

Chris Marvin, Donald Williams, Ken Kuntz, Paul Klawuun, Sean Backus, Terry Kolic, Corina Lucaciu, Karen MacPherson, and Eric Reiner

Abstract

197

Archived suspended sediment samples collected over the period 1980 - 2002 at Niagara-on-the-Lake in the Niagara River were analyzed to assess temporal trends in contaminants associated with historical industrial activities in the watershed (PCDDs/PCDFs, DLPCBs), compared to more modern industrial chemicals (PBDEs). The temporal trends for PCDDs/PCDDs and DLPCBs were generally similar, and showed a general trend toward decreasing concentrations, which was presumably due to implementation of control measures in the Niagara River watershed, including the remediation of hazardous waste facilities. The temporal trend in PBDEs contrasted with those of PCDDs/PCDFs and DLPCBs. Prior to 1988, PBDEs were generally detected at low-ppb concentrations, but showed a trend toward increasing concentrations over the period 1980 - 1988. After 1988, PBDE concentrations in the Niagara River showed a more rapidly increasing trend to a maximum of approximately 35 ng/g in 1995, with deca-BDE as the predominant congener detected. Samples collected over the period February 2003 to March 2004 at the head and mouth of the Niagara River were also analyzed for PBDEs; in all cases PBDE concentrations were higher at the mouth of the river at the outflow to Lake Ontario, indicating the Niagara River watershed is a source of PBDE contamination to Lake Ontario. However, PBDE concentrations in suspended sediments of the Niagara River were comparable to, or lower than, concentrations in bottom sediments in other industrialized/urbanized areas of the world. Based on these comparisons of global PBDE bottom sediment concentrations, the Niagara River watershed does not appear to be a significant local source of PBDEs to Lake Ontario, and concentrations in suspended sediments appear to be indicative of general PBDE contamination from a contamination of local, regional, and continental sources.

NWRI RESEARCH SUMMARY

Plain language title

Trends in Dioxins, dioxin-like PCBs, and brominated flame retardants in Niagara River suspended sediments

What is the problem and what do scientists already know about it?

Presence of contaminants in suspended sediments can be a primary source to higher trophic levels resulting in deleterious health impacts on fish and wildlife.

Why did NWRI do this study?

Research into the occurrence of contaminants in surface waters and suspended sediments of Great Lakes interconnecting channels and open-water lake areas has been ongoing since 1986 to track inputs, outputs, and in-lake concentrations of toxic chemicals. The Niagara River Upstream/Downstream Program has been conducted over the past 25 years to track trends in concentrations and loadings of contaminants in response to implemented control measures in the Niagara River watershed. The Niagara River is the primary discharger to Lake Ontario, contributing over 80% of the total tributary flow, 85% of the total input water budget, and roughly 50% of finegrained sediments entering the lake. Concentrations of pollutants are measured in both dissolved and particulate phases from biweekly water samples collected at the head of the river at Fort Erie, and the mouth at Niagara-on-the-Lake. Analyses have focused on a variety of priority toxics including PCBs, PAHs, organochlorine pesticides, industrial by-products, and metals. At a time when some toxic chemicals in the environment such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs) and dioxin-like PCBs (DLPCBs) are declining, newer classes of compounds such as polybrominated diphenyl ethers (PBDEs) are being found at increasing levels in the environment. In this study, we have analyzed archived particulate samples collected over the period 1980 - 2002 at Niagara-on-the-Lake in the Niagara River to assess temporal trends in contaminants associated with historical industrial activities in the watershed (PCDDs/PCDFs, DLPCBs), compared to more modern industrial chemicals (PBDEs).

What were the results?

The temporal trends for PCDDs/PCDDs and DLPCBs were generally similar, and showed a general trend toward decreasing concentrations, which was presumably due to implementation of control measures in the Niagara River watershed, including the remediation of hazardous waste facilities. The temporal trend in PBDEs contrasted with those of PCDDs/PCDFs and DLPCBs. Prior to 1988, PBDEs were generally detected at low-ppb concentrations, but showed a trend toward increasing concentrations over the period 1980 – 1988. After 1988, PBDE concentrations in the Niagara River showed a more rapidly increasing trend to a maximum of approximately 35 ng/g in 1995, with deca-BDE as the predominant congener detected. Samples collected over the period February 2003 to March 2004 at the head and mouth of the Niagara River were also analyzed for PBDEs; in all cases PBDE concentrations were higher at the mouth of the river at the outflow to Lake Ontario, indicating the Niagara River watershed is a source of PBDE contamination to Lake Ontario. However, PBDE concentrations in suspended sediments of the Niagara River were comparable to, or lower than, concentrations in bottom sediments in other industrialized/urbanized areas of the world. Based on these comparisons of global PBDE bottom sediment concentrations, the Niagara River watershed does not appear to be a significant local source of PBDEs to Lake Ontario, and concentrations in suspended sediments appear to be indicative of general PBDE contamination from a contamination of local, regional, and continental sources.

