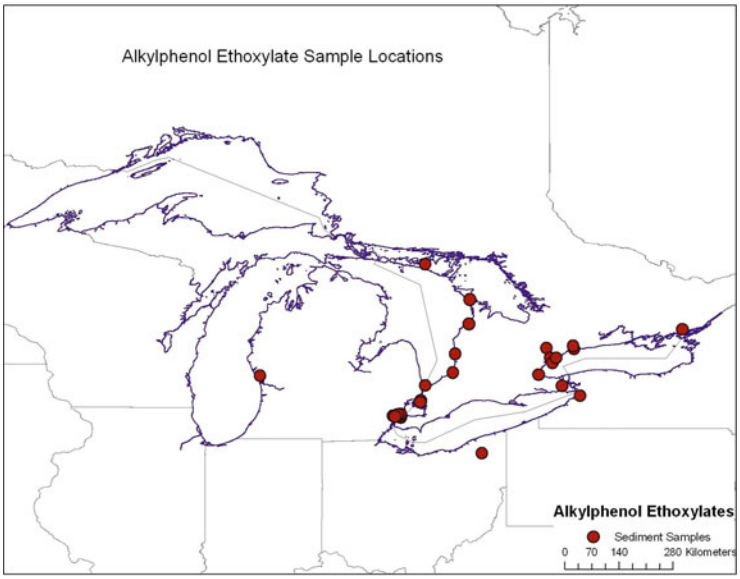


Fig. 5 Sampling locations for alkylphenol ethoxylates. **a** Surface waters and **b** sediments

NP and OP in the rivers suggested the presence of localized, but multiple, sources of contamination for each class of compounds. NP and OP were detected in 70% and 65% of the sediment samples with concentrations ranging from undetectable to as high as 60,000 and 4,050 μg/kg, respectively. Neither compound was detected in sediment samples collected from Lake Michigan.

Kannan et al. (2003) also conducted a survey of water, sediment, and fish samples from the Kalamazoo River. Samples were collected along transverse transects both upstream and downstream from wastewater discharges located in Battle Creek and Kalamazoo, MI, during July and August, 2000. Three of 36 sediment samples and 1 of 24 surface water samples contained detectable concentrations. NP and NP1EO concentrations in the water sample were 1.1 and 2.0 μg/L, respectively; measurable NP concentrations in the sediments ranged from 5.8 to 15.3 μg/kg dwt. Of the 10 fish caught during the study, 1 contained detectable concentrations of NP (3.4 μg/kg wwt).

Keith et al. (2001) reported the results of analysis of 183 fish (representing 8 species) collected in 1999 from the Kalamazoo River and Lake Michigan. NP concentrations were detectable in 41% of the samples; measured concentrations ranged from 3.3 to 29.1 μg/kg wwt. Traces of NP1EO were present in 11% of the fish, but the levels were not quantifiable. Higher mole NPEO were not detected.

Kolpin et al. (2002) analyzed for NP and low mole NPEO and OPEO in nine water samples from the Great Lakes Basin during the US nationwide reconnaissance study (1999–2000). NP was detected in 55% of the samples; measured concentrations ranged from 0.25 to 3 μg/L. NP1EO and NP2EO were detected less frequently (11%) with maximum concentrations of 1 μg/L. OP and low mole OPEO were detected in some samples at lower concentrations.

Mayer et al. (2007) analyzed for the presence of AP in the coastal marsh, Cootes Paradise, ON, Canada. This coastal wetland and nature sanctuary, located west of Hamilton Harbor, receives discharges from the Dundas, ON, wastewater treatment plant as well as inputs from several combined sewer overflows from the city of Hamilton, ON. Samples of water ($n = 6$) and sediment ($n = 21$) were collected from both open water and shoreline sites during 2001 and 2002. NP, OP, and NP1EO concentrations in water were low throughout the marsh, ranging from below the detection limit to 0.28 μg/L. However, one of the highest of the NP3–17EO concentrations in the Great Lakes Basin was reported (91.7 μg/L). The authors attributed this high concentration value to a heavy rainfall event that produced a large discharge from a combined sewer overflow on the day the samples were collected. Sediment concentrations for NP and NPEO were generally consistent, ranging from below the detection limit to 1.75 μg/g dwt.

Rice et al. (2003) examined the occurrence of a variety of AP and APEO in water, sediment, and fish collected along a 74-mile length of the Cuyahoga River, OH. Water and sediment samples, as well as 11 or 12 carp were collected from 8 sites along the river in the summer of 2000. Maximum AP/APEO concentrations in water and fish were observed downstream of the Akron wastewater treatment plant. NP concentrations in the water ranged from 0.1 to 0.5 μg/L; total NP0–3EO concentrations were slightly higher (0.13–5.1 μg/L). Total OP0–3EO concentrations were low (0.005–0.19 μg/L). Average total NP0–5EO concentrations in the fish ranged from

32 μg/kg at the upstream (clean) site to as high as 920 μg/kg; NP1EO was the predominant homolog detected. NP concentrations in fish varied from 7 to 110 μg/kg. According to the authors, the NP levels could be considered moderate when compared to maximum NP residues that have been reported in the literature. However, NP1EO and NP2EO concentrations were among the highest reported for fish in US waters. NP concentrations in the sediment ranged from 75 to 340 μg/kg, with total NP0–4EO ranging from 250 to 1,020 μg/kg. Total OP0–5EO levels in the sediment ranged from 20 to 74 μg/kg. Although AP/APEO concentrations increased below the wastewater discharge in Akron, OH, the highest concentrations were present at the most downstream site near Cleveland.

Sabik et al. (2003) examined the prevalence of APEO in surface water, sediment, and caged mussels from the St. Lawrence River at sites both upstream and downstream from the Montreal, QC, effluent outfall. At the time of the study (1999), the facility was the largest primary physico-chemical treatment plant in North America. In contrast to many of the other studies, the target analytes included a broad range of NPEO homologs (NP1EO–NP16EO) as well as NP, OP, and the ether carboxylates. The higher mole NPEO were predominant in the surface waters and were present in samples ($n = 4$) collected both upstream and downstream of the discharge. Concentrations of NP>7EO ranged from below the detection limit to as high as 10.3 μg/L. NP, OP, and the low mole NPEO were generally below the detection limit. In contrast, NP and the low mole NPEO were detected in the sediments ($n = 6$), with the highest concentrations occurring downstream of the discharge. To assess the potential for bioconcentration of APEO, mussels taken from a reference lake were caged and submerged for 62 days upstream and downstream of the facility. The authors noted a slight, but not significant bioconcentration of NP5EO–NP8EO in the mussels, which was more noticeable at the downstream site.

As presented in Table 10a, concentrations of APEO and their metabolites have been reported for 87 surface water samples obtained during the years from 1994 to 2002 at 43 locations throughout the Great Lakes Basin. As previously discussed, many of the sampling locations were downstream from the discharges of wastewater treatment plants. Although concentrations have been reported for as many as 24 different analytes, to facilitate interpretation, the analytes were first grouped into categories on the basis of structure and data availability, as follows: alkylphenols (NP, OP), low mole ethoxylates (NP1EO, NP2EO), higher mole ethoxylates (NP3–17EO, OPEO), and ether carboxylates (nonylphenol ether carboxylates (NPEC), octylphenol ether carboxylates (OPEC)). These groupings are intended to represent the majority of compounds found across all of the studies.

Of the 385 values reported for surface water, 46% were above the detection limits. NPEC were among the analytes detected most often in the samples (75%) with average concentrations of 0.97 ± 2.12 μg/L, which is consistent with the fact that ether carboxylates have been reported as the dominant biodegradation products of wastewater treatment (Melcer et al. 2007). Low and high mole NPEO were detected in 34–60% of the samples, with average concentrations ranging from 0.64 ± 1.22 to 2.01 ± 10.0 μg/L, respectively. The fact that high mole NPEO were detected at such levels is unusual. Further examination of the data indicated that samples were only analyzed for high mole NPEO in two studies (Mayer et al. 2007; Sabik et al. 2003).

Table 10 Summary statistics for alkylphenol ethoxylates

	n	Freq det (%)	Mean (μg/L)	SD (μg/L)	Median (μg/L)	95th percentile (μg/L)	Min (μg/L)	Max (μg/L)
A. Surface water								
NP	69	36	0.25	0.49	0.005	1.30	0.0005	3.00
NP1EO	69	54	0.64	1.22	0.159	2.18	0.0010	7.80
NP2EO	68	34	1.08	2.53	0.015	7.80	0.0010	11.00
NP3–17EO	87	60	2.01	10.00	0.063	8.90	0.0005	91.70
NPEC	20	75	0.97	2.12	0.395	2.85	0.0010	9.67
OP	48	25	0.02	0.07	0.003	0.07	0.0005	0.47
OPEO	14	50	0.11	0.06	0.100	0.24	0.0500	0.30
OPEC	10	60	0.06	0.12	0.027	0.25	0.0010	0.41
All alkylphenol ethxoyaltes (APE)	385	46	0.86	4.95	0.045	3.81	0.0005	91.70
	n	Freq det (%)	Mean (μg/g dwt)	SD (μg/g dwt)	Median (μg/g dwt)	95th percentile (μg/g dwt)	Min (μg/g dwt)	Max (μg/g dwt)
B. Sediment								
NP	113	81	5.60	14.94	0.30	30.00	0.003	110.00
NP1EO	51	82	5.22	13.13	0.28	32.50	0.005	70.00
NP2EO	51	69	0.76	2.91	0.12	2.50	0.001	20.00
NP3–17EO	33	76	0.62	0.94	0.09	2.88	0.015	2.88
NPEC	16	13	0.20	0.12	0.27	0.27	0.001	0.27
OP	76	71	0.56	2.75	0.02	1.44	0.001	23.70
OPEO	7	100	0.05	0.02	0.06	0.07	0.020	0.07
OPEC	14	0	0.02	0.01	0.02	0.02	0.003	0.02
All APE	361	71	2.78	10.12	0.12	20.00	0.001	110.00

Table 10 (continued)

	n	Freq det (%)	Mean (μg/g wwt)	SD (μg/g wwt)	Median (μg/g wwt)	95th percentile (μg/g wwt)	Min (μg/g wwt)	Max (μg/g wwt)
C. Biota								
Fish								
NP	284	63	0.025	0.035	0.007	0.102	0.002	0.11
NP1EO	284	29	0.095	0.157	0.008	0.400	0.008	0.55
NP2EO	284	29	0.038	0.064	0.009	0.150	0.009	0.24
NP3EO	203	0	0.010	0.000	0.010	0.010	0.010	0.01
OP	7	0	0.010	0.000	0.010	0.010	0.010	
OPEO	7	100	0.033	0.016	0.031	0.051	0.018	0.01
All APE	1,069	33	0.043	0.089	0.010	0.210	0.002	0.05
Mussels	*n*	Freq det (%)	Mean (μg/g wwt)	SD (μg/g wwt)	Median (μg/g wwt)	95th percentile (μg/g wwt)	Min (μg/g wwt)	Max (μg/g wwt)
NP	122	90	0.155	0.164	0.135	0.405	0.001	0.600
NP1EO	122	74	0.032	0.060	0.006	0.148	0.002	0.200
NP2EO	122	80	0.296	0.705	0.007	1.548	0.000	2.566
NP3–16EO	168	45	1.780	3.910	0.002	8.968	0.002	18.923
NPEC	12	0	0.002	0.000	0.002	0.002	0.002	0.002
OP	12	0	0.002	0.000	0.002	0.002	0.002	0.002
OPEC	12	0	0.002	0.000	0.002	0.002	0.002	0.002
All APE	570	65	0.877	2.752	0.002	4.157	0.000	18.923

In each case, the authors indicated that untreated or minimally treated wastewater was discharged into the receiving water. NP was detected in 36% of the surface water samples, with average concentrations of 0.25 ± 0.49 μg/L. OP, OPEO, and OPEC were detected in 25–60% of the samples, although the average concentrations were approximately 6–12 times lower than NP and NP>1EO. The latter findings are consistent with the fact that OP has significantly lower production volumes than NP, and the predominant use of OP does not result in its entry to the wastewater stream.

Figure 6a illustrates the frequency distribution for NP and NPEO concentrations in surface waters from the Great Lakes Basin. Concentrations of NP ranged from

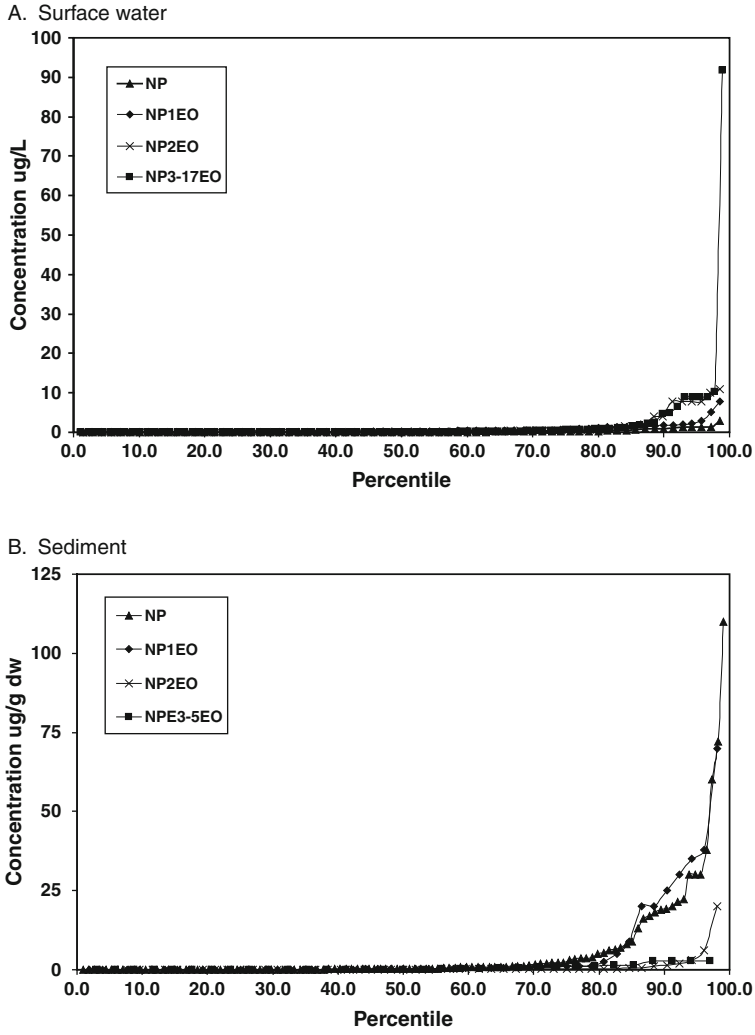


Fig. 6 Frequency distribution of nonylphenol and nonylphenol ethoxylates in surface waters and sediments. **a** Surface water and **b** sediment

below the detection limit to as high as 3.0 μg/L (95th percentile = 1.3 μg/L). Of the NP concentrations reported, six exceeded 1 μg/L. The highest value (3.0 μg/L) was reported by Kolpin et al. (2002) for a sample taken from the Chicago Sanitary and Ship Canal. Kannan et al. (2003) reported one measured value of 1.1 μg/L downstream of the Kalamazoo (MI) wastewater treatment plant, with the remaining four values reported as non-detect. However, based on the detection limit reported for the method (<2.6 μg/L), an estimated concentration of 1.3 μg/L was entered in the database for use in the statistical analysis. Concentrations of low mole and high mole NPEO ranged from below the detection limit to maximum values of 7.8 and 91.7 μg/L, respectively. The 95th percentile concentrations for NP1EO, NP2EO, and NP3–17EO were 2.2, 7.8, and 8.9 μg/L, respectively. Of the 224 reported concentrations for low and high mole NPEO, 42 were greater than 1 μg/L. Nearly all of these were from samples taken downstream from wastewater treatment plant discharges. The highest NPEO concentration (91.7 μg/L) was reported by Mayer et al. (2007) in a sample obtained from Cootes Paradise, ON. As previously discussed, the authors attributed the high concentrations to a heavy rainfall event resulting in a large discharge from a combined sewer overflow on the day the samples were collected.

As summarized in Table 10b, concentrations of APEO and their metabolites have been reported for 166 sediment samples obtained from 1994 to 2002 from 34 locations throughout the Great Lakes Basin. Of the 361 values in the database, 71% were above the detection limit. NP and NPEO were frequently detected, with average concentrations ranging from 0.62 ± 0.94 to 5.6 ± 14.9 μg/g (dwt). OP and OPEO were also detected in the samples (71–100%), although the average concentrations were about ten fold lower.

Figure 6b illustrates the frequency distribution for sediment concentrations of NP and NPEO. NP concentrations ranged from below the detection limit to as high as 110 μg/g dwt (95th percentile = 30 μg/g dwt). Concentrations of low mole NPEO and high mole NPEO ranged from below the detection limit to maximum values from 2.9 to 70 μg/g dwt; the 95th percentile concentrations for NP1EO, NP2EO, and NP3–17EO were 32.5, 2.5, and 2.9 μg/g dwt, respectively. The highest concentrations of NP and NPEO were found in Hamilton Harbor and in the Detroit and Rouge Rivers downstream from wastewater treatment plant discharges, or in areas of heavy urbanization and industrial activity (Bennett and Metcalfe 1998, 2000; Kannan et al. 2001).

The concentrations of AP and APEO which have been reported in biological tissues are summarized in Table 10c. Much of the biological data have been reported as means or ranges of concentrations (min–max). Fish ($n = 284$) have been collected from both the Kalamazoo River (MI) and the Cuyahoga River (OH). Of the 1,069 values, 33% were above the detection limit. Concentrations of NP and the low mole ethoxylates (NP1–3EO) ranged from below the detection limit to maximum concentrations of 0.55 μg/g wwt. Concentrations of NP and NPEO have been reported in mussels collected from a reference lake near Montreal, QC, as well as for specimens submerged near wastewater treatment plant discharges in the St. Lawrence River, Hamilton Harbor, and the Detroit River. NP and low mole NPEO concentrations in

mussels from the reference lake were below the detection limit, whereas detectable amounts of NP5–8EO (0.4–7.6 μg/g wwt) were reported. Concentrations of higher mole NPEO (NP>5EO), ranging from below the detection limit to 18.9 μg/g wwt, were reported in mussels submerged in the St. Lawrence river both upstream and downstream of the Montreal, QC, wastewater treatment plant. The absence of NP and low mole ethoxylates is consistent with the fact that the Montreal wastewater receives only primary physico-chemical treatment. Elsewhere, including mussels deposited in Hamilton Harbor and in the Detroit River downstream of the Windsor, ON, and Detroit, MI wastewater treatment plant discharges, maximum NP and NPEO concentrations were less than 1 μg/g wwt.

Regulatory criteria or guidelines have been developed in both the United States and Canada (Table 2). In the United States., the National Ambient Water Quality Criteria for NP in fresh water are 28 and 6.6 μg/L for acute and chronic exposures, respectively (US EPA 2005). In Canada, an Environmental Quality Guideline of 1 μg/L has been established for NP and NPEO in fresh water (Canadian Council of Ministers of the Environment (CCME) 2001). Considering the frequency distributions shown in Fig. 6a, all NP concentrations are below the US criterion, and 90% are below the Canadian guideline. In Canada, however, the guideline applies to aggregate NP equivalent concentrations, and the relative toxicity factors used to derive NP equivalent concentrations have been defined (CCME 2001). Lower mole NP*n*EO ($n = 1$–8) have been estimated to be less toxic than NP by a factor of two, and the higher mole NP*n*EO ($n > 9$), and NPEC were less toxic than NP by a factor of 200 (Servos et al. 2003). A similar approach was used for assigning relative toxicity factors for OPEO/OPEC, where OP was assigned a toxicity factor equal to NP. This methodology assumes that all compounds act with the same mode of action, and that the dose responses are additive. Based on the frequency distributions for AP and APEO in the Great Lakes, 78% of the NP equivalent concentrations in water are below the Canadian guideline. Although the US EPA has not specified a criterion based on aggregate concentrations, 95% of the NP equivalent concentrations are below 6.6 μg/L. These results are consistent with the recent work of Klečka et al. (2007), who reported the results of a statistical analysis for AP and APEO exposures in US aquatic environments.

Sediment quality guidelines have also been developed for Canada, but not in the United States. The current provisional Canadian guideline is 1.4 mg/kg dwt for NP equivalent concentrations (CCME 2001). Considering the frequency distributions, 69% of the NP equivalent sediment concentrations are below the guideline. A review of the database for the sites exceeding the guideline indicated that many of those with the highest concentrations are Canadian and are located in the immediate vicinity of wastewater treatment plant discharges. These sites (Windsor, Burlington, Hamilton, and Toronto) were sampled repeatedly during the period from 1995 to 1998 by several investigators (Bennett and Metcalfe 1998, 2000; Bennie et al. 1997). NP-equivalent sediment concentrations at these locations range from 16 to as high as 115 mg/kg dwt. Since the sediment samples were collected prior to implementation of the sediment quality guideline, it is unclear whether changes in regulations have had an impact on sediment exposures at these locations or not.

In summary, concentrations of AP and APEO have been reported for various media (water, sediment, biota) in samples collected throughout the Great Lakes Basin. Collectively, the frequencies with which the compounds have been detected range from 33 to 71%. Concentrations are generally low, with the exception of samples collected in the immediate vicinity of wastewater treatment plant discharges. Surface water concentrations were compared with United States and Canadian regulatory criteria and guidelines. None of the samples exceeded the US EPA Water Quality Criterion for NP. In contrast, 22% of the samples exceeded the NP-equivalent Canadian Water Quality Guideline. Sediment concentrations exceeded the NP-equivalent Canadian Sediment Guideline in 31% of the samples.

3.5 Synthetic Musks

Synthetic musks are used extensively in perfumes, cosmetics, detergents, cleaning products, and other personal care products. These compounds are commonly divided into two groups: nitro musks and polycyclic musks. There are other categories of synthetic fragrances, but they are used in much smaller quantities and therefore are not discussed here. The nitro musks include musk ketone (1-[4-(1,1-dimethyl-ethyl)-2,6-dimethyl-3,5-dinitrophenyl]-ethanone) and musk xylene (1-(1,1-dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene). The most common musks include 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(*g*)-2-benzopyran (HHCB), 6-acetyl-1,1,2,4,4,7-hexamethyltetralin (AHTN), 5-acetyl-3-isopropyl-1,1,2,6-tetramethylindane (ATII), 6-acetyl-1,1,2,3,3, 5-hexamethylindane (AHMI), 4-acetyl-6-*tert*-butyl-1,1-dimethylindane (ADBI), and 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5*H*)-indanone (DPMI) (Rimkus 1999). Nitro musks were first produced commercially in the 1900s as a substitute for the natural musk compounds, which were difficult to derive from their main source, the musk deer. In the 1950s, polycyclic musks were introduced commercially as another alternative to the natural musks. In 1996, worldwide production of synthetic musks was 8,000 t, with 5,600 t of this comprising polycyclic musks; of the latter, HHCB and AHTN accounted for 95% of the production (Gatermann et al. 2002).

Unlike their natural counterparts, synthetic musks have physical–chemical properties similar to those of other hydrophobic and semi-volatile organics, which are known to bioaccumulate and biomagnify in aquatic organisms. The environmental distribution and biological concentrations for musk ketone and musk xylene have been shown to correlate with their high octanol–water partition coefficients (K_{ow}; Rimkus et al. 1997). HHCB and AHTN have slightly lower K_{ow} values than the nitro musks (Rimkus 1999). Environmental concentrations of the synthetic musks were first reported in 1981 for European surface waters (Yamagishi et al. 1981) and have since been reported for sediments, aquatic biota, as well as in human adipose tissue and breast milk (Rimkus 1999; Rimkus et al. 1994; Winkler et al. 1998). Current studies from Europe and Canada suggest that effluents from wastewater treatment plants are a major source of synthetic musks that enter the environment (Dsikowitzky et al. 2002; Ricking et al. 2003; Simonich et al. 2000).

Concentrations of synthetic musks in the Great Lakes Basin have been reported in five papers, in which their concentrations in surface water, sediment, and biota were characterized. Information on the concentrations of synthetic musks in air and precipitation (e.g., Peck and Hornbuckle 2006) was not included in the analysis.

Peck and Hornbuckle (2004) characterized the concentrations of a variety of synthetic musk fragrances in the water column of western Lake Michigan and in the vicinity of Milwaukee, WI (locations not illustrated). Water samples ($n = 13$) were collected during the period from 1999 to 2001. Results of the water analysis showed that musks are found primarily in dissolved phase, as opposed to adsorbed on suspended particles. Concentrations ranged from 0.029 for ADBI to 4.7 ng/L for HHCB. A mass balance analysis indicated that wastewater treatment plants are important sources, while volatilization plays a major role in the loss of synthetic musks from Lake Michigan.

Peck et al. (2006) examined the distribution of synthetic musks in single sediment cores taken in 2003 from Lakes Erie and Ontario (locations not illustrated). Analysis of surface sediments showed HHCB to be present at the highest concentrations in Lake Ontario (16 ng/g dwt), whereas ADBI was present in the lowest amounts (0.10 ng/g); musk xylene and AHMI were not detected in the samples. Analysis of samples taken from various depths showed that the concentrations of synthetic musk fragrances have been increasing with time. The results suggested that the rate of increase in deposition of these compounds in Great Lakes sediments corresponded with the rates at which production increased.

O'Toole and Metcalfe (2006) analyzed fish ($n = 22$) from the Great Lakes for the presence of a variety of synthetic musks. Various fish species were collected in 2002 from Hamilton Harbor in western Lake Ontario and from western Lake Erie and the Detroit River (locations not illustrated). Fish from Hamilton Harbor showed maximum total musk concentrations of 498.0 $\pm$ 327.6 ng/g wwt, with nearly 80% attributed to HHCB. Fish from the Detroit River and western Lake Erie had lower total musk concentrations (maximum of 20.1 $\pm$ 4.0 ng/g wwt), with HHCB again being the dominant compound detected. Of the synthetic musks detected in the various fish, the synthetic musks HHCB, AHTN, and ATII were most often detected. None of the fish had detectable concentrations of the nitro musks.

Concentrations of HHCB, AHTN, musk ketone, and musk xylene were recently reported for water samples collected in the spring of 2005 from Hamilton Harbor, ON, and from the North Sea (Andresen et al. 2007). Total musk concentrations ranged from 0.3 to 3 ng/L in samples ($n = 14$) taken from the North Sea, with higher concentrations found in nearshore areas. Considerably higher concentrations were detected in the samples ($n = 4$) from Hamilton Harbor. For example, maximum concentrations of HHCB and AHTN were 41 and 5.5 ng/L, respectively. At both locations, the concentrations declined with increasing distance from the source. The authors noted that some of the musk fragrances exhibit half-lives exceeding the residence times of the water body, and thus could be considered persistent in these ecosystems.

As previously discussed, Tertuliana et al. (2008) measured the concentration of a wide variety of organic contaminants in sediment samples collected in the Tinkers Creek watershed from locations above and downstream of wastewater discharges. AHTN and HHCB were detected in over 50% of the samples ($n = 18$) at maximum concentrations of 80 and 390 ng/g dwt, respectively.

A statistical analysis of synthetic musk concentrations in the Great Lakes watershed was performed using a total of 465 data points. Concentrations in water ($n = 375$) represented the majority of the data. Limited information was available for the concentrations in biota ($n = 42$) and sediment ($n = 48$). As summarized in Table 11a and b, the frequencies of detection ranged from 16 to 100% for most compounds in the media, except for DPMI, which was not detected in any of the samples. Detection frequencies for the total musks were lowest in water samples (37%), as would be predicted from their hydrophobic nature and volatility. The musks were detected most frequently in biota (68%), followed by sediment (50–58%; data not shown). Of the various synthetic musks, HHCB and AHTN were most frequently detected.

Concentrations in the water column were generally low; mean concentrations for total musks were 2.2 ± 12.9 ng/L (Table 11a). HHCB and AHTN were frequently detected in the water samples, with concentrations ranging from of 0.08 to 180 ng/L and from 0.08 to 28 ng/L, respectively. Musk ketone was also present at comparable levels (range from 0.03 to 57.3 ng/L). The other synthetic musks were detected at lower concentrations (<1 ng/L).

Calculated mean concentrations for total synthetic musks in biota were 105.6 ± 122.2 ng/g wwt, and ranged from 5.6 to 498 ng/g wwt (Table 11b). The highest single analyte detected in biota was HHCB (mean = 80.3 ± 96.0 ng/g), representing about 76% of the total. The higher contributions for HHCB in biota are consistent with higher production volumes for this compound (Rimkus 1999). The mean concentration for three of the other synthetic musks, ATII, ADBI, and AHMI, were all 20–50-fold lower.

Limited data were available for sediment concentrations in the Great Lakes Basin. Based on the analysis of single sediment cores from both Lake Ontario and Lake Erie, concentrations of the various musks ranged from below the detection limit to 16.0 ng/g dwt. AHTN and HHCB were detected in sediments from Tinkers Creek at maximum concentrations of 80 and 390 ng/g dwt, respectively.

In general, the available data suggest that concentrations of the synthetic musks are somewhat higher in biota than in the other environmental matrices, consistent with their partitioning behavior. For all matrices, HHCB was the most frequently detected analyte as well as the one exhibiting the highest single analyte concentrations, reflecting the current status of the production volume of synthetic musks.

In the early 2000s, musk xylene was voluntarily removed from the market in some European countries after a report showed the compound causes hepatic toxicity in mice (Lehman-McKeeman et al. 1999). In 1999, the Centers for Disease Control supported research which showed developmental growth effects caused by musk xylene (Christian et al. 1999).

Table 11 Summary statistics for synthetic musks

	n	Freq det (%)	Mean (ng/L)	SD (ng/L)	Median (ng/L)	95th percentile (ng/L)	Min (ng/L)	Max (ng/L)
A. Water								
AHTN	50	66	1.525	4.800	0.334	4.770	0.075	28.000
HHCB	50	70	8.440	31.210	0.817	27.585	0.075	180.000
Acetyl-isopropyl-tetramethylindane (ATII)	44	30	0.078	0.049	0.075	0.113	0.018	0.361
Acetyl-*tert*-butyl-dimethylindane (ADBI)	44	16	0.071	0.021	0.075	0.075	0.018	0.155
Acetyl-hexamethylindane (AHMI)	44	41	0.132	0.117	0.075	0.292	0.045	0.617
Dihydro-pentamethyl-indanone (DPMI)	43	0	0.075	0.000	0.075	0.075	0.075	0.075
Musk ketone	50	50	5.990	14.083	0.075	42.171	0.030	57.335
Musk xylene	50	64	0.061	0.048	0.075	0.100	0.006	0.260
Total musks	375	37	2.177	12.904	0.075	37.066	0.006	180.000
	n	Freq det (%)	Mean (ng/g wwt)	SD (ng/g wwt)	Median (ng/g wwt)	95th percentile (ng/g wwt)	Min (ng/g wwt)	Max (ng/g wwt)
B. Biota								
ATHN	8	100	19.16	26.26	5.40	70.73	1.50	96.80
HHCB	8	100	80.34	95.85	8.85	303.71	1.70	391.10
ATII	8	63	3.70	4.40	0.45	9.62	0.20	9.90
ADBI	8	25	1.50	1.70	0.10	5.94	0.10	6.50
AHMI	8	50	1.45	4.42	0.15	5.42	0.10	5.80
Total musks	40	68	105.58	122.25	14.80	403.26	5.60	498.00

Risk assessments for musk xylene (EUC 2005a), musk ketone (EUC 2005b), AHTN (EUC 2008b), and HHCB (EUC 2008c) have been recently completed in Europe. PNECs have been developed for use in the calculation of risk quotients (Table 2). A comparison of the reported maximum concentrations of musk xylene, musk ketone, AHTN, and HHCB musk xylene, in environmental media from the Great Lakes, indicates that all values are below the PNEC values.