How will these results be used?

These results have further demonstrated that the focus of government agencies on the Niagara River is well justified. Further collaboration between State, Provincial and Federal agenices has been initiated to further study sources and loadings of contaminants that appear to be associated with local sources. These efforts are critical as elimination of sources is the only feasable management option for reducing deep water open-lake sediment contamination.

Who were our main partners in the study?

Ontario Region, MOE

Tendances temporelles des polychlorodibenzoparadioxines et des polychlorodibenzofuranes (PCDD/PCDF), des BPC de type dioxine (BPCTD) et des polybromodiphényléthers (PBDE) dans des sédiments en suspension de la rivière Niagara

Chris Marvin, Donald Williams, Ken Kuntz, Paul Klawuun, Sean Backus, Terry Kolic, Corina Lucaciu, Karen MacPherson et Eric Reiner

Résumé

Des échantillons archivés de sédiment en suspension recueillis de 1980 à 2002 à Niagara-on-the-Lake sur la rivière Niagara ont été analysés pour évaluer les tendances temporelles des contaminants liés à des activités industrielles passées dans le bassin hydrologique (PCDD/PCDF, BPCTD) comparativement à celles de produits chimiques industriels plus modernes (PBDE). Les tendances temporelles des PCDD/PCDF et des BPCTD étaient généralement similaires : la tendance générale des concentrations était à la baisse, ce qui est probablement attribuable à la mise en œuvre de mesures de surveillance dans le bassin hydrologique de la rivière Niagara, y compris la réparation d'installations de traitement de déchets dangereux. La tendance temporelle des PBDE contrastait avec celles des PCDD/PCDF et des BPCTD. Avant 1988, les PBDE étaient généralement détectés à de faibles concentrations, avec une tendance à la hausse des concentrations de 1980 à 1988. Après 1988, les concentrations de PBDE dans la rivière Niagara ont augmenté plus rapidement pour atteindre un maximum d'environ 35 ng/g en 1995, le décaBDE étant le congénère prédominant détecté. Des échantillons recueillis de février 2003 à mars 2004 à la source et à l'embouchure de la rivière Niagara ont été analysés pour déterminer des concentrations de PBDE; dans tous les cas, ces concentrations étaient plus élevées à l'embouchure sur le lac Ontario, indiquant que le bassin hydrologique de la rivière Niagara est une source de contamination par les PBDE pour celui-ci. Toutefois, les concentrations de PBDE dans les sédiments en suspension de la rivière Niagara étaient comparables ou inférieures à celles des sédiments de fond d'autres zones industrialisées ou urbanisées de la planète. Sur la base de ces comparaisons des concentrations de PBDE dans les sédiments de fond à l'échelle planétaire, le bassin hydrologique de la rivière Niagara ne semble pas être une source locale importante de PBDE pour le lac Ontario, et les concentrations dans les sédiments en suspension semblent indiquer une contamination générale par les PBDE par des sources locales, régionales et continentales.

Sommaire des recherches de l'INRE

Titre en langage clair

Tendances des dioxines, des BPC de type dioxine et des additifs ignifugeants bromés dans les sédiments en suspension de la rivière Niagara.

Quel est le problème et que savent les chercheurs à ce sujet?

La présence de contaminants dans les sédiments en suspension peut être une source primaire pour des niveaux trophiques plus élevés, qui a des effets délétères sur le poisson et les animaux sauvages.

Pourquoi l'INRE a-t-il effectué cette étude?