3.6 Perfluorinated Surfactants

The presence of perfluorinated surfactants in the environment and in biological tissues (Giesy and Kannan 2001; Giesy et al. 2010; Kannan et al. 2002) can be attributed to their widespread use over the past 50 years in a broad range of applications, including use as surface treatments for carpets, fabrics, and leathers for stain resistance, as well as coatings on various paper products. These surfactants have also found applications in semiconductor manufacturing, metal plating, and are used as components of hydraulic fluids in aviation, and in firefighting foams. There is growing concern over the environmental presence of perfluorinated surfactants, because representatives like perfluorooctane sulfonate (PFOS) have been shown to resist hydrolysis, photolysis, and biodegradation under environmental conditions. Perfluorinated surfactants, including PFOS and perfluorooctanoic acid (PFOA), are also of concern because they have been found to accumulate in biological tissues (Kannan et al. 2002). PFOS and related fluoroalkyl substances have been detected in blood plasma of non-occupationally exposed humans collected from around the world and have even been found in sparsely populated regions that have no apparent sources (Schultz et al. 2003).

Perfluorinated surfactants are currently synthesized by two distinct processes, namely electrochemical fluorination (ECF) and telomerisation, which yield different types of fluorinated reaction products (Hekster et al. 2002). Electrochemical fluorination products are branched or straight-chain polymers that contain a sulfonyl group; perfluorooctanesulfonyl fluoride (POSF) is the most important manufacturing intermediate. POSF is a precursor of many fluorinated sulfonyl surfactants found in the environment, including PFOS, perfluorooctane sulfinate (PFOSulfinate), perfluorooctane sulfonamide (FOSA or PFOSA), perfluorooctane sulfonamido acetic acid (PFOSAA), *N*-ethylperfluorooctane sulfonamido acetic acid (*N*-EtFOSAA), and *N*-ethylperfluorooctane sulfonamidoethanol (*N*-EtFOSE). The telomerisation process is distinct from electrochemical fluorination as it produces only linear polymer chains that are typically fluorotelomer olefins, epoxides, or fluorotelomer alcohols (FTOHs). The alcohols are precursors to many perfluorinated carboxylic acids (PFAs), such as PFOA and perfluorononanoic acid (PFNA). In commercial products, the fluoroalkyl chain length can vary from 4 to 20 carbon atoms, although most products contain chain lengths between 6 and 10. The homologous series of PFAs found in the environment include C4 (perfluorobutyric acid; PBFA), C5 (perfluoropentanoic acid; PFPeA), C6 (perfluorohexanoic acid, PFHxA), up to and

including C15 (perfluoropentadecanoic acid, PFPA). Short-chain fluorinated acids such as trifluoroacetic acid (TFA) and the C3–C9 PFAs are also reported to be atmospheric oxidation products of fluorotelomer alcohols and perfluorosulfonamido alcohols (Martin et al. 2006).

The complex structure of perfluorinated surfactants makes it difficult to predict their environmental behavior solely from examining their physical–chemical properties. These structures have both a hydrophobic head and a hydrophilic carbon chain tail. Although this structural configuration lends itself to being a highly effective surfactant, it also thwarts scientific attempts to understand the potential environmental fate and bioconcentration potential for members of the class. For example, unlike organic chemicals that bioaccumulate by partitioning into lipids, perfluorinated surfactants have been shown to bind to proteins and are slowly excreted (Kannan et al. 2005a). Because PFOS has the potential to accumulate in the liver, it has been shown to be a potential carcinogen in rats and has displayed significant increases in hepatocellular adenomas in animals exposed orally to dietary concentrations of 20 mg/kg (Organisation for Economic Co-operation and Development (OECD) 2002).

The present analysis focused on those studies which reported concentrations in surface waters and biota. However, a number of studies were identified in the literature search which included analysis of perfluorinated surfactants in air and precipitation (e.g., Boulanger et al. 2005; Scott et al. 2006).

Boulanger et al. (2004) were among the first to analyze for perfluorinated surfactants in the waters of the Great Lakes. Surface water samples were collected in August 2003 from four locations in Lake Erie ($n = 8$) and four locations in Lake Ontario ($n = 8$) and were analyzed for a PFOS, PFOA, and six other PFOS precursors. Concentrations of PFOS and PFOA in Lake Erie and Lake Ontario ranged from 11 to 47 ng/L and from 15 to 121 ng/L. The analysis also revealed the presence of various PFOS precursors, including *N*-EtFOSAA (4.2–11 ng/L), and FOSA (0.6–1.3 ng/L). PFOSAA and PFOSulfinate were detected in some samples at concentrations ranging from below the detection limit to maximum levels of 6.5 and 17 ng/L, respectively. *N*-EtFOSE and *N*-EtFOSAA were not detected in surface waters from the two lakes.

In a related study, Boulanger et al. (2005) used the data from their previous work to develop a mass budget for the eight perfluorooctane surfactants found in Lake Ontario. The mass balance showed that inflows from Lake Erie, as well as contributions from wastewater treatment plants, were the major sources of perfluorooctane surfactants in Lake Ontario. Outflow through the St. Lawrence River was shown as the predominant loss mechanism. Based on the analysis, the authors concluded that the steady state and measured mean concentrations in the lake are the same at the 95% confidence level.

Scott et al. (2006) described the development of a sensitive analytical method for PFAs and application of these methods to analyze surface water samples collected from varying locations in the Great Lakes Basin. Lake water samples were obtained in 2001 at varying depths from Lakes Superior (4 and 260 m; $n = 6$), Huron (125 m; $n = 2$), and Ontario (4–200 m; $n = 9$). The total PFA concentrations

found in Lake Ontario were relatively constant at depths from 4 to 150 m, ranging from 112 to 162 ng/L, whereas total concentrations in the deeper water samples were higher (233 ng/L). TFA was the dominant PFA detected; TFA concentrations ranged from 100 to 200 ng/L, with the levels increasing with depth. Concentrations of the other analytes (C3–C8; PFPrA to PFOA) were lower, ranging from below the detection limit to 8.9 ng/L. PFOA and PFNA concentrations in Lakes Superior and Huron ranged from below the detection limit to 1.8 ng/L.

Martin et al. (2004) analyzed the bioaccumulation and trophic magnification of a variety of perfluorinated compounds in a Lake Ontario food web. Biological specimens consisting of invertebrates (*Diporeia* and *Mysis* spp.), forage fish (slimy sculpin, alewife, rainbow smelt), and lake trout were collected in 2002 and analyzed for PFOS and its precursor FOSA, as well as the homologous series of PFAs (C8–C15). Total PFOS concentrations ranged from 50 to 460 ng/g wwt and were highest in *Diporeia* and sculpin. The distribution in the food web was similar for the PFAs. Total PFA concentrations ranged from 12 to 260 ng/g wwt and were also highest in *Diporeia* and sculpin. Total PFOS and PFA concentrations in the trout were 186 and 30 ng/g wwt, respectively. Analysis of concentration versus trophic level for the various analytes did not reveal any significant associations when all of the organisms were included in the regression analysis. For the PFAs, the benthic macroinvertebrate (*Diporeia*) and sculpin showed wide and consistent divergence from the other organisms. When these organisms were excluded, strong associations with trophic level were observed. Trophic magnification factors exceeded unity for PFOS, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorotridecanoic acid (PFTrA), ranging from 2.45 to 5.88. Trophic magnification factors were equal to or less than one for FOSA, PFOA, PFNA, and PFDoA. Archived lake trout samples from the Great Lakes Specimen Bank were also analyzed for PFOS to determine any temporal trends in Lake Ontario. PFOS concentrations increased from 43 to 180 ng/g during the period from 1980 to 2001. The authors noted that the increase was not linear and may have been influenced by the invasion and proliferation of zebra mussels.

Kannan et al. (2005b) examined the trophic transfer of PFOS, PFSOA, perfluorohexane sulfonate (PFHxS), and PFOA in a wide range of aquatic and terrestrial wildlife collected from Michigan and the surrounding region in 1998–2001. Average PFOS concentrations in amphipods (1.6 ng/g wwt), zebra mussels (1.4 ng/g wwt), and crayfish (3.5 ng/g wwt) were approximately 1000-fold greater than those in the surrounding water (1.9–3.9 ng/L). PFOS concentrations in round gobies (mean = 10.6 ng/g wwt) and smallmouth bass (mean = 9.1 ng/g wwt) were 2- to 4-fold greater than those measured at lower trophic levels. Similar trends were noted for PFOSA at the lower trophic levels. PFOS accumulation in predatory fish was determined on the basis of liver analysis, since the compound has been shown to preferentially accumulate in this tissue. Livers from lake whitefish and Chinook salmon contained average PFOS concentrations of 67 and 100 ng/g wwt, respectively, which is approximately 6–10-fold greater than that detected in round gobies, and 10–20-fold higher than present in zebra mussels and amphipods. Carp from the Saginaw Bay contained PFOS concentrations as high as 297 ng/g wwt in muscle

tissue. Although the concentrations were quite variable, concentrations in mink and bald eagles were, on average, five to tenfold greater than those measured in salmon, carp, or snapping turtles. Overall, the results suggest a bioaccumulation factor of approximately 1,000 for benthic invertebrates, and a biomagnification factor of 10–20 for mink and bald eagles. Eggs from several fish collected in the study contained detectable concentrations of PFOS (64 ng/g wwt), suggesting the potential for oviparous transfer. In contrast, although PFOA concentrations in water ranged from 4.4 to 14.7 ng/L, the compound was detected in few of the biological specimens, suggesting a biomagnification potential lower than PFOS.

Sinclair et al. (2006) reported the occurrence of PFOS and several related compounds in water, fish, and birds from New York State. Water samples ($n = 51$) were obtained from nine water bodies located throughout the state in 2004. In addition, sport fish ($n = 66$) were collected from 20 inland lakes, and 10 species of waterfowl ($n = 87$) were obtained from the Niagara River region. Residues of PFOS, PFOA, and PFHxS were ubiquitous in the surface waters. Average PFOA concentrations ranged from 14 to 49 ng/L and were typically higher than concentrations for PFOS (means range from 1.6 to 6.4 ng/L) or PFHxS (means range from 0.9 to 7.4 ng/L). Elevated concentrations of PFOS were found in Lake Onondaga (198–1,090 ng/L), and higher concentrations of PFOA (22–173 ng/L) were detected in the Hudson River. Of the various analytes, PFOS was the most abundant perfluorinated compound present in all of the wildlife samples. PFOS concentrations in fish and bird livers ranged from 9 to 315 ng/g wwt and from 11 to 882 ng/g wwt, respectively, and the concentrations were greater in piscivorous birds. PFOA and PFOSA were also detected in 62–90% of the fish livers at concentrations ranging from below the detection limit to 11.4 ng/g wwt. However, PFOA and PFOSA residues were not found in any of the bird samples. Based on the results of the study, a bioconcentration factor of 8,850 was estimated for PFOS accumulation in fish, and a biomagnification factor of 8.9 was estimated for the accumulation of PFOS in the common merganser.

The spatial distribution of various perfluoroalkyl contaminants in lake trout from the Great Lakes was recently reported by Furdui et al. (2007). Lake trout of the same age class (4 years) were collected in 2001 from Lakes Superior, Michigan, Huron, Erie, and Ontario. Between 6 and 10 fish were obtained from each lake, and whole fish homogenates were analyzed for a broad range of perfluorinated sulfonates (PFHxS, PFOS, PFDS, and PFOSA) and carboxylates (perfluoroheptanoic acid (PFHpA) to perfluoropentadecanoic acid (PFPA); C7–C15). Fish from Lake Superior contained the lowest total concentrations (13.1 ± 1 ng/g wwt), while the highest levels were found in samples from Lake Erie (152 ± 14 ng/g wwt). Fish from Lakes Ontario and Huron showed similar total concentrations, 60 ± 5 ng/g wwt and 58 ± 10 ng/g wwt, respectively, whereas samples from Lake Michigan were lower (27 ± 3 ng/g wwt). The predominant perfluorinated compounds detected were PFOS followed by perfluorodecane sulfonate (PFDS); mean concentrations for these analytes ranged from 5 to 121 ng/g wwt and from 0.7 to 9.8 ng/g wwt, respectively. Average concentrations for the perfluorinated carboxylic acids were lower, ranging from below the detection limit to 4.9 ng/g wwt. Of the PFAs detected, PFOA and PFDA were typically present at higher concentrations.

The statistical analysis of perfluorinated surfactant concentrations in the Great Lakes watershed was based on the data obtained from seven publications in which the concentrations in surface water and biological tissues were reported. The samples were collected during the period from 1998 to 2003, and the locations are illustrated in Fig. 7a and b. Water samples were collected from Lakes Erie, Huron, Ontario, and Superior. Biological samples have been obtained from locations throughout the Great Lakes watershed. For the analysis, the various perfluorinated compounds were subdivided into two major categories based on the manufacturing process used for their synthesis.

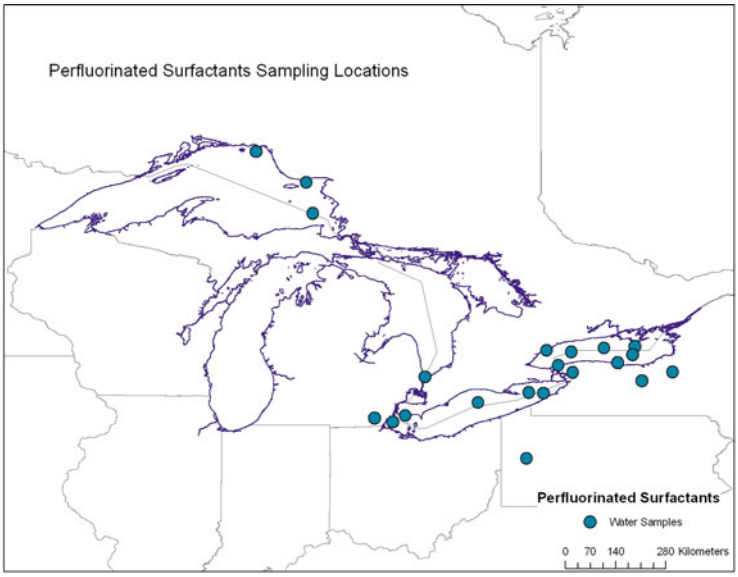
As shown in Table 12a and b, detection frequencies for total perfluorinated sulfonyls (PFS) were highest in water (65%), followed by biota (47%). Detection frequencies for the PFAs were higher in all media in which they were analyzed.

PFS and PFA were prevalent in surface waters, with all but four compounds detected in 50% or more of the samples. The total concentrations of PFS and PFA in water were low, with mean concentrations of 0.0126 ± 0.0662 μg/L and 0.0206 ± 0.0377 μg/L, respectively (Table 12a). PFOS and PFOA were the predominant analytes detected in water. Analysis of the database for information on the spatial distribution of perfluorinated surfactants in Great Lake waters suggests that the highest concentrations are found in Lake Ontario.