La recherche sur la présence de contaminants dans les eaux de surface et les sédiments en suspension dans les voies interlacustres et les eaux libres du réseau des Grands Lacs se poursuit depuis 1986 pour suivre les intrants, les extrants et les concentrations lacustres de produits chimiques toxiques. Depuis 25 ans, le Programme de surveillance amont/aval de la rivière Niagara suit les tendances des concentrations et des charges de contaminants après la mise en œuvre de mesures de surveillance dans le bassin de la rivière Niagara. Celle-ci est la principale source de rejets dans le lac Ontario, contribuant pour plus de 80 % à l'écoulement tributaire total, pour 85 % au bilan hydrique entrant total et pour environ 50 % aux sédiments fins qui entrent dans le lac. Les concentrations de polluants sont mesurées dans les phases dissoute et particulaire au moyen d'échantillons d'eau prélevés toutes les deux semaines à la source de la rivière à Fort Erie, et à l'embouchure à Niagara-on-the-Lake. Les analyses se sont concentrées sur divers toxiques d'intérêt prioritaire, dont les BPC, les HAP, les pesticides organochlorés, les sous-produits industriels, et les métaux. Au moment où certains produits chimiques toxiques dans l'environnement, comme les polychlorodibenzoparadioxines et les polychlorodibenzofuranes (PCDD/PCDF), et les BPC de type dioxine (BPCTD) sont en baisse, de nouvelles classes de composés, comme les polybromodiphényléthers (PBDE), sont détectées dans l'environnement à des concentrations croissantes. Dans ces études, nous avons analysé les échantillons de particules archivés recueillis entre 1980 et 2002 dans la rivière Niagara, à Niagara-on-the-Lake, pour évaluer les tendances temporelles des contaminants liées à des activités industrielles historiques dans le bassin hydrologique (PCDD/PCDF, BPCTD), comparativement à celles de produits chimiques industriels plus modernes (PBDE).

Quels sont les résultats?

La tendance temporelle des PBDE contrastait avec celles des PCDD/PCDF et des BPCTD. Avant 1988, les PBDE étaient généralement détectés à de faibles concentrations, avec une tendance à la hausse des concentrations de 1980 à 1988. Après 1988, les concentrations de PBDE dans la rivière Niagara ont augmenté plus rapidement pour atteindre un maximum d'environ 35 ng/g en 1995, le décaBDE étant le congénère prédominant détecté. Des échantillons recueillis de février 2003 à mars 2004 à la source et à l'embouchure de la rivière Niagara ont été analysés pour déterminer des concentrations de PBDE; dans tous les cas, ces concentrations étaient plus élevées à l'embouchure sur le lac Ontario, indiquant que le basin hydrologique de la rivière Niagara est une source de contamination par les PBDE pour le lac Ontario. Toutefois, les concentrations de PBDE dans les sédiments en suspension de la rivière Niagara étaient comparables ou inférieures à celles des sédiments de fond d'autres zones industrialisées ou urbanisées de la planète. Sur la base de ces comparaisons des concentrations de PBDE dans les sédiments de fond à l'échelle planétaire, le bassin hydrologique de la rivière Niagara ne semble pas être une source locale importante de PBDE pour le lac Ontario, et les concentrations dans les sédiments en suspension semblent indiquer une contamination générale par les PBDE provenant de sources locales, régionales et continentales.

Comment ces résultats seront-ils utilisés?

Ces résultats ont montré une fois de plus que l'intérêt porté à la rivière Niagara par les organismes gouvernementaux est entièrement justifié. Une collaboration plus poussée entre les organismes des États et les organismes provinciaux et fédéraux a été amorcée afin d'étudier de façon plus approfondie les sources et les charges de contaminants qui semblent liées à des sources locales. Ces efforts sont cruciaux car l'élimination des sources est la seule option de gestion réalisable pour réduire la contamination des sédiments en eau profonde au large.

Quels étaient nos principaux partenaires dans cette étude?

Région de l'Ontario, MEO.

Temporal Trends in Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans, Dioxin-like PCBs, and Polybrominated Diphenyl Ethers in Niagara River Suspended Sediments

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Abstract

Archived suspended sediment samples collected over the period 1980 – 2002 at Niagaraon-the-Lake in the Niagara River were analyzed to assess temporal trends in contaminants associated with historical industrial activities in the watershed (PCDDs/PCDFs, DLPCBs), compared to more modern industrial chemicals (PBDEs). The temporal trends for PCDDs/PCDDs and DLPCBs were generally similar, and showed a general trend toward decreasing concentrations, which was presumably due to implementation of control measures in the Niagara River watershed, including the remediation of hazardous waste facilities. The temporal trend in PBDEs contrasted with those of PCDDs/PCDFs and DLPCBs. Prior to 1988, PBDEs were generally detected at low-ppb concentrations, but showed a trend toward increasing concentrations over the period 1980 – 1988. After 1988, PBDE concentrations in the Niagara River showed a more rapidly increasing trend to a maximum of approximately 35 ng/g in 1995, with deca-BDE as the predominant congener detected. Samples collected over the period February 2003 to March 2004 at the head and mouth of the Niagara River were also analyzed for PBDEs; in all cases PBDE concentrations were higher at the mouth of the river at the outflow to Lake Ontario, indicating the Niagara River watershed is a source of PBDE contamination to Lake Ontario. However, PBDE concentrations in suspended sediments of the Niagara River were comparable to, or lower than, concentrations in bottom sediments in other industrialized/urbanized areas of the world. Based on these comparisons of global PBDE bottom sediment concentrations, the Niagara River watershed does not appear to be a significant local source of PBDEs to Lake Ontario, and concentrations in suspended sediments appear to be indicative of general PBDE contamination from a contamination of local, regional, and continental sources.