PFS and PFA were widely detected in a variety of aquatic and terrestrial wildlife, as shown in Table 12b. The frequencies with which the various analytes were detected ranged from 4 to 100%. The total PFS concentrations in biota were higher than those of PFA; their mean concentrations ranged from 119.2 ± 1,170.9 ng/g wwt to 7.19 ± 12.44 ng/g wwt, respectively. PFOS and PFOA were the predominant contaminants detected in biota, with concentrations ranging from below the detection limit to maximum values of 18,000 and 90 ng/g wwt, respectively. From the analysis of lake trout collected from each of the five Great Lakes, the concentrations of PFS and PFA are highest in Lake Erie, followed by Lakes Ontario and Huron, with Lake Michigan and Lake Superior showing lower concentrations. From the analysis of archived fish, temporal trends in PFOS concentrations in biota appear to be increasing with time (Martin et al. 2004).

Risk assessments for PFOS and PFOA have been conducted by authorities in various geographies (Department for Environment, Food and Rural Affairs; DEFRA 2004; EC 2006a; Hekster et al. 2002). Environment Canada has derived an estimated no effect value (ENEV) of 0.491 μg/L for PFOS in freshwater. PNECs have also been derived in Europe for PFOS in fresh water (2.5 μg/L) and for secondary poisoning by ingestion of food (0.0167 mg/kg food). The PNEC for water is comparable to the proposed Dutch Quality Objective for water of 3.8 μg/L. Comparison of the available data for PFOS and PFOA concentrations in water versus the various regulatory standards (Table 2) suggests that all exposures are well below the no effect values derived in Europe. Mean and 95th percentile values for water are also below the Canadian ENEV, although the maximum reported PFOS concentration (0.76 μg/L) is higher. It is important to note that the highest concentration in the database was measured in Lake Onondaga in New York, which, according to the authors, is a Superfund site that is influenced by several industries that exist along

A. Surface waters



B. Biota

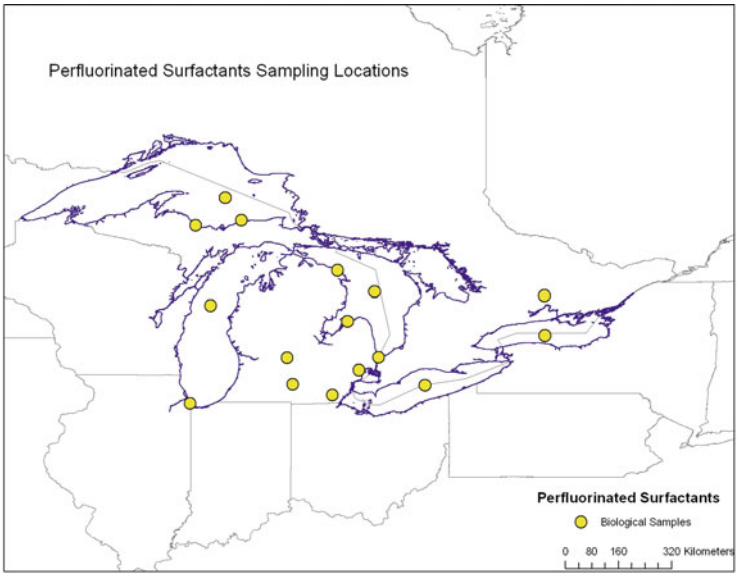


Fig. 7 Sampling locations for perfluorinated surfactants. **a** Surface waters and **b** biota

Table 12 Summary statistics for perfluorinated surfactants

	n	Freq det (%)	Mean (μg/L)	SD (μg/L)	Median (μg/L)	95th percentile (μg/L)	Min (μg/L)	Max (μg/L)
A. Water								
Perfluorohexane sulfonic acid (PFHxS)	11	82	0.0017	0.0020	0.0012	0.0050	0.0005	0.0074
Perfluorooctane sulfonic acid (PFOS)	27	100	0.0550	0.1428	0.0310	0.1039	0.0016	0.7560
Perfluorooctane sulfinate (PFOSulfinate)	16	69	0.0031	0.0057	0.0011	0.0173	0.0001	0.0180
Perfluorooctane sulfonamide (PFOSA)	18	78	0.0014	0.0014	0.0011	0.0050	0.0001	0.0050
Perfluorooctane sulfonamido acetic acid (PFOSAA)	16	38	0.0006	0.0016	0.0001	0.0020	0.0001	0.0065
N-Ethylperfluorooctane sulfonamide (*N*-EtFOSA)	16	6	0.0003	0.0001	0.0003	0.0003	0.0001	0.0003
N-Ethylperfluorooctane sulfonamido acetic acid (*N*-EtFOSAA)	16	94	0.0066	0.0036	0.0073	0.0110	0.00001	0.0110
N-Ethylperfluorooctane sulfonamido ethanol (*N*-EtFOSE)	16	6	0.0010	0.0003	0.0011	0.0011	0.0001	0.0011
Total perfluorinated sulfonyls (PFS)	136	65	0.0126	0.0662	0.0011	0.0418	0.00001	0.7560
Trifluoroacetic acid (TFA)	8	100	0.1344	0.0371	0.1200	0.1913	0.1000	0.2000
Perfluoropropionic acid (PFPrA)	9	100	0.0036	0.0020	0.0031	0.0068	0.0023	0.0089
Perfluorobutyric acid (PFBA)	9	100	0.0054	0.0014	0.0049	0.0077	0.0045	0.0091
Perfluoropentanoic acid (PFPeA)	9	100	0.0017	0.0019	0.0013	0.0047	0.0004	0.0065
Perfluorohexanoic acid (PFHxA)	9	100	0.0017	0.0009	0.0012	0.0032	0.0011	0.0037
Perfluoroheptanoic acid (PFHpA)	9	78	0.0015	0.0015	0.0008	0.0035	0.0001	0.0036
Perfluorooctanoic acid (PFOA)	44	93	0.0218	0.0195	0.0190	0.0499	0.00013	0.0700
Perfluorononanoic acid (PFNA)	8	38	0.0002	0.0001	0.0003	0.0003	0.00003	0.0004
Total perfluorinated carboxylic acids (PFA)	105	90	0.0206	0.0377	0.0035	0.1080	0.00003	0.2000

Table 12 (continued)

	n	Freq det (%)	Mean (ng/g wwt)	SD (ng/g wwt)	Median (ng/g wwt)	95th percentile (ng/g wwt)	Min (ng/g wwt)	Max (ng/g wwt)
B. Biota[a]								
PFHxS (PFHS)	72	4	4.5	5.7	1.0	17.0	0.5	21.0
PFOS	82	85	328.2	1,998.6	13.5	449.8	1.0	18,000.0
Perfluorodecane sulfonic acid (PFDS)	5	100	3.3	3.8	1.6	8.5	0.7	9.8
PFOSA (FOSA)	82	43	18.1	32.7	2.6	70.3	0.3	180.0
Total PFS	241	47	119.2	1,170.9	4.1	168.0	0.3	18,000.0
PFOA	82	16	8.66	13.87	2.25	36.00	0.01	90.00
PFNA	11	100	10.26	7.29	2.80	45.00	0.57	57.00
Perfluorodecanoic acid (PFDA)	11	100	7.84	3.16	2.20	30.50	0.72	32.00
Perfluoroundecanoic acid (PFUnA)	11	100	9.76	3.77	2.70	40.00	0.74	41.00
Perfluorododecanoic acid (PFDoA)	11	100	3.91	1.46	1.80	14.00	0.37	14.00
Perfluorotridecanoic acid (PFTrA)	11	100	4.57	1.27	3.30	14.00	1.10	15.00
Perfluorotetradecanoic acid (PFTeA)	11	82	1.74	0.57	1.00	5.65	0.25	7.30
Perfluoropentadecanoic acid (PFPA)	11	64	0.67	0.46	0.46	1.54	0.25	1.90
Total PFA	159	53	7.19	12.44	1.60	36.00	0.01	90.00

[a] The results represent concentrations reported for multiple trophic levels (invertebrates, small fish, large fish, birds, mammals)

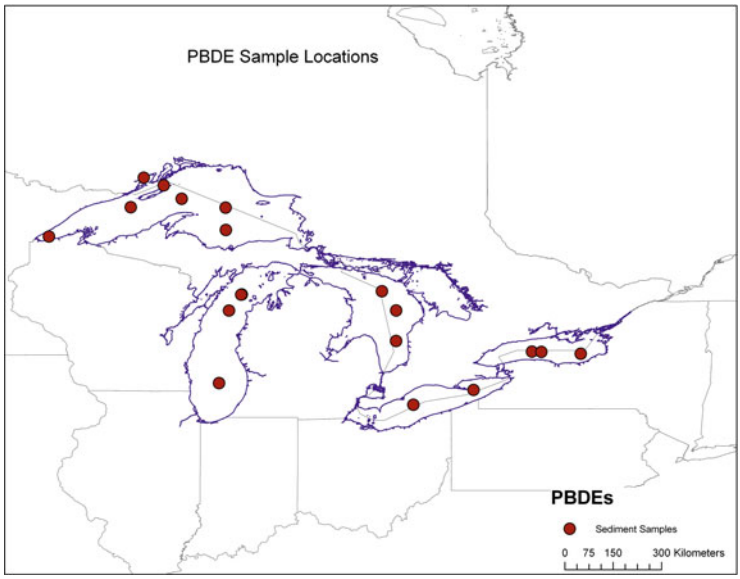
the lake (Sinclair et al. 2006). As a result, concentrations measured at this location may have no relevance to the Great Lakes. However, PFOS and total PFS concentrations in biota exceed the criteria for secondary poisoning from the ingestion of food. As summarized in Table 12b, mean and 95th percentile concentrations for PFOS and total PFS are 0.33 and 0.45 mg/kg wwt and 0.12 and 0.17 mg/kg wwt, respectively.

3.7 Polybrominated Diphenyl Ethers

PBDEs are a class of additive halogenated flame retardants used in numerous commercial products to impart fire retardant properties. The flame retardant within the polymer is not covalently bonded (to the polymer). Rather, these additive flame retardants are mixed with the polymer resin and therefore have the potential to continually migrate out of the final product. This tendency for PBDEs to leach out of treated materials or to enter the environment during production, formulation, and use has contributed to the detection of PBDE globally, as environmental contaminations. These compounds have become chemicals of emerging concern in recent years, because of their high production volume during the period from the 1970s to the 1990s and their detection in surface waters, sediments, air, biota, and humans. These compounds are hydrophobic, lipophilic, and therefore have the potential for accumulation in sediments and wildlife, with biomagnification occurring within the food web.

The most common PBDEs identified in the environment are comprised predominately of the tetrabrominated congener, BDE-47, followed by lower levels of two pentabrominated congeners, BDE-99 and BDE-100 (Rice et al. 2002). PBDEs are structurally similar to the PCBs, and thus the numbering of PBDE congeners follows the system used to identify PCB congeners. As a result of the similarities between PBDEs and PCBs, researchers have examined and compared concentrations in fish and sediment samples in attempts to correlate contaminant distributions and loading rates for these two compounds in the Great Lakes. Production of the commercial penta-PBDE and octa-PBDE products was banned in Europe in 2003 (EUC 2003c), and current efforts are focused on phasing out these brominated flame retardants in North America. With the regulatory ban of the penta-PBDE and octa-PBDE products, the production of other brominated flame retardants, such as decabromodiphenyl ether (deca-PBDE product), has increased. As summarized below, numerous researchers have attempted to track changes in PBDE concentrations and congener profiles. In many of these studies, attempts have been made to establish the temporal trends for these compounds in the Great Lakes, by using archived fish and egg samples that were collected as part of the Great Lakes Fish Monitoring Program or by the US Geological Survey Great Lakes Science Center. More recent studies have focused on the analysis of fresh fish and bird eggs along with sediment samples. The locations of the sampling sites are shown in Fig. 8a and b.

A. Sediments



B. Biota

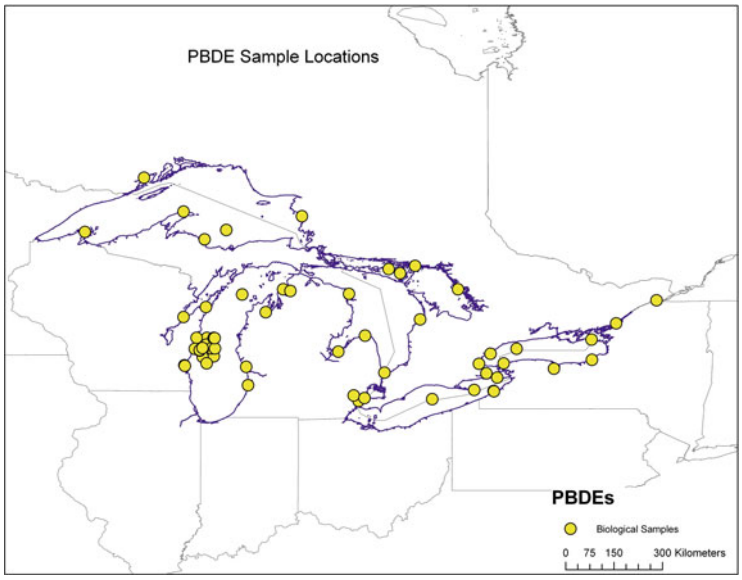


Fig. 8 Sampling locations for polybrominated diphenyl ethers. **a** Sediments and **b** biota

The present analysis focused on those studies which reported concentrations in sediments and biota. However, a number of studies were identified in the literature search which described the analysis of brominated diphenyl ethers in the atmosphere over the Great Lakes (e.g., Gouin et al. 2005; Hoh and Hites 2005; Shen et al. 2006; Strandberg et al. 2001; Venier and Hites 2008).

Manchester-Neesvig et al. (2001) compared the levels of PCBs and PBDEs in coho (*Oncorhynchus kisutch*) and chinook (*Oncorhynchus tshawytscha*) salmon collected from two southern Lake Michigan tributaries in the fall of 1996. The average concentration for total PBDEs in salmon was 80.1 ng/g wwt and consisted predominantly of BDE-47, BDE-66, BDE-100, BDE-99, BDE-154, and BDE-153. This concentration was compared to the average total PCB concentration which was approximately 18 times higher at 1,450 ng/g wwt. When the most abundant single congeners for PBDEs and PCBs were compared, the values became more similar with an average BDE-47 concentration of 52.1 ng/g wwt, compared to 149 ng/g wwt for PCB-153. Since the concentrations of PBDE and PCB were correlated in individual fish, the authors suggested that PBDE concentrations are as prevalent as PCBs in Lake Michigan.

Luross et al. (2002) determined the concentration of two types of brominated flame retardants, including PBDEs and polybrominated biphenyls (PBBs) in a single age class of lake trout (*Salvelinus namaycush*), collected in 1997 from Lakes Superior, Huron, Erie, and Ontario. Total PBDE concentrations in lake trout were reported to be significantly higher in trout collected from Lake Ontario (95 ng/g wwt), than in all other lakes except Lake Superior (56 ng/g wwt). Concentrations for Lake Huron and Lake Erie were 50 and 27 ng/g wwt, respectively. The three most dominant congeners representing the penta-PBDE formulation, BDE-47, BDE-99, and BDE-100, accounted, respectively, for 57, 15, and 8% of the total PBDEs measured. Lake Huron trout had the highest levels of PBBs with maximum concentrations of 3.1 ng/g wwt. The authors concluded that higher concentrations of PBDEs versus PBBs may be attributed to a North American ban on PBB production that was implemented approximately 20 years ago. Differences observed in concentrations of these two flame retardants within the Great Lakes were attributed to probable different sources of input.