Keywords: Polychlorinated dibenzo-p-dioxins; Polybrominated diphenyl ethers, Niagara River, suspended sediment; Great Lakes

1. Introduction

Research and monitoring of contaminants in surface waters of Great Lakes interconnecting channels (St. Clair, Niagara and St. Lawrence Rivers, Williams et al., 2000, Merriman, 1988) and open-water lake areas (Williams et al., 1998a, Williams et al., 1998b, Williams et al., 2001) has been ongoing since 1986 to track inputs, outputs, and in-lake concentrations of toxic chemicals. The Niagara River Upstream/Downstream Program has been

conducted over the past 25 years to track trends in concentrations and loadings of contaminants in response to implemented control measures in the Niagara River watershed. The Niagara River is the primary discharger to Lake Ontario, contributing over 80% of the total tributary flow (Eadie and Roberston, 1976), 85% of the total input water budget, and roughly 50% of finegrained sediments entering the lake (Kemp and Harper, 1976). Concentrations of pollutants are measured in both dissolved and particulate phases from biweekly water samples collected at the head of the river at Fort Erie, and the mouth at Niagara-on-the-Lake (Figure 1). Analyses have focused on a variety of priority toxics including PCBs, PAHs, organochlorine pesticides, industrial by-products, and metals.

At a time when some toxic chemicals in the environment such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) and dioxin-like PCBs (DLPCBs) are declining, newer classes of compounds such as polybrominated diphenyl ethers (PBDEs) are being found at increasing levels in the environment. During the 1970s, production of brominated flame retardants (BFRs) increased due to growing demand for better fire retardants, which was due in part to more stringent fire safety standards. BFRs typically constitute between 10% - 30% by weight of plastics, polymers, and resins used in manufacturing a variety of consumer products. BFRs are produced for the textile and paint industries and used in automobile upholstery, insulation, and building materials. PBDEs constitute roughly a third of the BFRs manufactured. As consumer products are discarded, PBDEs can be potentially released into the environment. PBDEs, like PCBs, have 209 possible congeners, and are similar in behaviour to PCDDs/PCDFs and PCBs in that they are persistent and lipophilic. PBDEs exhibit low water solubility and have a tendency to bind strongly with particulates including soils and sediments.

Hale et al. (2003), Alaee et al. (2003) and de Wit (2002) have published excellent overviews of BFRs in the environment.

In this study, we have analyzed archived particulate samples collected over the period 1980 – 2002 at Niagara-on-the-Lake in the Niagara River to assess temporal trends in contaminants associated with historical industrial activities in the watershed (PCDDs/PCDFs, DLPCBs), compared to more modern industrial chemicals (PBDEs).

2. Experimental

Water at the head (Fort Erie) and mouth (Niagara-on-the-Lake) of the Niagara River was collected using a large-volume 24-hour time-integrated dissolved/particulate phase sampling protocol under the auspices of the Niagara River Upstream/Downstream Program (Williams et al. 2001). Descriptions of sampling protocols and analyses for contaminants have been detailed elsewhere (NLET, 1997, NRAP, 1992, NRSP, 1995). Sampling times at the head and mouth of the river were offset by 15-18 hours to compensate for travel time of water between the two sampling points. Samples were collected using a submersible pump connected to an intake line and Westphalia centrifuge assembly connected to a Goulden Large Sample Extractor (GLSE, Goulden and Anthony 1985).

The freeze-dried archived samples analyzed in this study represent single weekly/biweekly samples collected between April and/or May. Samples were spiked with ¹³Clabelled surrogates for 15 of the 2,3,7,8-substituted PCDD/PCDF isomers and all 12 DLPCBs, and then Soxhlet extracted in toluene for 16 hrs followed by a three-stage open column cleanup. These procedures have been described in detail elsewhere (Ontario Ministry of the Environment, 2002),. The first column contained 1.5 g 10% silver nitrate; 1.0 g activated silica; 2.0 g 33%

sodium hydroxide/silica; 1.0 g activated silica; 4.0 g sulphuric acid/silica; 2.0 g activated silica, and; 2.0 g anhydrous sodium sulphate. The column was eluted with hexane and transferred to a column containing 5.0 g of activated alumina and 2.0 g of anhydrous sodium sulphate. The column was eluted with hexane followed by 10% carbon tetrachloride/hexane (v/v) to collect most mono-ortho PCBs (Fraction A). The PCDDs/PCDFs, co-planar (Co-PCBs), and remaining mono-ortho PCBs were eluted with 10% methanol/dichloromethane (v/v) (Fraction B). Fraction B was loaded onto a column containing 0.35 g 5% Amoco PX21-activated silica (w/w), eluted with 40 mL 25% dichloromethane/hexane and added to Fraction A. The column was inverted and eluted with 160 mL of toluene to isolate a PCDD/PCDF/Co-PCB fraction. The GC-HRMS system was tuned to 10,000+ RP (10% valley definition). Co-PCBs (BZ# - 77, 81, 126, 169) and PCDDs/PCDFs (fraction B), and mono-ortho PCBs (fraction A) were analyzed in separate GC-HRMS runs. Analyses for PCDDs/PCDFs and DLPCBs were performed on a Micromass Autospec HRMS with a Hewlett-Packard HP6890 gas chromatograph using a 40m DB-5 column (0.18 mm i.d, 0.18 µm film thickness, J&W Scientific)

PCDD/PCDF and DLPCB extracts were analysed in splitless mode with He carrier gas at a linear velocity of 1.5 cm/s; injector temperature and transfer line temperature were maintained at 280°C and 300°C, respectively. Temperature program for Fraction A was: 150°C for 1 min; 150°C to 200°C at 5°C/min; 200°C to 235°C at 3°C/min; 235°C for 10 min; 235°C to 300°C at 12°C/min; 300°C for 1 min. Temperature program for Fraction B was: 100°C for 1 min; 100°C to 200°C at 30°C/min; 200°C to 235°C at 3°C/min; 235°C for 10 min; 235°C to 300°C at 6°C/min; 300°C for 1 min. All PCDD/PCDF and DLPCB data was corrected for surrogate recoveries. Method blanks and standard reference materials (SRMs) were processed with each

set of 10 field samples. Toxic equivalents (TEQs) were calculated using the International Toxicity Equivalency Factor (ITEF) method (Van den Berg et al. 1998).

Methods for analysis of PBDEs are described in detail elsewhere (Ontario Ministry of the Environment, 2003). Samples were fortified with ¹³C-labelled PBDE quantification standards with one congener for each homologue group. Fortified samples were Soxhlet extracted overnight in toluene for approximately 12-16 hours. Cleanup was performed using an acid/base/silver nitrate silica column. After initial elution with hexane, the PBDEs were eluted with hexane followed by hexane/DCM (50:50). Chromatographic separation for the tri-BDEs to deca-BDE was achieved on a DB-5HT 15m X 0.25mm X 0.10 µm (J&W Scientific, USA, Table 1, Figure 1), and the GC-HRMS system was tuned to greater that 9000 RP. Total PBDEs represent the sum total of the following 16 congeners: BDE-17; BDE-28; BDE-47; BDE-49; BDE-66; BDE-71; BDE-77; BDE-85; BDE-99; BDE-100; BDE-119; BDE-126; BDE-138; BDE-153; and BDE-183. Figure 2 shows the complete separation of the 17 PBDE congeners on a15-meter DB-5HT column (5% phenyl-high temperature). The complete run took 17.25 minutes to separate tri- to deca-BDE. Within a calibration series 5-point curve for the tri- to hepta-BDEs, the percent RSD's were less than 10% for both the ¹²C and ¹³C responses. The percent RSD for the response factor of isotopically labelled ¹³C deca-BDE was relatively higher than the other compounds within the series. However, the percent RSD for the relative response factor (RRF) of the native deca-BDE was within 10%. BDE extracts were analysed in splitless mode with He carrier gas at a linear velocity of 1.2 cm/s; injector temperature and transfer line temperature were maintained at 270°C. The Temperature program was: 110°C for 1 min; 110°C to 200°C at 40°C/min; 200°C to 330°C at 10°C/min; 300°C for 10 min.