The historical and geographical distribution of 15 PBDE congeners and 1 PBB (PBB-153) was examined in archived lake trout (*S. namaycush*) and walleye (*Stizostedion vitreum*) collected from the Great Lakes during the sampling period 1980–2000 by Zhu and Hites (2004). Lake Michigan and Lake Ontario trout had the highest total PBDE concentrations (ΣPBDEs = BDE-47, BDE-99, BDE-100, BDE-153, BDE-154). An exponential increase in PBDE concentrations was shown from 1980 to 2000 in fishes from all five of the Great Lakes; this increase had a calculated doubling time of 3–4 years, which is similar to results reported by other studies (Norstrom et al. 2002). The authors reported no change in PBB-153 concentrations over the period of 1980–2000, except in Lake Huron where the concentrations have decreased.

Carlson and Swackhamer (2006) analyzed composite samples of 820 lake trout (*S. namaycush*), walleye (*S. vitreum*), steelhead (variant of rainbow trout,

Oncorhynchus mykiss), chinook (*O. tshawytscha*) and coho (*O. kisutch*) from the Great Lakes collected in 1999 and 2000, as part of the Great Lakes Fish Monitoring Program. Concentrations of PBDE congeners (355 ng/g wwt) were greatest in lake trout from Lake Michigan (sum of BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, and BDE-154), followed by Lake Ontario and Lake Superior. The trout from Lake Huron had the lowest concentrations of these compounds. The authors reported on the differences in contamination patterns among lakes, between sites within a lake, and between fish from the same site.

Chernyak et al. (2005) evaluated time trends (1983–1999) for a variety of organochlorines and PBDEs, using the rainbow smelt (*Osmerus mordax*) as an indicator organism for detection of the biomagnification of these substances. The smelt collected in Lakes Michigan, Huron, and Superior between 1983 and 1999 were archived. The most abundant congener was BDE-47, and time trends for total PBDE (sum of BDE-47, BDE-99, BDE-100, and BDE-153) concentrations indicated exponential increases at all sites, with doubling times varying from 1.58 to 2.94 years in Lake Huron, 2.16 years for Lake Superior, and 1.75 years for Lake Michigan. The authors concluded that the initiation of build-up of PBDEs occurred in 1980.

Batterman et al. (2007) analyzed trends in PBDE concentrations and congener profiles in rainbow smelt (*O. mordax*), and lake trout (*S. namaycush*) collected in Lakes Michigan, Superior, Huron, Ontario, and walleye (*S. vitreum*) from Lake Erie between 1979 and 2005. Their analyses focused on the four most common congeners (BDE-47, BDE-99, BDE-100, and BDE-153). This research is an update to trend data determined by a previous analysis by Chernyak et al. (2005). Trend analysis indicated increasing concentrations of PBDE in fish from all Great Lakes starting in the early to mid-1980s. Although the doubling times were 2–4 years, differences were reported by congener, fish species, and source lake. From the more recent data, the authors concluded that PBDE concentrations are no longer exponentially increasing in the Great Lakes as was reported by other studies. The data suggest that accumulation rates are slowing and concentrations of penta and hexa-congeners may be decreasing. This trend was most evident in Lake Ontario and Lake Michigan, beginning in the mid-1990s.

Streets et al. (2006) examined the partitioning and bioaccumulation of PBDEs and PCBs in the Great Lakes and were the first to determine bioaccumulation factors (BAFs) in fish. The researchers analyzed 6 PBDE and 110 PCB congeners in lake trout collected as part of the Great Lakes Fish Monitoring Program during 2000, 2001, and 2002 from all five Great Lakes and water samples collected from five locations in Lake Michigan. Four PBDE congeners (BDE-47, BDE-66, BDE-99, and BDE-100) were detected in the dissolved phase of water samples and had concentrations ranging from 0.13 to 10 pg/L. In the particulate phase, three PBDE congeners (BDE-47, BDE-99, and BDE-100) were measured at concentrations ranging from 0.18 to 1.4 pg/L. Fish samples contained six congeners that included BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, and BDE-154, with the highest values reported for lake trout collected in Lake Michigan, followed by Lakes Ontario, Superior, and Huron. Log BAFs for the PBDE congeners ranged from 6.7 to 7.5 for lake trout.

The levels and patterns of PBDE congeners were evaluated by Rice et al. (2002) in carp and largemouth bass collected from the Detroit River, MI, and in carp collected at two locations in the Des Plaines River, IL, in May and June 1999. Both are major rivers that receive industrial and municipal effluents. The average total concentrations of PBDEs in carp and bass from the Detroit River were 5.39 and 5.25 ng/g wwt, respectively. Higher total PBDE concentrations were reported for carp collected in the Des Plaines River, with an average total concentration of 12.48 ng/g wwt. The tetrabromo congener, BDE-47, represented 53 and 56% of the relative proportion of the seven detected congeners in carp and largemouth bass, respectively; these fish were collected from the Detroit River. In carp collected from the Des Plaines River, the most prominent congeners were BDE-183 and BDE-181 (20 and 22%, respectively, of the total PBDE residue), whereas the heptabromo congener BDE-190 was present in Des Plaines River samples and represented 12% of the total amount of PBDE. The authors also reported positive correlations between PBDE congener concentrations and increasing lipid levels, in both fish species. The authors suggested that the differences in dominant congener types between the two locations were probably related to differences in industrial and municipal discharges entering these systems.

Valters et al. (2005) assessed the concentrations of PBDEs and their metabolites, which included hydroxylated-PBDEs (OH-PBDEs) and methoxylated-PBDEs (MeO-PBDEs), in benthic and pelagic fish taken from the Detroit River collected in 2001 and 2002. Several other compounds were included in the study, including triclosan and its metabolites (methylated triclosan analogue). The dominant PBDE congeners were BDE-47, BDE-99, and BDE-100, and these accounted for 85% of the ΣPBDE concentration and individually ranged from 0.155 to 21.1 ng/g wwt. For comparison, triclosan concentrations ranged from 0.750 to >100 ng/g wwt. The dominant hydroxylated-PBDE was 6-OH-BDE-47 and had ΣOH-PBDE concentrations ranging from 0.003 to 0.198 ng/g wwt. MeO-PBDEs were below detection limits in all samples. The resulting ΣPBDE to ΣOH-PBDE ratio ranged from 0.0005 to 0.02. The authors suggested that OH-PBDEs are likely derived as metabolites from PBDE precursors and are retained in the blood.

The herring gull (*Larus argentatus*) is a good indicator organism for studying the bioaccumulation of organic compounds in ecosystems, because it fills the niche of facultative piscivore. Norstrom et al. (2002) studied the geographical distribution of PBDE flame retardants in herring gulls in 2002 by analyzing eggs collected at 15 locations in the Great Lakes. Temporal trends for the period from 1981 to 2000 were explored by analysis of archived egg homogenates from gull colonies in Lakes Michigan, Huron, and Ontario. A total of 25 di-BDE to hepta-BDE congeners were identified, with 7 congeners representing 97.5% of the ΣPBDEs. The dominant congener distributed throughout the Great Lakes was BDE-47, followed by BDE-99. Concentrations of ΣPBDE ranged from 192 to 1,400 ng/g wwt. The two highest concentrations were measured in gull colonies located in Lake Michigan (1,400 and 1,366 ng/g wwt), followed by Toronto Harbor in Lake Ontario (1,003 ng/g wwt). The lowest ΣPBDE concentrations were found in colonies in Lake Erie (192 ng/g wwt). An increase in ΣPBDE concentrations ranging from 20-fold to

75-fold occurred from 1981 to 2000 in herring gull eggs taken from colonies in Lake Michigan, Lake Huron, and Lake Ontario. The three most common congeners, BDE-47, BDE-99, and BDE-100, ranged from 5 to 12 ng/g wwt in 1981–1983, and then increased to 400–1,100 ng/g wwt from 1983 to 2000. The doubling times of these three congeners ($\Sigma PBDE_{47,99,100}$) were 2.8 years in Lake Ontario, 2.6 years in Lake Michigan, and 3.1 years in Lake Huron. The authors concluded that, if the present rate of change continued, the concentrations of ΣPBDE would equal or surpass those of ΣPCBs in Great Lakes herring gull eggs in 10–15 years.

Herring gull eggs were examined by Gauthier et al. (2007) for the presence of a variety of PBDE congeners (hepta-BDE to nona-BDE and BDE-209), including those that were not reported in spatial and temporal assessments of PBDEs from 1981 to 2000. The study included the analysis of other brominated and chlorinated flame retardants. BDE-209 and seven other heptabromo-BDE to nonabromo-BDE congeners were detected. The authors reported a trend of decreasing concentrations of Σ_7PBDEs when compared to data collected in 2000 (Norstrom et al. 2002). Of the other flame retardants that were included in the analysis, six were quantifiable in the egg samples pooled from all six colonies in 2004.

Gauthier et al. (2008) continued to utilize herring gull eggs to analyze the temporal trends of PBDEs, specifically BDE-209 in pooled samples from seven gull colonies in the Laurentian Great Lakes from 1982–2006. The authors reported that 39 congeners were quantifiable in the pooled egg samples, and the highest Σ_{39}PBDE concentration was detected in samples from Gull Island (1,191 ng/g wwt). In 2006, BDE-209 concentrations ranged from 4.5 to 20 ng/g wwt and constituted 0.6–4.5% of the Σ_{39}PBDE concentrations. The doubling time for BDE-209 between 1982 and 2006 was determined to be 2.1–3.0 years. Concentrations of Σ_{octa}BDEs and Σ_{nona}BDEs congeners detected in herring gull eggs may have resulted from the debromination of BDE-209 formed metabolically, either in the herring gulls or in the environment, and then accumulated through the diet and transferred to their eggs. The authors determined that congeners derived from the penta-PBDE and octa-PBDE mixtures (BDE-47, BDE-99, BDE-100) showed increases in concentrations up until 2000 with no increasing trend thereafter.

To assess sediment concentrations of various flame retardants, Qiu et al. (2007) reported the analysis of Dechlorane Plus (DP), PBDEs, and 1,2 bis(2,4, 6-tribromophenoxy)ethane (TBE) in sediment cores taken from the central basin of Lake Ontario. Of the PBDE concentrations detected, $\Sigma PBDE_{3–7}$ (sum of tri-BDE to hepta-BDE congeners) and BDE-209 were found at average concentrations of 2.8 and 14 ng/g dwt, respectively. BDE-209 was the dominant PBDE congener measured in sediment samples. The analysis of concentration profiles with depth suggested that BDE-209 accumulation in sediments increased beginning in the early 1980s.

Sediment core samples were taken from each of the Great Lakes in 2001–2002 and analyzed for the presence of PBDEs and PCBs. The results were published in a series of three papers by Song et al. (2004, 2005a, b). In the first paper, Song et al. (2004) sampled 6 locations in Lake Superior in 2001 and 2002 and reported the results for 10 PBDEs and 19 PCBs. $\Sigma PBDE_9$ (sum of nine congeners, excluding

BDE-209) concentrations ranged from 0.49 to 3.1 ng/g dwt in surficial sediments. ΣPCB (sum of all 19 PCB congeners) concentrations in surficial sediments were in the range of 2–27 ng/g dwt. BDE-209 was the predominant PBDE congener and represented 83–94% of the total concentration of PBDEs detected in the sediments. The authors estimated that the loading rate of all ten PBDE congeners to Lake Superior sediments was 80–160 kg/yr.

In subsequent work, sediment cores were collected at 6 sites in Lakes Michigan and Huron in 2002 and analyzed for the same 10 PBDE congeners, as well as 39 PCB congeners (Song et al. 2005b). The concentration of $\Sigma PBDE_9$ in surface sediments of Lake Michigan ranged from 1.7 to 4 ng/g dwt, whereas Lake Huron sediments contained $\Sigma PBDE_9$ congeners that ranged from 1.0 to 1.9 ng/g dwt. Sediment concentrations of PBDE showed a trend of increasing levels with decreasing depth. BDE-209 was the dominant congener representing 96 and 91% (by mass) of the PBDEs found in Lake Michigan (average of 63 ng/g dwt) and Lake Huron (average of 15.9 ng/g dwt), respectively. The total load of PBDEs in Lake Michigan, including BDE-209, was estimated to range from 29,000 to 50,000 kg with a total loading of 390–1,200 kg/yr. For Lake Huron, the total load was estimated to range from 6,000 to 15,000 kg (including BDE-209) and the loading rate from 400 to 840 kg/yr. Of the lower congeners, BDE-47 and BDE-99 were the most abundant. PCB concentrations were shown to be stable at most locations rather than continually increasing with decreasing sediment depth. Variations in the PCB data suggested that potential non-point source inputs of PCBs remain, although production and usage of PCBs were banned in the 1970s.

In 2002, sediment core samples were collected for evaluation of PBDE concentrations in Lakes Ontario and Erie (Song et al. 2005a). Sediment cores were obtained from 4 locations and analyzed for the same 10 PBDE congeners and 39 PCB congeners. $\Sigma PBDE_9$ concentrations (excluding BDE-209) ranged from 4.85 and 6.33 ng/g dwt, in Lake Ontario and from 1.83 and 1.95 ng/g dwt, in Lake Erie, respectively. BDE-209 concentrations were higher in Lake Ontario at 242 and 211 ng/g dwt, compared to 50 and 55 ng/g dwt, in Lake Erie. In Lake Ontario, PBDE concentrations followed a clear increasing trend from the bottom of sediment cores to the surface, where maximum concentrations were detected. In Lake Erie, the trends were not as clear, although the data were consistent with increasing concentrations of PBDE in surface sediments. The authors hypothesized that resuspension of sediments occurs in the shallow waters of Lake Erie from the action of wind and waves. The observation that PBDE concentration increases with decreasing sediment depth supports the view that there has been a continuous input of PBDEs since the 1970s. Although average PBDE concentrations were reported to be higher for Lake Ontario than for Lake Erie, organic carbon normalized data were similar between the lakes. The current load of PBDEs, including BDE-209, was 22 and 18 t for Lake Ontario and Lake Erie, respectively, in 2002. Loading rates were determined to be 3,400 kg/yr in Lake Ontario for total PBDEs (all ten congeners) and 32 kg/yr and 1,311 kg/yr for $\Sigma PBDE_9$ and BDE-209, respectively, in Lake Erie. BDE-209 was the dominant PBDE congener measured in sediments in both lakes, and respectively, represented 91 and 96% of the measured total PBDE

concentrations in Lakes Erie and Ontario. Of the remaining nine PBDE congeners, BDE-47 and BDE-99 were the most common. PCB concentrations peaked in the 1960s and 1970s and showed a trend of decreasing levels in surface sediments. In 2002, sediment cores from Lake Ontario exhibited surface PCB concentrations ranging from 58.3 to 63.6 ng/g dwt, whereas Lake Erie had lower concentrations of 23–28.3 ng/g dwt.

A database of 2,197 data points was created from 19 published studies in which the concentrations of PBDEs in the various environmental media were evaluated. Although concentrations have been reported for as many as 28 different congeners, groups of congeners, or metabolites, to facilitate the interpretation, the analytes were first grouped into categories on the basis of data availability. For the present analysis, metabolite data were not included. When possible, individual BDE congeners were grouped to derive concentrations representative of the commercial products (penta-PBDE, octa-PBDE, or deca-PBDE). For the herring gull egg data, individual congeners were grouped according to the degree of bromination (i.e., total Br_3, total Br_4, total Br_5, total Br_6, etc.). As presented in Table 13a and b, concentrations in biological tissues ($n = 673$) represented the majority of the data; fewer data were available for sediment ($n = 45$).

Table 13a presents the analysis of concentrations of PBDEs in fish. Note that, for this dataset, concentrations of individual congeners were reported, and these were grouped into categories representative of the commercial products. Penta-PBDE concentrations in fish ranged from 0.005 to 354.7 ng/g wwt; mean and 95th percentile values were 35.1 and 122.7 ng/g wwt, respectively. Concentrations of octa-PBDE detected in fish were lower, ranging from 0.77 to 1.92 ng/g wwt. Mean and 95th percentile octa-PBDE concentrations were 1.45 and 1.81 ng/g wwt, respectively.