3. Results and Discussion

3.1. Trends in Polychlorinated Dibenzo-p-dioxins and Dibenzofurans and Dioxin-like PCBs

Assessment of homologue profiles from bottom sediment surveys of the major depositional basins of Lake Ontario have implicated non-point source discharges within the Niagara River as primary contributors to PCDD/PCDF and DLPCB contamination in Lake Ontario. Lake Ontario sediments were enriched in the higher-chlorinated PCDF homologs and 2,3,7,8-tetrachlorodibenzodioxin and 1,2,3,4,7,8-hexachlorodibenzofuran congeners (Marvin et al. 2002). Pearson et al. (1998) attributed 65 – 95% of PCDD accumulation and greater than 95% of PCDF accumulation in Lake Ontario to non-atmospheric sources, including the Niagara River. Substantial inventories of PCDDs/PCDFs may still reside in hazardous waste disposal sites. including the Hyde Park Dump that discharges into the Niagara River via Bloody Run Creek. The Hyde Park facility was closed in 1975; however, Howdeshell and Hites (1996) reported that sediment sampling conducted in 1993 indicated that contamination continued to migrate from the dump. More recent data from sediment and biomonitoring studies in the Niagara River at sites including Bloody Run Creek and Pettit Flume (City of Tonawanda) showed elevated PCDD/PCDF levels (Richman 1999, Woodfield and Estabrooks 1999), indicating that hazardous waste sites continued to discharge PCDDs/PCDFs to the Niagara River.

Temporal trends in PCDDs/PCDFs and DLPCBs at the mouth of the Niagara River over the period 1980 – 2002 are shown in Figure 3. Data for 1980 have been omitted, as inclusion of these relatively high concentrations (43.6 pg/g TEQ for PCDDs/PCDFs and 39.5 ng/g for DLPCBs) made trend analysis more difficult. The temporal trends for PCDDs/PCDDs and DLPCBs were generally similar, and showed a general trend toward decreasing concentrations, which was presumably due to implementation of control measures in the watershed, including remediation of hazardous waste facilities. Based on a previous study of sediment contamination in Lake Ontario, maximum accumulation of PCDDs/PCDFs and DLPCBs occurred in the early 1950s to the late 1960s; levels subsequently declined from the late 1960s to the early 1980s, but further significant declines since the 1980s were not apparent (Marvin et al. 2002). The current data generally corroborate the open-lake data; concentrations of PCDDs/PCDFs and DLPCBs are decreasing over time, and further reductions in contamination by these compounds on a lakewide basis can be expected.

3.2. Trends in Polybrominated Diphenyl Ethers

Total PBDEs were expressed as the total of 18 individual congeners. Although all samples were collected discreetly in both particulate and aqueous phases, analyses for PBDEs were confined to the particulate samples due to the tendency of these compounds to partition to sediments and soils (Gouin and Harner 2003). The temporal trend in PBDEs in suspended sediments at the mouth of the Niagara River (Figure 4) contrasted with those of PCDDs/PCDFs and DLPCBs (Figure 3). Prior to 1988, PBDEs were generally detected at low-ppb concentrations, but appeared to show a trend toward increasing concentrations over the period 1980 – 1988. Prior to 1989, most of the PBDE burden was attributable to deca-BDE (Figure 4); average contribution of deca-BDE to total PBDEs over this period was 89%. Similarly, Song et al. (2004) found that surficial concentrations of deca-BDE represented 79% - 98% on a mass basis of total PBDEs in Lake Superior sediments. The deca-BDE reportedly accounts for greater than 70% of total PBDE production in North America (Hale et al. 2003), due to its incorporation in textiles and consumer products requiring denser plastics such as televisions and computers (Alcock et al. 2003). After 1988, PBDE concentrations in the Niagara River showed a more

rapidly increasing trend to a maximum of approximately 35 ng/g in 1995, with the deca-BDE continuing to be the predominant congener detected. An increase in PBDEs in the late-1980s and early 1990s was similarly observed by Luross et al. (2002) in Lake Trout from the Great Lakes, which was attributed to increased PBDE usage as a result of the banning of polybrominated biphenyls (PBBs) and Mirex in the late-1970s. Zhu and Hites (2004) and Lebeuf et al. (2004) made similar observations in lake trout from Lake Ontario and beluga whales from the St. Lawrence Estuary, respectively; PBDE doubling times in both of these studies were estimated to be 3 – 4 years. Song et al. (2004) observed an increase in PBDE fluxes in Lake Superior beginning in the 1970s, which was correlated with PBDE commercial production patterns. Despite the considerable inter-year variability in PBDE concentrations in the Niagara River suspended sediment samples during the mid- to late-1990s, there was still a definitive trend toward increasing concentrations. An explanation for this variability is that spring samples are influenced to varying extents by sediments originating upstream in Lake Erie; future work will focus on the summer sample archives with correspondingly greater contributions of particulate derived locally within the watershed, which may result in a more consistent temporal trend.

Samples collected over the period February 2003 to March 2004 at both Fort Erie and Niagara-on-the-Lake were also analyzed for PBDEs. The comparison of PBDE concentrations in these paired samples is shown in Figure 5. In all cases, PBDE concentrations were higher at the Niagara-on-the-Lake station, compared to Fort Erie. Total PBDEs at Niagara-on-the-Lake typically ranged from 5 ng/g to 20 ng/g, while concentrations at Fort Erie were generally less than 5 ng/g. Song et al. (2004) reported levels of total PBDEs (with the exclusion of deca-BDE) in Lake Superior surficial sediments to range from 0.49 ng/g to 3.14 ng/g, dry weight, while

surficial concentrations of BDE 209 ranged from 4.3 ng/g to 17.5 ng/g dry weight. Lake Superior is a remote area unimpacted by significant local sources of PBDEs, and loadings are primarily the result of atmospheric deposition. Lake Superior is also a deep-water northern lake characterized by cold temperatures and very long residence times.

The typical PBDE congener distribution pattern for spring (April/May) 2003 – 2004 suspended sediments at Niagara-on-the-Lake is shown in Figure 6. In addition to the deca-BDE, BDE 47 and BDE 99 were prevalent and detected in all samples. Minor contributors to the total PBDE burden in these samples included BDE 100, BDE 153, and BDE 154. The BDE-47, 99, 100, 153, and 154 congeners are major components of the commercial penta-PBDE mixture, which accounts for roughly 25% of North American demand (Hale et al. 2003). There was a dramatic increase in production and use of the penta-PBDE mixture in North America in the early 1990s, which stands in contrast to Europe where use of the penta-formulation was restricted and subsequently banned (Alcock et al. 2003). Luross et al. (2002) determined BDE 47, BDE 99, and BDE 100 to be the predominant PBDE congeners in Lake Ontario lake trout, which was attributed to the penta-BDE formulation. In addition, Lake Ontario lake trout concentrations of total PBDEs were highest of all the Laurentian Great Lakes.

Zhu and Hites (2004) used the ratio of the sum of BDE-47 + BDE-99 + BDE-100 to the ratio of BDE 153 + BDE 154 to assess the relative contributions of the penta-BDE commercial product vs the octa-BDE commercial product, respectively, in influencing PBDE congener patterns in Great Lakes fish. This ratio increased over the period 1980 – 2000, which reflected increased use of the octa-BDE product in the 1980s relative to the penta-BDE product, and subsequent increased use of the penta-BDE product in the 1990s relative to the octa-BDE product. The temporal trend in this ratio for the Niagara River suspended sediments at Niagara-

on-the-Lake is shown in Figure 7. Similar to the results of Zhu and Hites for fish, this shift in PBDE usage is reflected in the trend for the congener ratio in suspended sediments, which showed a distinct increase over time ($r^2 = 0.660$). Similar to the results in fish, the ratios in Niagara River suspended sediments were much higher (5- to 15-fold) than the corresponding ratios calculated based on global demand of the penta- and octa-BDE products. Zhu and Hites proposed differences in bioavailability of PBDE congeners as a potential factor, which does not explain our observations for suspended sediments. In addition, BDE 183 is reported to be a marker for the octa-BDE commercial product (Zegers et al. 2003). Although BDE 183 was detected in all samples from 1980 – 2002, there was no temporal trend in this congener in the Niagara River samples. Future work will focus on generating a temporal data set for PBDEs at Fort Erie over the period 1980 – 2002 in order to measure any differences in ratios of individual PBDE congeners at the upstream and downstream sampling sites that could provide evidence of local sources of PBDEs.

The PBDEs are reported to be susceptible to seasonal effects due to variations in temperature in terms of surface – air exchange (Gouin and Harner 2003). There did not appear to be any definitive seasonal trends in PBDE concentrations or congener distributions for the 2003 – 2004 suspended sediment samples at Niagara-on-the-Lake; however, the highest concentrations were generally observed in the spring samples from March to early-June (Figure 5). These results contrast with those for other primarily particulate-bound contaminants in the Niagara River, such as PCBs, where concentrations are lowest in winter and highest in summer (Williams et al. 2003). This seasonal patterns in PCBs was attributed to the effect of both quantity and composition of suspended particulate material in the Niagara River water column.

Future work will focus on analyzing greater numbers of biweekly samples for further investigation of seasonal trends.