The most abundant single congener detected in fish was BDE-47, followed by BDE-99 and BDE-100 (Fig. 9a and b). The predominance of congener data available for commercial penta-PBDE is evident in Table 13a, with 235 values as compared to 22 for the octa-PBDE product. The higher concentrations of these lower-brominated congeners may reflect the increased production and use of the penta-PBDE products or differences in bioavailability.

In Table 13a, we also summarize the analysis of concentrations of various congener groups in herring gull eggs. Of the various congeners, total Br_4 BDE and total Br_5 BDE were predominant. Concentrations for these groups ranged from 0.06 to 708 ng/g wwt; mean and 95th percentile ranged from 106 to 437 ng/g wwt. The prevalence of Br_4 and Br_5 congeners in the gull eggs is consistent with the distribution of PBDE congeners in fish. Although fewer data were available, concentrations of the higher brominated congeners were lower in the gull eggs, reflecting either differences in production and use or decreased bioavailability of the higher congeners.

As discussed above, numerous researchers have documented trends of increasing PBDE concentrations in biota dating back to 1979 and continuing through 2000. The data suggested that PBDEs initially began to accumulate in biota around 1980, which corresponds to increasing production and use of these flame retardants.

Table 13 Summary Statistics for Polybrominated diphenyl ethers (PBDE)

	n	Freq det (%)	Mean (ng/g wwt)	SD (ng/g wwt)	Median (ng/g wwt)	95th percentile (ng/g wwt)	Min (ng/g wwt)	Max (ng/g wwt)
A. Biota								
Fish								
Penta[1]	235	NA	35.1	54.1	10.4	122.7	0.005	354.7
Octa	22	NA	1.45	0.299	1.53	1.81	0.77	1.92
Gull eggs	*n*	Freq det (%)	Mean (ng/g wwt)	SD (ng/g wwt)	Median (ng/g wwt)	95th percentile (ng/g wwt)	Min (ng/g wwt)	Max (ng/g wwt)
Total Br_3 BDE	55	NA	3.03	2.34	2.7	7.03	0.1	8.2
Total Br_4 BDE	55	NA	171	144	128	437	2.8	602
Total Br_5 BDE	103	NA	106	128	63.4	364	0.6	708
Total Br_6 BDE	103	NA	44.9	45.2	31.8	142	1.4	235
Total Br_7 BDE	61	NA	11.9	18.8	7.1	43.5	0.2	125
Total Br_8 BDE	13	NA	6.85	4.67	5.4	15.4	2.6	19
Total Br_9 BDE	13	NA	2.65	2.48	2.3	6.78	0.1	8.5
BDE-209	13	NA	6.35	7.31	4.5	18.8	0.05	20
	n	Freq det (%)	Mean (ng/g dwt)	SD (ng/g dwt)	Median (ng/g wwt)	95th percentile (ng/g dwt)	Min (ng/g dwt)	Max (ng/g dwt)
B. Sediment								
Penta PBDE[2]	22	100	2.23	1.42	1.83	4.81	0.49	6.33
Deca PBDE	23	100	71.3	88.5	36	239	4.30	315

[1]Penta-PBDE and octa-PBDE concentrations were calculated by summing values for brominated diphenyl ether (BDE) isomer BDE-47 through BDE-154 and BDE-153 through BDE-190, respectively

[2]Penta-PBDE concentrations were calculated by summing values for BDE-28 through BDE-183

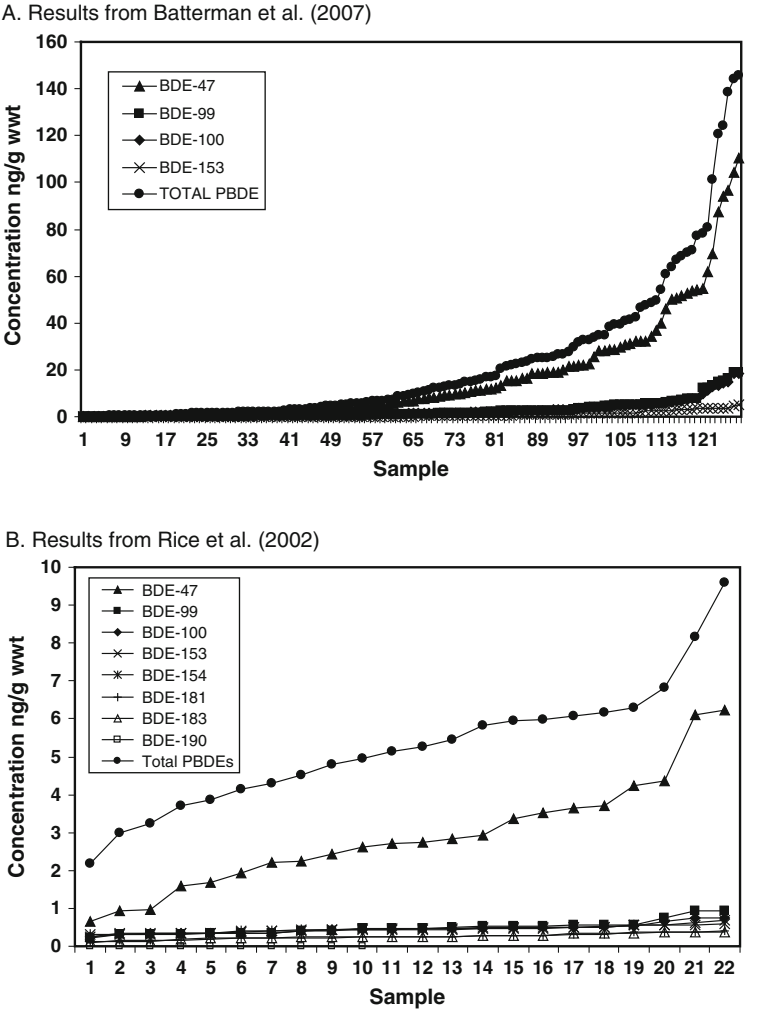


Fig. 9 Distribution of BDE congeners in fish compared with total PBDE concentrations. **a** Results from Batterman et al. (2007) and **b** results from Rice et al. (2002)

However, these data are biased, because few if any pre-1980 archived biota samples are available for analyses. Nonetheless, the trend of increasing PBDE concentrations through the 1980s into the 1990s is consistent with the findings of Batterman et al. (2007), Chernyak et al. (2005), and Zhu and Hites (2004). More recent data (post-2000) suggest that concentrations in biota have leveled-off or are declining, particularly for penta-PBDE and octa-PBDE, which likely reflects changes in use of these products as a consequence of regulatory bans or, for some products, voluntary decisions to stop manufacture.

Deca-PBDE (BDE-209) was not reported in any fish samples from the Great Lakes. Possible explanations include the exclusion of this specific congener from analyses, the limited manufacture and release of BDE-209 in the early to mid-1980s, or the reduced bioavailability and bioaccumulation potential of BDE-209 in fish. However, several researchers have noted that a potential source of hepta-BDE congeners (BDE-181, BDE-183, and BDE-190) may be from the environmental transformation of BDE-209. Some researchers have suggested that the debromination of deca-PBDE may result in the formation of hepta-BDE and octa-BDE congeners, which become more bioavailable to accumulate in fish and other organisms.

Norstrom et al. (2002) performed analysis of herring gull eggs collected from 1981 to 2000 and reported that nona-BDEs and BDE-209 were not detected in eggs collected from 15 locations around the Great Lakes. However, low concentrations of BDE-209 were detected at quantifiable levels in some samples that were collected at the same locations in 2004 (Gauthier et al. 2007). From the statistical analysis, mean concentrations of BDE-209 in gull eggs were 6.35 ± 7.31 ng/g wwt ($n = 13$), with minimum and maximum concentrations of 0.05–20 ng/g wwt, respectively. These values were similar to the 5th and 95th percentile values (0.05 and 18.8 ng/g wwt).

Although the data are more limited, penta-PBDE and deca-PBDE have been detected in sediment cores, and concentrations in such cores appear to be increasing over time. As summarized in Table 13b, penta-PBDE concentrations range from 0.049 to 6.33 ng/g dwt; mean and 95th percentile concentrations were 2.23 and 4.81 ng/g dwt, respectively. In contrast, BDE-209 was the dominant congener detected, representing over 85% of the PBDEs analyzed in sediment samples. The BDE-209 concentrations ranged from 4.3 to 315 ng/g dwt (mean and 95th percentile of 71.3 and 239 ng/g dwt, respectively). Increasing trends in sediment deca-PBDE concentrations may be due to the increased production of deca-PBDE in the late 1990s combined with the propensity to partition to sediment particles because of having a high K_{ow}.

Risk assessments for commercial PBDEs have been conducted by authorities in various geographies (EC, 2006b; EUC 2001, 2003b). Estimated no effect values and PNECs have been developed for use in the calculation of risk quotients (Table 2). Comparison of the available data for sediment concentrations (Table 13b) versus the various regulatory criteria suggests that all exposures are below effect concentrations developed in Canada and Europe. Maximum penta-PBDE and deca-PBDE concentrations in sediment are 0.006 and 0.315 mg/kg dwt, respectively, which are below the most stringent criteria. Maximum and 95th percentile values for penta-PBDE in fish are 0.35 and 0.12 mg/kg wwt, respectively (Table 13a). These concentrations exceed the Canadian ENEV for secondary poisoning via the food chain, although they are below the PNEC value derived in Europe (Table 2). In contrast, all octa-PBDE concentrations in fish (maximum = 0.002 mg/kg food) are below the regulatory criteria.

The lower brominated congeners were more prevalent in gull egg samples, with the tetra-BDE and penta-BDE congeners being present at the highest concentrations. Mean values were 0.17 and 0.11 mg/kg wwt, and the corresponding maximum concentrations were 0.6 and 0.71 mg/kg wwt, respectively. These concentrations exceed

the Canadian ENEV criteria value for secondary consumers (0.0084 mg/kg food). The remaining PBDE congeners reported for gull eggs were below the regulatory criteria for both Canada and Europe, including BDE-209 concentrations, which had mean and maximum values of 0.006 and 0.02 mg/kg wwt, respectively.

3.8 Other Flame Retardants

The use of flame retardants in commercial and consumer goods has grown over the last 40 years as a result of increasingly stringent fire safety regulations. As discussed in the previous section, PBDE flame retardants were widely used for many years in a variety of applications. However, because of increased environmental and human health concerns, several of the PBDEs (e.g., penta-BDE and octa-BDE) have been recently banned in Europe and in other countries. The major manufacturer in the United States stopped production of these compounds in 2004. As flame retardants are taken off the market, they are replaced by others to enable manufacturers of commercial and consumer goods to continue to meet government safety standards.

The substances discussed in this category include a variety of other flame retardants, many of which have been produced for more than 40 years. As presented below, environmental concentrations have been reported for a variety of these substances, particularly for Dechlorane Plus (DP) and hexabromocyclododecane (HBCD) in sediments and biota. Limited information is available for various other substances and for other environmental media.

In the present analysis we focused on those studies that reported concentrations in surface waters, sediment, and biota (sampling locations not illustrated). However, a number of studies that were identified in the literature included analytical results for flame retardants in air (e.g., Hoh and Hites 2005; Hoh et al. 2005, 2006; Venier and Hites 2008).

Hoh et al. (2005) analyzed for TBE and pentabromoethylbenzene (PBEB) in a single sediment core taken from northern Lake Michigan in April 2004. TBE was detected in the sediment core from Lake Michigan at about 9 ng/g dwt, whereas PBEB was not detected. Based on the analysis of sediment samples taken at various depths, TBE first appeared in the core at a depth corresponding to the year 1973, consistent with the beginning of production. Levels in the core increased toward the shallower depths with a doubling time of approximately 2 years until 1985, when concentrations stabilized. TBE was not detected in the surficial (top) layer of the core which represented 1993–2004. According to US EPA Inventory Update Rule, TBE production increased from 1986 to 1994 and then decreased substantially after 1998.

Hoh et al. (2006) summarized the analysis of DP in sediment and fish collected throughout the Great Lakes Basin. DP is a chlorinated flame retardant introduced in the mid-1960s as a substitute for Dechlorane (or Mirex) and is incorporated into polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material. Two sediment cores were taken from eastern Lake Erie in August 2003, and one each was taken from northern and southern Lake Michigan

in April 2004. Archived fish samples, taken from Lake Erie throughout 1980–2000 (seven sampling periods), were also analyzed. DP was detected in sediment cores taken from Lakes Michigan and Erie. Concentrations in the cores appeared to peak during the period between 1976 and 1981, and since then have declined by about 50% in surface layers. The highest historical DP concentration in Lake Erie (40 ng/g dwt) was about ten times higher than observed in the sediment core profiles for Lake Michigan. Concentrations in the surface layers of Lakes Michigan and Erie sediments were in the range of 2–5 ng/g dwt.

Because of the higher concentrations of DP in air and sediments from Lake Erie, Qiu et al. (2007) speculated that Lake Ontario may receive atmospheric contributions of DP from a manufacturing facility in Niagara Falls, NY. To address this, a sediment core was obtained in 2004 from the central basin of Lake Ontario and analyzed for DP and other brominated flame retardants. Results showed that DP concentrations increased rapidly in the mid-1970s and reached a peak concentration (310 ng/g dwt) in the mid-1990s. DP concentrations near the surface were lower (150 ng/g dwt). Measurements of TBE in the sediment core showed increased levels starting after the early 1980s, with a maximum concentration of 6.7 ng/g dwt in the surficial sediment.

Sverko et al. (2008) reported the results of a survey of DP concentrations in sediments collected during the period from 1997 to 1998 from 40 locations in Lakes Erie and Ontario. Archived samples of Niagara River suspended sediments were also analyzed. Total DP concentration in surface sediments from Lakes Erie and Ontario ranged from 0.061 to 8.62 ng/g and from 2.23 to 586 ng/g dwt, respectively. Lake-wide average DP concentrations in Lake Ontario were about 50 times greater than observed in Lake Erie. Analysis of archived sediments collected from the Niagara River, during the period from 1980 to 2002, showed a declining total DP concentration from 89 to 7 ng/g dwt, suggesting a possible decrease in production or the reduction of DP released to the environment from the manufacturing facility. The spatial distribution of DP in Lake Ontario was generally related to the bathymetry, with the highest concentrations associated with fine-grained sediments in the three major deep-water depositional basins. The non-depositional sill zones, where the sediments were characterized by coarse sands, exhibited the lowest levels. Although the Niagara River has been suggested as a primary source of DP, the spatial distribution of DP was noted as being similar to that of other contaminants, including PCBs. The highest concentration measured in Lake Ontario was near the city of Toronto, which is unusual if one considers the river as the primary source and the counterclockwise flow pattern of the lake. The authors concluded that in addition to the Niagara River, other sources may also be important contributors to DP concentrations in Lake Ontario, and that greater spatial resolution is required.

The distribution of HBCD isomers in Detroit River sediments was reported by Marvin et al. (2006). HBCD is the principal flame retardant in extruded and expanded polystyrene foams and is used as insulation in the building industry. The substance is also used in upholstery textiles, including residential and commercial furniture, draperies, and wall coverings. Suspended sediment samples ($n = 63$) were

collected monthly (from May to November, 2001) from the Detroit River from single-point sediment-trap moorings sited at nine stations, located from the headwaters in southern Lake St. Clair to the mouth of the outflow to western Lake Erie. Suspended sediments were sampled instead of bottom sediments because of the non-depositional nature of the upper and middle reaches of the river. Individual HBCD isomers were found at relatively low concentrations ranging from < 0.025 to 1.9 ng/g dwt for the alpha isomer, to < 0.025 to 2.3 ng/g dwt for the gamma isomer; concentrations of the beta isomer were lower (< 0.025–0.28 ng/g dwt). Approximately 66% of the suspended sediment samples were dominated by the gamma isomer in which the isomeric profiles were similar to the commercial technical mixture. The isomer profiles in the remaining samples were dominated by the alpha isomer. The highest monthly concentrations of total HBCD were detected in samples from the upper reaches of the river near Belle Isle (2.6 ng/g dwt, in October), near the mouth of the Rouge River (3.65 ng/g dwt, in August), and near the head of the Trenton Channel (2.6 ng/g dwt, in August). The authors noted that the distribution and occurrence of HBCD in suspended sediments of the Detroit river were commensurate with land use patterns (i.e., general urbanization and industrialization) and do not provide evidence of the presence of significant point sources. The widespread occurrence of relatively low concentrations of HBCD in the sediments suggests that large urban areas can act as diffuse sources.