Song et al. (2004) found that the ratio of BDE 47 to BDE 99 in Lake Superior sediments was greater than 1.0 in over 60% of the samples collected, whereas this ratio was roughly 0.5 in sediments in a lake (Hadley Lake, IN) impacted by potential local PBDE sources. The mean ratio of BDE 47 to BDE 99 in the 2003 – 2004 Fort Erie suspended sediments was 0.89 while the corresponding mean ratio at Niagara-on-the-Lake was 0.75. Based on a paired t-test, the ratios at Fort Erie and Niagara-on-the-Lake in 2003 – 2004 were not significantly different. The ratios for Niagara River suspended sediments were intermediate in relation to sediments from an area impacted primarily by PBDEs derived from atmospheric deposition (Lake Superior), and an area potentially impacted by PBDEs derived from local sources (Hadley Lake, IN). The Niagara River BDE 47 to BDE 99 ratios at both Fort Erie and Niagara-on-the-Lake did not appear to exhibit any seasonal trends.

4. Conclusions

Temporal trends in PCDDs/PCDFs and DLPCBs at Niagara-on-the-Lake over the period 1980 – 2002 indicate that sources of these compounds in the watershed have been substantially reduced, which speaks to the effectiveness of remedial activities associated with hazardous waste facilities. The observation of higher PBDEs at Niagara-on-the-Lake vs Fort Erie in 2003 – 2004 indicates that the Niagara River watershed is a source of PBDE contamination to Lake Ontario; however, PBDE concentrations in suspended sediments of the Niagara River were comparable to, or lower than, concentrations in bottom sediments in other industrialized/urbanized areas of the world (Song et al. 2004). Previous reports based on temporal data from the Niagara River

Upstream/Downstream Program for contaminants including hexachlorobenzene, octachlorostyrene, and mirex also implicated the Niagara River as a source of persistent toxics to Lake Ontario (Williams et al. 2000, Marvin et al., 2004).

Given the heavy usage of PBDEs in manufactured and consumer products by modern society, and the high degree of industrialization and urbanization in the Niagara River watershed compared to eastern Lake Erie, the observations of higher concentrations of PBDEs in suspended sediments at Niagara-on-the-Lake were expected. In addition, the range of concentrations of total PBDEs at Niagara-on-the-Lake in 2003 – 2004 (2.4 ng/g to 34 ng/g) was similar to the range of concentrations in surficial sediments at six sites in Lake Superior (5.3 ng/g – 21 ng/g, Song et al. 2004). Based on comparisons of global PBDE bottom sediment concentrations, the Niagara River watershed does not appear to be a significant local source of PBDEs to Lake Ontario, as concentrations in suspended sediments appear to be indicative of general PBDE contamination from regional or continental sources.

The results of this study highlight the critical importance of upstream/downstream monitoring programs in major connecting interconnecting channels of the Great Lakes for providing information on temporal trends not only for legacy compounds such as PCBs and PCDDs/PCDFs, but for contaminants of new and emerging concern. In the case of PBDEs, which have been heavily produced in the last 20 years, contamination in the Niagara River appears to reflect a combination of local, regional, and continental influences. The apparent lack of significant local sources of PBDEs in the Niagara River area limits the scope of remedial actions that can mitigate potential environmental impacts in the open-water areas, since PBDE contamination in Lake Ontario appears to represent a cumulative societal impact.

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Figure 1. Map showing the Niagara River area sampling locations for the Niagara River Upstream/Downstream Program.

Figure 2. Separation of polybrominated diphenyl ethers on a DB-5HT ($15m \times .25 mm \times 0.10 \mu m$) column.

Figure 3. Concentrations of PCDDs/PCDFs (top) and DLPCBs (bottom) in Niagara River suspended sediments over the period 1981 – 2002.

Figure 4. Concentrations of PBDEs in Niagara River suspended sediments over the period 1980 – 2002. Bottom panels also show trends for total PBDEs without decaBDE (left), and decaBDE exclusively (right).

Figure 5. Comparison of total polybrominated diphenyl ether concentrations at the head (Fort Erie) and mouth (Niagara-on-the-Lake) of the Niagara River.

Figure 6. Typical polybrominated diphenyl ether profile in suspended sediments sampled at Niagara-on-the-Lake, Niagara River in spring, 2003.

Figure 7. Temporal trend in the ratio of the sum of the concentrations of BDE 47 + BDE 99 + BDE 100 to the sum of the concentrations of BDE 153 + BDE 154. The correlation coefficient (r^2) for the trend line was 0.660, which was significant.











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