Tomy et al. (2004) analyzed the bioaccumulation and trophic magnification of HBCD isomers in a Lake Ontario pelagic food web. Lake trout ($n = 5$), alewife (composites of 5 fish, $n = 3$), rainbow smelt (composites of 5 or 20 fish, $n = 3$), and slimy sculpin (composites of 10 or 15 fish, $n = 3$), were collected between June and September of 2002 at offshore stations in Lake Ontario. Invertebrate species, including samples of *Mysis* (composites of >100, $n = 2$) and amphipods (*Diporeia*, composites of >100, $n = 2$), as well as plankton grab samples ($n = 2$), were collected at the same locations. Concentrations of the alpha isomer were consistently higher than that of the gamma isomer, while levels of the beta isomer were always below the detection limit. Measured concentrations of alpha (0.4–3.8 ng/g wwt) and gamma HBCD (0.1–0.8 ng/g wwt) were highest in the lake trout samples. For the prey fish species, trends in alpha and gamma levels were on the order of slimy sculpin > smelt > alewife. Because of their benthic association and higher lipid content, it is reasonable that levels of HBCD were higher in sculpin compared to the other two forage fish species. Mean concentrations in *Mysis* and *Diporeia* were similar (0.14–0.16 ng/g) and about twofold higher than concentrations measured in plankton (0.06 ng/g wwt). Biomagnification factors were variable between the trophic levels and feeding relationships and ranged from 0.2 to 10.8. The trophic magnification factor (TMF) of 6.3, derived for HBCD, is comparable to those reported for DDE (6.1) and the PCBs (5.7).

In a related study, Tomy et al. (2007) examined the bioaccumulation and trophic magnification of DP in a Lake Ontario pelagic food web. Biological specimens consisting of plankton, invertebrates, forage fish, and lake trout were collected between June and September of 2002, using the sampling protocols discussed above. Concentrations of the *anti*-isomer were generally higher than that of the *syn*-isomer.

The extent of bioaccumulation of the isomers was greater in the lower trophic levels in Lake Ontario. For example, measured concentrations of *anti*-DP and *syn*-DP were the highest in *Diporeia* (3.1 ± 0.9 ng/g lipid wt and 1.3 ± 0.6 ng/g lipid wt, respectively) and were approximately 10–30-fold lower in lake trout. For the prey fish species, *anti*-isomer and *syn*-isomer concentrations ranged from 7 to 901 ng/g lipid wt, and the trends in total DP concentrations were on the order of slimy sculpin > alewife > smelt. Biomagnification factors were variable between the trophic levels and feeding relationships and ranged from 0.1 to 12. However, no statistically significant trophic magnification factor for either isomer was determined for the Lake Ontario food web. In contrast, related work conducted in Lake Winnipeg resulted in trophic magnification factors of 2.5 and <1 for the *anti*-isomer and *syn*-isomer, respectively. Further analysis of the results suggested that interspecies differences in bioaccumulation and biotransformation are probable key factors in determining the distribution of DP isomers in the environment.

Gauthier et al. (2007) analyzed for the presence of a variety of flame retardants in gull eggs that were collected throughout the Laurentian Great Lakes. Eggs (n = 10–13) were collected from six colonies in April–May of 2004, and pooled homogenates were prepared and analyzed for each colony. As illustrated in Fig. 10, concentrations of the flame retardants, including PBEB, DP, and HBCD, ranged among the colonies from 0.03 to 1.4 ng/g wwt, from 1.5 to 4.5 ng/g wwt, and from <0.01 to 20.7 ng/g wwt, respectively. Concentrations of other flame retardants, including hexabromobenzene (HBB), pentabromotoluene (PBT), and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE or TBE) were all less than 1 ng/g wwt. Whether the latter substances are still used commercially was unclear. In contrast, total PBDE

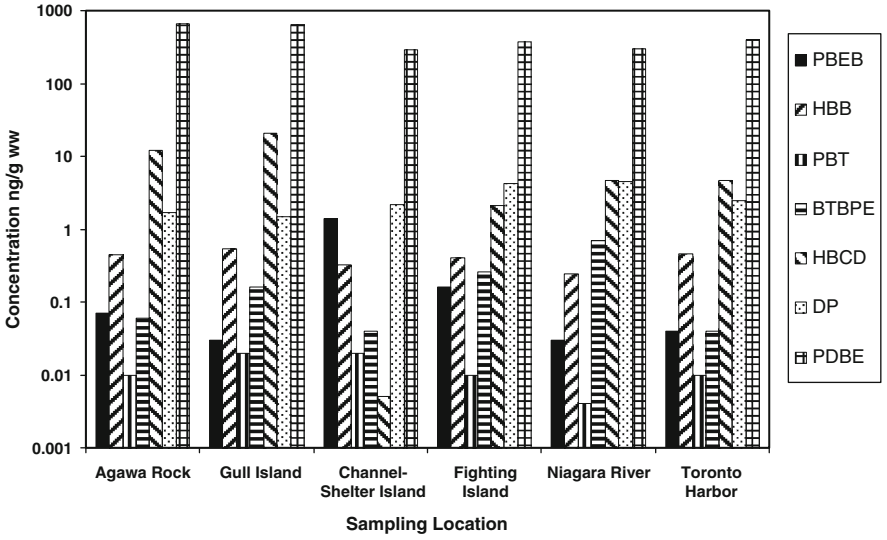


Fig. 10 Distribution of flame retardants in gull eggs from the Laurentian Great Lakes

concentrations in the eggs from all colonies were substantially higher, ranging from 293 to 663 ng/g wwt. The most abundant PBDE congeners detected were those associated with penta-PBDE mixtures. Concentrations of total hepta-BDE, octa-BDE, and nona-BDE were generally less than 10 ng/g wwt, whereas deca-BDE was typically below the detection limit. When PBDE concentrations measured in the current study were compared with those determined in 2000 for eggs collected from the same colonies, the trend appears to suggest that concentrations have decreased considerably. The limited data precludes an analysis of trends in concentrations for the remaining compounds. The authors concluded that mother herring gulls are exposed to several current-use flame retardants via their diet, and that in ovo transfer occurs to their eggs.

Only limited information was available for the presence of several chlorinated phosphate flame retardants in surface waters of the Great Lakes. Kolpin et al. (2002) reported concentrations in water samples ($n = 7$) from the Lake Michigan watershed that ranged from below the detection limit to 0.27 μg/L for tri-(2-chloroethyl)phosphate and tri-(dichloroisopropyl)phosphate. Andresen et al. (2007) reported concentrations for these two as well; tri-(dichloropropyl) phosphate ranged from 0.002 to 0.08 μg/L in samples ($n = 6$) from Hamilton Harbor, ON. According to the authors, these compounds were previously used as flame retardants in polyurethane foam and have been phased out because of toxicity concerns.

The statistical analysis of the flame retardant data in this category was performed on a total of 660 data points. As summarized in Table 14a–c, the concentrations reported in biological tissues ($n = 509$) represented the majority of the data. Fewer data were available for sediments ($n = 119$) and only for a few of the compounds. Limited data were available for surface waters.

Concentrations of DP have been reported for sediment and biological samples collected throughout the Great Lakes Basin. Several of the studies focused on the potential contributions of a manufacturing facility located in the Niagara River region. Information on the concentrations and spatial distribution of DP in sediments was available from three studies, although the majority of samples were obtained from Lakes Erie and Ontario. A survey conducted in 1997 and 1998 showed that DP levels were the highest in Lake Ontario, ranging from 2.2 to 586 ng/g dwt. Analysis of a single core from Lake Ontario in 2003 showed comparable results; the DP concentration in the surface layer was 150 ng/g dwt. DP levels found in Lake Erie in 1997 and 1998 ranged from 0.06 to 8.6 ng/g dwt and were reported to be approximately 50-fold lower than levels reported in Lake Ontario. Analysis of a single core in 2003 showed similar levels (3 ng/g dwt), which were reported as being comparable to BDE-209 concentrations in the same core. Limited results are available for DP concentrations in sediments from Lake Michigan, where the levels were found to be lower than those in Lake Erie, and considerably lower than PBDE levels in the same samples. DP was detected in 100% of the aquatic biota collected from Lake Ontario (Table 14c). The concentrations ranged from 0.02 to 4.4 ng/g wwt (mean $= 1.27 \pm 1.59$ ng/g wwt) and were highest in *Diporeia*. Lower levels in lake trout (approximately 0.02 ng/g wwt) were consistent with decreased bioaccumulation of

Table 14 Summary statistics for other flame retardants

	n	Freq det (%)	Mean (μg/L)	SD (μg/L)	Median (μg/L)	95th percentile (μg/L)	Min (μg/L)	Max (μg/L)
A. Surface water								
Tri (2-chloro-ethyl) phosphate	13	85	0.086	0.095	0.035	0.240	0.004	0.270
Tri (di-chloro-isopropyl) phosphate	13	62	0.052	0.033	0.050	0.104	0.003	0.110
Tri(dichloro-propyl phosphate)	6	100	0.015	0.014	0.011	0.033	0.002	0.035
	n	Freq det (%)	Mean (ng/g dwt)	SD (ng/g dwt)	Median (ng/g dwt)	95th percentile (ng/g dwt)	Min (ng/g dwt)	Max (ng/g dwt)
B. Sediment								
Total Dechlorane Plus (DP)	48	100	107.8323	217.7972	5.0000	455.2000	0.2060	586
Total HBCD	66	64	0.4702	0.7273	0.1825	2.2275	0.0008	3.65
Pentabromoethyl benzene (PBEB)	1	0	0.01	0.00	0.01	0.01	0.01	0.01
Tribromophenoxy ethane (TBE)	4	75	5.27	4.62	6.70	8.77	0.10	9.00

Table 14 (continued)

	n	Freq det (%)	Mean (ng/g wwt)	SD (ng/g wwt)	Median (ng/g wwt)	95th percentile (ng/g wwt)	Min (ng/g wwt)	Max (ng/g wwt)
C. Biota[a]								
Aquatic								
Total DP	21	100	1.27	1.59	0.50	3.71	0.02	4.42
Total HBCD	20	100	0.56	1.01	0.20	1.57	0.02	4.51
Gull Eggs	*n*	Freq det (%)	Mean (ng/g wwt)	SD (ng/g wwt)	Median (ng/g wwt)	95th percentile (ng/g wwt)	Min (ng/g wwt)	Max (ng/g wwt)
Bis-tribromophenoxy ethane (BTBPE)	78	100	0.210	0.255	0.110	0.590	0.040	0.700
Total DP	78	100	2.77	1.28	2.35	4.43	1.50	4.50
Hexabromobiphenyl (HBB)	78	100	0.400	0.104	0.425	0.513	0.240	0.530
Total HBCD	78	83	7.39	7.71	4.66	18.56	0.01	20.67
PBEB	78	100	0.288	0.547	0.055	1.090	0.030	1.400
Pentabromotoluene (PBT)	78	100	0.012	0.006	0.010	0.020	0.004	0.020

[a] The results represent concentrations reported for multiple trophic levels (invertebrates, small fish, large fish)

DP at higher trophic levels that were reported for this lake. DP was also detected in 100% of the gull eggs collected throughout the basin. Concentrations ranged from 1.5 to 4.5 ng/g wwt (mean = 2.8 ± 1.3 ng/g wwt). The highest concentration in gull eggs was measured in samples collected from sites near the Niagara River.

Fewer data were available for the concentrations of HBCD in the Great Lakes Basin. In one study, sediment concentrations obtained from various locations along the Detroit River were analyzed. As shown in Table 14b, HBCD (total) was detected in 64% of these sediment samples at concentrations ranging from below the detection limit to 3.65 ng/g dwt (0.47 ± 0.73 ng/g dwt). The highest concentrations were present at the confluence of the Rouge and Detroit Rivers. The authors noted that HBCD concentrations in the Detroit River represent the contributions from diffuse sources and were three orders of magnitude lower than were PCB concentrations in this region. HBCD was detected in 100% of the aquatic biota collected from Lake Ontario. HBCD concentrations ranged from 0.02 to 4.5 ng/g wwt (mean 0.56 + 1.0 ng/g wwt) and increased in samples from the various trophic levels (invertebrates, prey fish, and large fish). The highest concentrations were reported in lake trout, consistent with the calculated trophic magnification factor of 6.3. HBCD was detected in 83% of the gull eggs collected from locations throughout the basin. Concentrations ranged from non-detectable to 20.7 ng/g wwt. The highest concentrations were measured from eggs collected from northern Lake Michigan (20.7 ng/g wwt) and Agawa Rock (12.2 ng/g wwt) in Lake Superior (Fig. 10). Elsewhere, HBCD concentrations ranged from 2.1 to 4.7 ng/g wwt and were not detectable in eggs collected from Channel Island in Saginaw Bay.

Only limited data were available for the remaining flame retardants examined in this category. Low concentrations of TBE (also referred to as BTBPE) were measured in sediments, ranging from 0.1 to 9 ng/g dwt. BTBPE was detected in 100% of the gull eggs at concentrations ranging from 0.04 to 0.7 ng/g wwt. PBEB was detected in all of the gull eggs sampled at concentrations ranging from 0.03 to 1.4 ng/g wwt and was not detected in the single sediment sample which was analyzed.

In contrast to the PBDEs, few risk assessments have been performed for the flame retardants discussed in this section. The European Chemicals Bureau of the EUC (EUC 2008 g) has recently completed a comprehensive risk assessment for HBCD. Although no risks were indicated for certain uses, risk quotients greater than one were concluded for others, including general uses in textile back coating and certain uses of expanded polystyrene. Further, although the data are equivocal and under debate, HBCD was considered to meet criteria for persistence, bioaccumulation, and toxicity (PBT), and an overall conclusion of risk was indicated for secondary poisoning. As a result, HBCD has recently been nominated for evaluation under the United Nations Economic Commission for Europe Long Range Transboundary Air Pollution Convention (UNECE LRTAP) and under the United Nations Environment Program (UNEP) Stockholm Convention. In the EU risk assessment, PNECs for HBCD are reported for surface waters, sediments, and for secondary poisoning by ingestion of food. These PNEC values are 0.31 μg/L, 0.86 mg/kg dwt, and 15.3 mg/kg food, respectively (Table 2). When compared to the limited data for

the Great Lakes Basin, maximum reported concentrations of HBCD in sediments (0.0037 mg/kg dwt) and biota (0.02 mg/kg wwt) are well below these PNEC values.

3.9 Chlorinated Paraffins

Chlorinated paraffins are complex mixtures of chlorinated alkanes produced since 1930 by direct chlorination of normal paraffins fractions. Commercial products are usually differentiated into three categories depending on chain length; short chain ($C_{10–13}$), medium chain ($C_{14–17}$) and long chain ($C_{18–30}$). Short-chain chlorinated paraffins (SCCP) are primarily used as extreme temperature additives in metal-working fluids, although they are also used in paints and sealants, and in the leather-working industry. Medium- (MCCP) and long-chain (LCCP) products are used as flame retardant plasticizers and as additives to improve the water resistance and flame retardancy of adhesives, paints, and sealants. SCCPs have attracted the greatest attention owing to their toxicity, persistence, and bioaccumulation potential. Environmental releases of these products may occur during production, storage, transportation, and use of chlorinated paraffin-based products, or from emissions from wastewater treatment plants, landfills, and other waste disposal sites.

Compared to monitoring data for other halogenated organics in the Great Lakes, the number of studies and the geographical distribution of data for chlorinated paraffins are rather limited. Factors contributing to the lack of measurements have been the availability of standards and the development of analytical techniques for these complex mixtures. The majority of the available data for water and sediment are for samples from Lake Ontario, although some surface water data are also available for the St. Lawrence River (sampling locations not illustrated). Limited data are available for the presence of SCCPs in biological tissues from Lakes Michigan and Ontario.

Muir et al. (2001) summarized the analytical results of surface waters, sediments, and biota collected from Lake Ontario. Surface sediments were collected from three harbor areas (Toronto, Port Credit, and Hamilton, ON), in 1996. Carp were also collected in 1996 from Hamilton Harbor, and lake trout were obtained from two locations in western Lake Ontario (Port Credit and Niagara on the Lake). Large volume samples of lake water were obtained in July 1999 from the western basin of Lake Ontario. SCCPs were present in the surface water samples; sum SCCP concentrations were 1.75 ng/L and were dominated by C_{12} congeners. Analysis of atmospheric data and fugacity ratios suggested that $C_{10–12}$ homologs were volatilizing from water to air. SCCPs were measured in all surface-sediment samples from the three harbors. Sum SCCP concentrations in sediment ranged from 7.3 to 290 ng/g dwt. The highest concentrations were found at an industrialized location (Windermere basin in Hamilton Harbor), which has documented heavy metal, PAH, and PCB concentrations. SCCPs were detectable in all samples of carp and lake trout. Average concentrations in carp (sum SCCP $= 2{,}630 \pm 2{,}560$ ng/g wwt) were higher than those detected in lake trout (59 ± 51–73 ± 47 ng/g wwt); these

values were consistent with the observation that SCCP congeners are metabolized and have short half-lives and low biomagnification factors in juvenile rainbow trout. For comparison, the mean sum PCB concentrations in the same trout ranged from 2,180 to 5,150 ng/g wwt.

Moore et al. (2004) described the development of a sophisticated GC/MS method for quantifying SCCP concentrations in environmental samples. The method was applied to the analysis of high volume water samples from the St. Lawrence River. Samples were collected in April, September, and October in 1999 from the drinking water intake of the municipality of Levis, QC. Concentrations of sum SCCP ranged from 3.48 to 38.44 ng/L. No apparent seasonal differences in concentrations were noted.

Marvin et al. (2003) reported the results of a survey of SCCP concentrations in sediments collected in 1998 from 27 stations in Lake Ontario. Selected stations in each of the depositional basins exhibited the highest concentrations, ranging from 147 to 410 ng/g dwt. The average sum SCCP concentration lakewide was 49 ng/g dwt. Because of the limited sampling frequency, the distribution of SCCPs did not exhibit a definitive spatial trend. Assessment of core profiles and estimates of SCCP fluxes indicated that an area in the western basin of the lake was heavily impacted and potentially influenced by local industrial sources. Maximum accumulation of SCCPs in the western basin occurred in the mid-1970s. In contrast, SCCP concentrations in cores from the central basin of the lake exhibited characteristics that were more similar to remote locations that were primarily impacted by atmospheric sources.

Houde et al. (2008) examined the distribution, bioaccumulation, and trophic biomagnification of SCCP and MCCP in Lake Ontario and northern Lake Michigan. Water samples ($n = 10$) were collected from three sites in Lake Ontario (western, central, and eastern basins) during the period from October 2000 to July 2004. Net plankton, forage fish, and lake trout (n varies from 2 to 7) were collected in northern Lake Michigan (near Charlevoix, MI) and from locations in western Lake Ontario in July 2001. Total sum SCCP and sum MCCP concentrations in lake water from Lake Ontario were 1,190 and 0.9 pg/L, respectively. Despite different sampling techniques, different years, and different analytical methods, the total SCCP concentrations in the water samples from the two lakes were similar. Chlorinated paraffins were also detected in invertebrates and fish from both lakes. SCCP predominated in organisms from Lake Michigan, with the highest mean concentrations detected in lake trout (123 ± 35 ng/g wwt). In contrast, MCCPs dominated most species in Lake Ontario, with the highest levels detected in slimy sculpin (108 ng/g wwt). Log bioaccumulation factors for lake trout ranged from 4.1 to 7.0 for SCCPs and from 6.3 to 6.8 for MCCPs. SCCP and MCCP were found to biomagnify between prey and predators from both lakes. Trophic magnification factors for invertebrates–forage fish–lake trout food webs ranged from 0.41 to 2.4 for SCCPs and from 0.06 to 0.36 for MCCPs.

Preliminary results for SCCP and MCCP concentrations in Lake Ontario biota have been recently reported by Tomy et al. (2007). The study focused primarily on the bioaccumulation of Dechlorane Plus in Lake Ontario food webs, but included

the analysis of SCCPs and MCCPs in extracts from archived samples of invertebrates, forage fish, and lake trout collected between 2000 and 2003. Limited details were provided in the paper, and future publication of the data was indicated. Sum SCCP concentrations (normalized-to-lipid content) ranged from 30.43 to 520.8 ng/g lipid wt. The lowest and highest SCCP concentrations were found in *Mysis* and sculpin, respectively. Sum MCCP concentrations ranged from below the detection limit (*Mysis* and plankton) to as high as 2,250 ng/g lipid weight (sculpin). Note that the higher levels of sum MCCP concentrations observed in this study are consistent with the previous work of Houde et al. (2008). Because of the preliminary nature of the findings, and the difference in units relative to the other biological data, these results were not included in the statistical analysis.

As presented in Table 15a–c, limited data are available for the concentrations of chlorinated paraffins in the environment. SCCPs have been detected in all of the surface water samples ($n = 16$) from Lake Ontario and the St. Lawrence River and appear to be dominated by the C_{10} and C_{11} congeners (Table 15a). Total SCCP concentrations ranged from 0.0012 to 0.0384 μg/L; median and 95th percentile values were 0.012 and 0.0349 μg/L, respectively. MCCPs were also present in surface waters of Lake Ontario at substantially lower concentrations. SCCPs were present in all of the surficial sediment samples (Table 15b). Muir et al. (2001) provided concentrations for the SCCP congeners for eight samples, while only summary data were reported by Marvin et al. (2003). Total SCCP concentrations in Lake Ontario sediments range from 5.9 to 410 ng/g dwt; median and 95th percentile concentrations were 30 and 306.5 ng/g dwt, respectively. The residues of the C_{12} congeners appear to be dominant based on limited data.

The results of mean concentrations reported for chlorinated paraffins in biological tissues are summarized in Table 15c. Note that the summary statistics represent concentrations for multiple trophic levels, ranging from invertebrates to small fish to predatory fish. Total SCCP concentrations ranged from 1.02 to 2,630 ng/g wwt, with median and 95th percentile concentrations of 24 and 624.4 ng/g wwt, respectively. In contrast to surface waters, both C_{12} and C_{13} congeners are predominant in biological tissues. As previously discussed, SCCP concentrations in fish vary considerably, depending on species and sampling location. The highest concentrations were observed in carp (2,630 ng/g wwt) as compared to lake trout (34–123 ng/g wwt). Total MCCP concentrations were lower, ranging from 0.05 to 109 ng/g wwt. However, as previously discussed, MCCP may be important in biota in certain lakes. The data for SCCPs in fish suggest that SCCP contamination appears to be widespread, but the concentrations are relatively low compared to other organic compounds (e.g., PCBs).

Risk assessments for exposure to the chlorinated paraffins (SCCP and MCCP) have been conducted by authorities in various geographies (EC 2008; EUC 2005c, 2008d; US EPA 1991, 1993). Although some risk assessments (United States, UK) have concluded that there is low ecological risk, others (Canada, Europe) have determined that these products pose a risk to aquatic life and should be phased out. Europe has recently completed risk assessments for both SCCP and MCCP (EUC 2005c, 2008d). Although no risks were indicated for certain uses, risk reduction

Table 15 Summary statistics for chlorinated paraffins

	n	Freq det (%)	Mean (μg/L)	SD (μg/L)	Median (μg/L)	95th percentile (μg/L)	Min (μg/L)	Max (μg/L)
A. Surface water								
C10	16	100	0.0045	0.0049	0.0032	0.0119	0.0001	0.0133
C11	16	100	0.0059	0.0059	0.0050	0.0143	0.0004	0.0155
C12	16	100	0.0032	0.0028	0.0018	0.0068	0.0007	0.0071
C13	16	100	0.0014	0.0016	0.0009	0.0037	0.00004	0.0038
Total SCCP	16	100	0.0150	0.0143	0.0123	0.0349	0.0012	0.0384
Total MCCP	10	100	0.0000009		0.0000009	0.0000009	0.0000009	0.0000009
	n	Freq det (%)	Mean (ng/g dwt)	SD (ng/g dwt)	Median (ng/g dwt)	95th percentile (ng/g dwt)	Min (ng/g dwt)	Max (ng/g dwt)
B. Sediment								
C10	8	100	2.88	3.44	1.80	8.31	0.60	11.00
C11	8	100	13.59	17.91	6.90	42.00	2.20	56.00
C12	8	100	27.58	41.98	10.50	96.90	2.20	127.00
C13	8	100	18.16	29.80	8.50	65.85	0.30	90.00
Total SCCP	38	100	69.24	97.28	30.00	306.50	5.90	410.00

Table 15 (continued)

	n	Freq det (%)	Mean (ng/g wwt)	SD (ng/g wwt)	Median (ng/g wwt)	95th percentile (ng/g wwt)	Min (ng/g wwt)	Max (ng/g wwt)
C. Biota[a]								
C10	47	100	8.44	12.56	3.80	29.40	0.21	51.00
C11	47	100	30.64	85.29	8.60	96.00	0.42	360.00
C12	47	100	75.96	261.61	8.30	250.00	0.34	1,090.00
C13	47	100	70.59	283.33	0.68	242.80	0.05	1,170.00
Total SCCP	47	100	185.55	630.74	24.00	624.40	1.02	2,630.00
C14	44	61	7.30	11.39	2.60	28.90	0.05	38.00
C15	44	61	10.55	21.30	0.48	57.50	0.05	64.00
C16	44	36	2.87	6.06	0.05	15.75	0.05	19.00
C17	44	14	0.25	0.48	0.05	1.28	0.05	1.60
Total MCCP	44	61	21.04	38.47	3.55	108.35	0.05	109.00

[a] The results represent concentrations reported for multiple trophic levels (invertebrates, small fish, large fish)

strategies have been implemented for their use in metal-working fluids, leather fat liquors, and in the production of polyvinylchloride. Europe has also concluded that SCCPs, but not MCCPs, meet criteria for persistence, bioaccumulation, and toxicity (PBT).

ENEVs and PNECs have been developed for chlorinated paraffins to be used in the calculation of risk quotients (exposure vs. effect). Comparison of the concentration distributions for SCCP and MCCP is summarized in Table 15a–c. These values, when compared with the ENEV and PNEC values shown in Table 2, suggest that all exposures are below the no effect values. However, Environment Canada (EC 2008) has recently concluded that, because of limitations in the available exposure and effects data, the absence of risk quotients greater than unity cannot be considered proof that these persistent and bioaccumulative substances do not cause ecological harm.

4 Summary

This review and statistical analysis was conducted to better understand the nature and significance of environmental exposures in the Great Lakes Basin and watershed to a variety of environmental contaminants. These contaminants of interest included current-use pesticides, pharmaceuticals, organic wastewater contaminants, alkylphenol ethoxylates, perfluorinated surfactants, flame retardants, and chlorinated paraffins. The available literature was critically reviewed and used to develop a database containing 19,611 residue values for 326 substances. In many papers, sampling locations were characterized as being downstream from municipal wastewater discharges, receiving waters for industrial facilities, areas susceptible to agricultural or urban contamination, or harbors and ports. To develop an initial assessment of their potential ecological significance, the contamination levels found were compared with currently available regulatory standards, guidelines, or criteria.

This review was prepared for the IJC multi-board work group, and served as background material for an expert consultation, held in March, 2009, in which the significance of the contaminants found was discussed. Moreover, the consultation attempted to identify and assess opportunities for strengthening future actions that will protect the Great Lakes.

Based on the findings and conclusions of the expert consultation, it is apparent that a wide variety of chemicals of emerging concern have been detected in environmental media (air, water, sediment, biota) from the Great Lakes Basin, although many are present at only trace levels. Although the presence of these contaminants raises concerns in the public and among the scientific community, the findings must be placed in context. Significant scientific interpretation is required to understand the extent to which these chemicals may pose a threat to the ecosystem and to human health. The ability to detect chemicals in environmental media greatly surpasses our ability to understand the implications of such findings. As advances in analytical technologies occur, it is probable that substances previously found to be

non-detectable will be detected. However, their presence in environmental media should not be construed to mean that they are necessarily toxic or hazardous.

Current-use pesticides are tightly regulated and extensive efforts have been made to analyze for their presence in surface waters from the Great Lakes Basin. The concentrations found in surface waters for many of the pesticides are below current regulatory criteria. However, the concentrations of certain pesticides exceeded current criteria in 6–32% of the samples analyzed.

Detectable concentrations of pharmaceutical compounds were present in 34% of the surface water samples. Various prescription and non-prescription drugs were detected, most frequently at locations that were proximate to the point of discharge from wastewater treatment plants or agricultural operations. At present, there are no standards, guidelines, or criteria with which to compare these contaminant concentrations.

Concentrations of alkylphenol ethoxylates and their metabolites have been well studied. All surface water nonylphenol concentrations were below US ambient water quality criteria. However, the concentrations reported for some locations exceeded Canadian guidelines for water or sediment.

Only limited data were available for a wide variety of organic wastewater contaminants. Measured concentrations in Great Lakes waters were generally low. Where criteria exist for comparison, the concentrations found were generally below the associated regulatory standards. However, exceedences were noted for some classes of compounds, including phthalates and polycyclic aromatic hydrocarbons.

The highest environmental concentrations were reported in biota for a number of persistent, bioaccumulative, and toxic compounds (e.g., polybrominated diphenyl ethers, perfluorinated surfactants). Various stewardship as well as government risk assessment and risk management programs have been implemented over the past years for many of these compounds. Because risk management strategies for some of these contaminants have been implemented only recently, their impact on environmental concentrations, to date, remains unclear. Current evidence suggests that the concentrations of some brominated flame retardants are trending downward, while the concentrations of others appear to be increasing.

Regulatory criteria are not available for many of the chemicals of emerging concern that were detected in the Great Lakes Basin. When criteria do exist, it is important to recognize that they were developed based on the best available science at the time. As the science evolves, regulatory criteria must be reassessed in light of new findings (e.g., consideration of new endpoints and mechanisms of action). Further, there are significant scientific gaps in our ability to interpret environmental monitoring data, including the need for: (a) improving the understanding of the effects of mixtures, (b) information on use of, and the commercial life cycle of chemicals and products that contain them, (c) information on source contributions and exposure pathways, and (d) the need for thoughtful additional regulatory, environmental, and health criteria.

Discharges from wastewater treatment plants were identified as an important source of contaminants to surface waters in the Great Lakes Basin. Combined sewer overflows and agricultural operations were also found to be important contributors

to concentrations in surface waters. Concentrations of many of the chemicals were generally the highest in the vicinity of these sources, decline with increasing distance from sources, and were generally low or non-detectable in the open waters of the Great Lakes.

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